

Recent Advances in Transition Metal Complexes and Light-Management Engineering in Organic Optoelectronic Devices

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Two of the recent major research topics in optoelectronic devices are discussed: the development of new organic materials (both molecular and polymeric) for the active layer of organic optoelectronic devices (particularly organic light-emitting diodes (OLEDs)), and light management, including light extraction for OLEDs and light trapping for organic solar cells (OSCs). In the first section, recent developments of phosphorescent transition metal complexes for OLEDs in the past 3–4 years are reviewed. The discussion is focused on the development of metal complexes based on iridium, platinum, and a few other transition metals. In the second part, different light-management strategies in the design of OLEDs with improved light extraction, and of OSCs with improved light trapping is discussed.

due to the limitation of space, two of the recent major research topics in these optoelectronic devices: the development of new organic materials (both molecular and polymeric) for the active layer of organic optoelectronic devices (particularly OLEDs), and the light management including light extraction for OLEDs and light trapping for OSCs will be discussed. In the first section, recent developments in phosphorescent transition metal complexes for OLEDs in the past 3–4 years are reviewed. The discussion is focused on the development of metal complexes based on iridium, platinum, and a few other transition metals. In the second part, different

light-management strategies in the design of OLEDs with improved light extraction and OSCs with improved light trapping is discussed.

1. Introduction

Organic optoelectronic devices including organic light-emitting diodes (OLEDs) and organic solar cells (OSCs) have been potential candidates for the emerging technologies of solid-state lighting and green-energy applications. Since the pioneering reports of OLEDs and OSCs device with reasonable performance in the 1980s,^[1] research in this areas has been growing very rapidly due to the promising application potential. In the past decade, research on these organic optoelectronic devices has mainly been divided into two major aspects. From the molecular design point of view, it is essential to develop new organic/organometallic materials (molecular- or polymer-based) with improved light absorption/emission and charge-transport properties. In addition, improvement in device performance can also be realized by the fabrication of novel device structure so that light emitted (or absorbed) can be better managed. It has truly demonstrated the interdisciplinary effort by scientists and engineers from different areas. In this review,

2. Phosphorescent Transition Metal Complexes

The early examples of emissive materials in OLEDs were singlet emitters. One of the most commonly used emitter was tris(8-hydroxyquinoline)aluminum (Alq₃), which is a green-light-emitting aluminum complex. The emission is from the singlet excited states of the quinoline ligand. In early 1990s almost all emissive materials developed, either molecular or polymeric, were singlet emitters. The performance of OLEDs with singlet emission only are bounded by the maximum external quantum efficiency of 25% because only 25% of the excited states generated after exciton formation are singlet in nature. The rest of the excited states are triplet in nature, from which most of the organic compounds do not emit. In principle, if the triplet excited states can be harvested for light emission, the efficiency of the devices can be significantly improved. In 1998, Ma et al. reported the fabrication of phosphorescent light emitting devices in which the emissive materials were osmium complexes doped in PVK.^[2] In the same year, Thompson and Forrest reported the use of platinum porphyrin doped in Alq₃ host as the emissive materials in phosphorescence light emitters.^[3] In these devices, the singlet excited states of the complexes undergo a rapid intersystem crossing to the strongly emissive triplet excited states due to the presence of a heavy metal center. Since then, research in the development of phosphorescent light emitting materials based on transition metal complexes

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DOI: 10.1002/adma.201306133

had grown rapidly. In 2000, it was reported by Thompson et al. that a green-light emitter based on cyclometalated iridium (III) complex $\text{Ir}(\text{ppy})_3$ (**Scheme 1**)^[4] exhibited an external quantum efficiency of 8%. Thereafter, iridium complexes have been one of the most extensively studied phosphorescence emitter for OLEDs, and complexes with a variety of emission colors have been reported.^[5]

In recent years, research in phosphorescence materials has been focused on blue-light-emitting materials and optimization of green/red emitters for white-light-emitting devices. These materials are of important applications for multicolor displays and for lighting purposes. In this aspect, the tuning of the excited state energy is essential because it directly affects the emission color as well as the efficiency of the device. This can be achieved by designing new molecules with specifically tailored characters, or by novel device engineering.

2.1. Iridium Complexes

2.1.1. Molecular Complexes Based on Cyclometalated Ligands

Cyclometalated iridium complexes have been the most commonly used triplet emitters due to the high phosphorescence quantum yield, optimum triplet state lifetime (in the order of μs), high thermal stability for purification and fabrication by vacuum deposition technique, and versatility in tuning the excited state properties by modifying the structure of the ligands. Since the first report of cyclometalated iridium triplet emitter,^[4,b] most of the complexes reported were mainly red or green light emitters. The energy level of the emissive excited states can be tuned by varying the structure and substituents of the cyclometalated and/or ancillary ligands. In addition, their short triplet excited state lifetimes are also desirable due to the less significant triplet-triplet annihilation. In general, the HOMO of the complex mainly localizes at the π orbital of the phenyl moiety and the iridium d orbitals, while the LUMO is mainly contributed by the pyridyl moiety that is more electron deficient in nature. The optical absorption of these complexes comprises of both metal-to-ligand charge transfer (MLCT) ($d\text{-}\pi^*$) at around 450 nm, and ligand-centered (LC) ($\pi\text{-}\pi^*$) transitions between 250–350 nm.^[6] The phosphorescence usually originates from the lowest energy triplet excited states, which may be the triplet ^3LC ($^3\pi\text{-}\pi^*$) state or the triplet $^3\text{MLCT}$ ($^3d\text{-}\pi^*$) state. In general, the phosphorescence energy will decrease when an electron donating group is attached to the phenyl moiety, or an electron withdrawing group is attached to the N -heterocycle of the cyclometalated ligand. In 2001, a blue-light-emitting complex based on difluorophenylpyridine and ancillary picolate ligands (FIRpic) was reported.^[7] When doped in 4,4'- N,N' -dicarbazole-biphenyl (CBP) host (6% w/w), an emission peak at 475 nm and two shoulders at 495 and 540 nm were identified in the EL spectrum of the device. Since then, work done was focused on the development of new blue light phosphorescent emitters with improved efficiency and color purity. The development of high energy or deep blue phosphorescent materials has been one of the major challenges in this area, and it will be discussed later in this section. Most of the work has been focused on introducing different substituents at the arene and/or



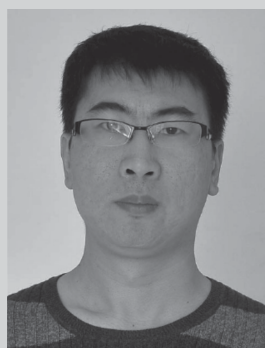
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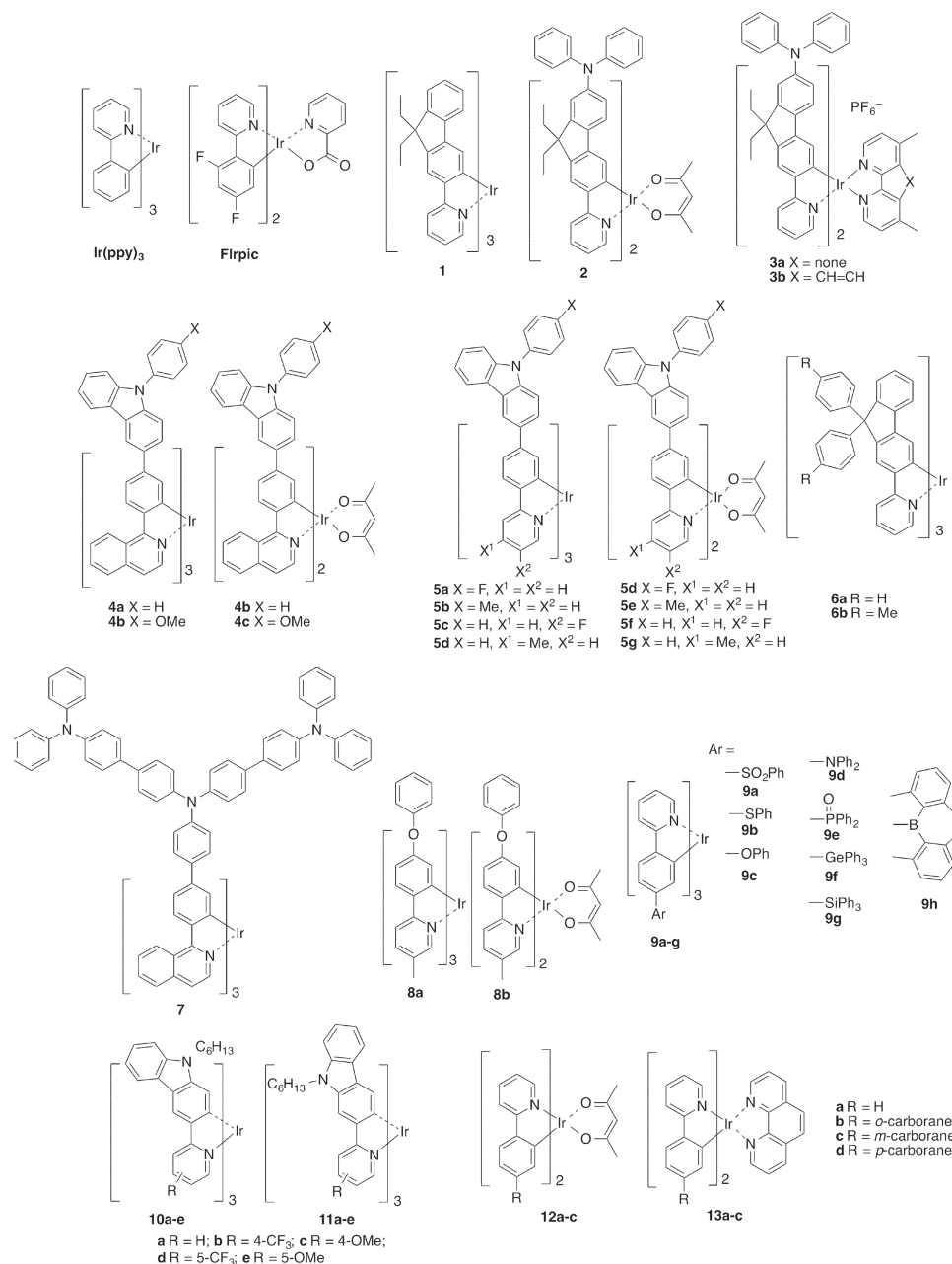
metal complexes for optoelectronic applications.



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pyridyl moieties, or by modifying the ancillary ligands, yielding complexes that are neutral or ionic. Reviews on the development of iridium complexes in 2000s have been published.^[8] In this section, we will present an overview on the recent development in the design and application of new iridium complexes for organic phosphorescence light emitting devices.

Most of the phosphorescent iridium complexes reported to date are cyclometalated complexes with C^*N type donor



Scheme 1. Cyclometalated iridium complexes with various emission colors.

ligands. Other than improving efficiency and color purity, efforts have also been paid on the improvement in charge-carrier mobilities of the emissive materials so that a balance hole/electron injection can be maintained. This can be addressed by the fabrication of multilayer devices with improved charge-injection and transport properties, or by optimizing the host material with optimized electronic energy levels. Various host materials based on aromatic amines or carbazole for OLED have been developed.^[9] The incorporation of electron donating units on the C^N ligands is another strategy in enhancing the hole-transporting properties of iridium complexes. Iridium complexes based on C^N ligands substituted with a variety of electron rich functional units have been reported (Scheme 1).

Cyclometalated iridium complexes based on triarylamine functionalized ligands were reported.^[10] These complexes exhibited with different emission colors and improved charge-transport properties. Complexes **1** and **2** of the type Ir(L)₃ and IrL₂L' (L = C^N ligand, L' = acetylacetonate, acac) were synthesized from diphenylaminofluorenylpyridine. Complex **1** is highly amorphous in nature, resulting in a good compatibility with various phosphorescent hosts and organic dopants. The OLED device exhibited a strong orange color emission power efficiency $PE = 21 \text{ lm W}^{-1}$, current efficiency $CE = 30 \text{ cd A}^{-1}$, and external quantum efficiency $EQE = 10\%$, and the performance of the device based on **1** is higher than that of the hetero-leptic complex **2**. A white-light-emitting OLED based on **1**

was also fabricated.^[11] Multilayer device with the structure ITO/NPB/1:CBP/FIrpic:mCP/TPBI/LiF/Al was fabricated [NPB = *N,N'*-bis(naphthalen-1-yl)-*N,N'*-bis(phenyl)benzidine, TPBI = 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene], in which the FIrpic (Scheme 1) was responsible for blue light emission. Maximum *CE* and *PE* of 17.8 cd A⁻¹ and 7.6 lm W⁻¹ (CIE coordinates = 0.31, 0.41) were reported. In a later report, charged complexes **3a–b** based on the same C[^]N ligand were synthesized.^[12] The N[^]N type ancillary ligand was based on 4,4'-dimethyl-2,2'-bipyridine or 4,7-dimethyl-1,10-phenanthroline. The resulting organic light-emitting device from **3a** demonstrated an improved current and power efficiency of 20 cd A⁻¹ and 19 lm W⁻¹, respectively. Other than improvement in the color purity and hole-transport properties, it was later demonstrated that the carrier mobilities of complexes was also enhanced.^[12] The issues of balanced charge injection and improvement of carrier mobilities have long been challenges in the design of OLEDs. It has previously been demonstrated that some transition metal complexes based on ruthenium and rhenium could serve as both hole and electron carrier when fabricated into an optoelectronic devices.^[13] Complex **3b** was fabricated into light emitting electrochemical transistor, of which the hole and electron drift mobilities were measured to be 0.20 and 0.22 cm²V⁻¹s⁻¹, respectively.^[14] It was suggested that the two diarylamine ligands served as the hole carriers, while the ancillary phenanthroline ligand served as the electron carriers. The amphipolar character observed could greatly facilitate a balance injection of charges from the respective electrodes.

C[^]N ligands bearing fused carbazole moieties were also used in the synthesis of orange light emitting iridium complexes.^[15] The design strategy of these molecules was to attach a fused *N*-phenyl- or *N*-methoxyphenyl-carbazoyl moieties on the phenyl group, and the N donor was modified to isoquinoline (complexes **4a–d**). TDDFT calculation and electrochemical experimental results showed that introduction of carbazole moieties raised the HOMO energy level, but the introduction of methoxy group had little effect. No experimental data about the carrier mobilities of the complexes were presented. In a later report, the isoquinoline unit in the ligand was replaced by pyridyl unit substituted with methyl or fluoro groups (complexes **5a–h**).^[16] The presence of methyl or fluoro group on the pyridine ring had strong influence to the LUMO level of the complexes, and the emission peaks observed in the EL spectra were in the range from 500 to 533 nm. Maximum *CE* and *PE* measured were 43.4 cd A⁻¹ and 33.4 lm W⁻¹ for the device from **5b**.

Other examples of C[^]N ligand incorporated with electron rich (or hole carrying) units were reported. Complexes **6a–b** were used as the yellow and red emitters in the fabrication of white-light OLED.^[17] **6a** was blended with FIrpic together with poly(9-vinylbarbazole) (PVK) host in different ratios, and the best performed device exhibited a maximum *PE* of 494 lm W⁻¹ (CIE = 0.37, 0.53). The color quality of the devices was further improved by using complexes with improved carrier mobilities. When **6b** was blended with FIrpic (as blue emitter), Ir(mppy)₃ (as yellow emitter), and complex **7** (red emitter with dendritic arylamine unit) together in the emissive layer, the resulting devices emitted white light with maximum *PE* of 30.7 and 20.7 lm W⁻¹ at 100 and 1000 cdm⁻², respectively (CIE =

0.299, 0.483). The performance of the device was attributed to the balance in charge carriers. In a more recent example, phenoxy group was used as the electron donating group in the C[^]N ligand (complexes **8a–b**).^[18] Despite the presence of the strongly electron donating phenoxy group, the energy of the triplet emissive excited state was still in the green light region after introducing the methyl group to the pyridine ring. OLEDs were fabricated by both vacuum deposition and spin coating techniques. In the optimized device ITO/NPB/**8b**(acac): CBP/BCP/Alq3/LiF/Al, a very high *PE* of 72.8 lm W⁻¹ was recorded.

Since obtaining high purity color is of highly practical importance in OLED research, it would be ideal if a wide range of emission color can be achieved by systematic modification of complexes with similar structures. Wong et al. demonstrated the tuning of emission color by synthesis a series of iridium complexes in which the C[^]N ligands were modified by introducing different organic main group moieties derived from sulfur, phosphorus, silicon, boron, germanium, nitrogen, and oxygen (complexes **9a–g**).^[19] The emission color of the complexes spanned in the range between bluish-green (**9c**, Ar = -OPh; $\lambda_{\text{max, em}}$ = 505 nm) to red (**9h**, Ar = -B(mesityl)₂; $\lambda_{\text{max, em}}$ = 605 nm). Complex **9h** with a dimesityl borane group behaved quite differently from other complexes that the empty p orbital tends to stabilize the MLCT states (a strong π acceptor). The sulfonyl group in **9a** does not lower the LUMO level significantly, as the electron withdrawing is mainly by inductive effect. In other complexes the MLCT states are more localized at the pyridine ring.

The tuning of emission color was also demonstrated by the synthesis of two isomeric carbazole ligands with different substituents.^[20] Complexes **10a–e** and **11a–e** are based on 2-(carbazol-3'-yl)- and 2-(carbazol-2'-yl)-pyridine. The HOMOs of these complexes were described as mixed ligand-metal orbitals with significant contribution from the carbazole, in particular for complexes **11a–d**. In complexes **10b,d** and **11b,d**, introduction of trifluoromethyl group substantially decreased the HOMO–LUMO gap as the LUMO energy levels were decreased. Complexes **10a–e** exhibited higher emission energy and phosphorescence quantum yield than those of complexes **11a–e**. The color of these complexes ranged from green (**10c**, R = 4-OMe) to red (**11d**, R = 5-CF₃). OLEDs fabricated by blending with PVK host polymer in a solution process, and a maximum *PE* of 10 lm W⁻¹ (*CE* = 36.5 cd A⁻¹) was observed in **10d**.

Recently, carborane was also used as the substituent in an attempt to tune the emission energy of iridium complexes.^[21] Both neutral (**12a–d**) and cationic (**13a–d**) iridium complexes with *o*-, *m*-, and *p*-carborane substituted C[^]N ligands were synthesized. It was envisaged that the bulky and cage-like carborane moieties could enhance the thermal stability. They did not show significant difference in emission energies (λ_{em} $\approx$ 516–543 nm). Emission quenching was observed in the neutral complex **12b**, which was attributed to the quenching of excited states by the C–C bond in the *o*-carborane moiety. For the cationic complex **13b**, the LUMO was largely located at the N[^]N ligand, which was not affected by the carborane. For *m*- and *p*-carboranes complexes (**12c–d**, **13c–d**), they showed an emission enhancement in both solid and solution states, and the quantum efficiencies are in the range between 44 to 67%.

The development of blue light phosphorescent complexes is essential to both multicolor display as well as white-light-emitting devices. This has been a particularly challenging area in OLED research because the operational lifetimes of blue-light-emitting materials are in general shorter than their red- or yellow-light-emitting counterparts. This is mainly due to the requirement that a high energy excited states for the charge-transport/host/light-emitting materials have to be generated. They are subject to degradation by various oxidative/reductive processes. To date, one of the most representative blue-light-emitting iridium complexes, FIrpic, was designed by introducing a fluoro group on the phenyl ring and replacing the acetylacetonate ancillary ligand by picolinate, which resulted in an increase in the HOMO-LUMO gap. Different strategies in designing blue emitting iridium complexes have been discussed.^[5a] Since then, attempts in improving the performance of blue-light-emitting cyclometalated iridium complexes were mainly achieved by introducing electron withdrawing groups on the phenyl ring or electron donating groups on the pyridine ring of the C^N ligand. The structures of some iridium complexes for the fabrication of blue- or white-light-emitting devices are shown in **Scheme 2**. Based on the FIrpic core, Cao et al. introduced phosphoryl or sulfonyl group groups on the fluoro-/difluoro-substituted phenyl ring in the C^N ligand (complexes **14a–b**).^[22] OLEDs were fabricated from solution process, and the performances were comparable to that fabricated from FIr6, a blue-light-emitting iridium complex with poly(pyrazolyl)-borate ancillary ligand.^[23] The detailed device performance data of some blue- and white-light-emitting devices fabricated by iridium complexes discussed in this paper are summarized in **Table 1**. When complex **14a** was blended with complexes with other emitting colors [Ir(ppy)₃ and (piq)₂Ir(acac)] in one single active layer with PVK host, a white-light OLED with high current efficiency ($CE = 25 \text{ cd A}^{-1}$ at 100 cd m^{-2}) and EQE (14% at 0.40 mA cm^{-2}) was obtained and the color-rendering index was enhanced to 82 (CIE = 0.17, 0.30). The introduction of diphenylphosphoryl group to pyridine instead of phenyl ring had a significant effect to the emission color. The work was reported by Li et al. in the same year.^[24] Complex **15a** emitted at lower energy compared with **14a**, and complexes **15b–d** showed lower emission energy when there is no fluoro group on the phenyl ring. When **15d** was blended with FIrpic in a two component OLED, the device emitted white light with a high CE of 23.9 cd A^{-1} ($PE = 13.9 \text{ lm W}^{-1}$, CIE = 0.29, 0.43).

The C^N ligand in complex **16** was isoelectronic with FIrpic, in which the phenyl group was replaced with a pyridyl unit. The resulting difluorosubstituted bipyridine was adopted as an C^N ligand, and the complex exhibited a blue emission with high color purity ($\lambda_{\text{max, em}} = 438 \text{ nm}$) and PL quantum efficiency (71%).^[25] When bulky groups such as mesityl, *t*-butyl, *n*-heptyl and 3-(ethyl)heptyl groups were introduced to the pyridine ring, the complexes obtained (**17a–e**) could be processed by solution method.^[26] It was found that the introduction of bulky group on the difluorophenyl group (**17e**) could enhance the quantum yield than those complexes (a–d) with bulky group (**17a–d**) on the pyridine ring. The bulky mesityl group is not coplanar with the phenyl group, which prevents the red shift of the PL, and its bulkyness also reduces the quenching of excited states significantly (PL quantum yield = 92%). Blue light OLED fabricated

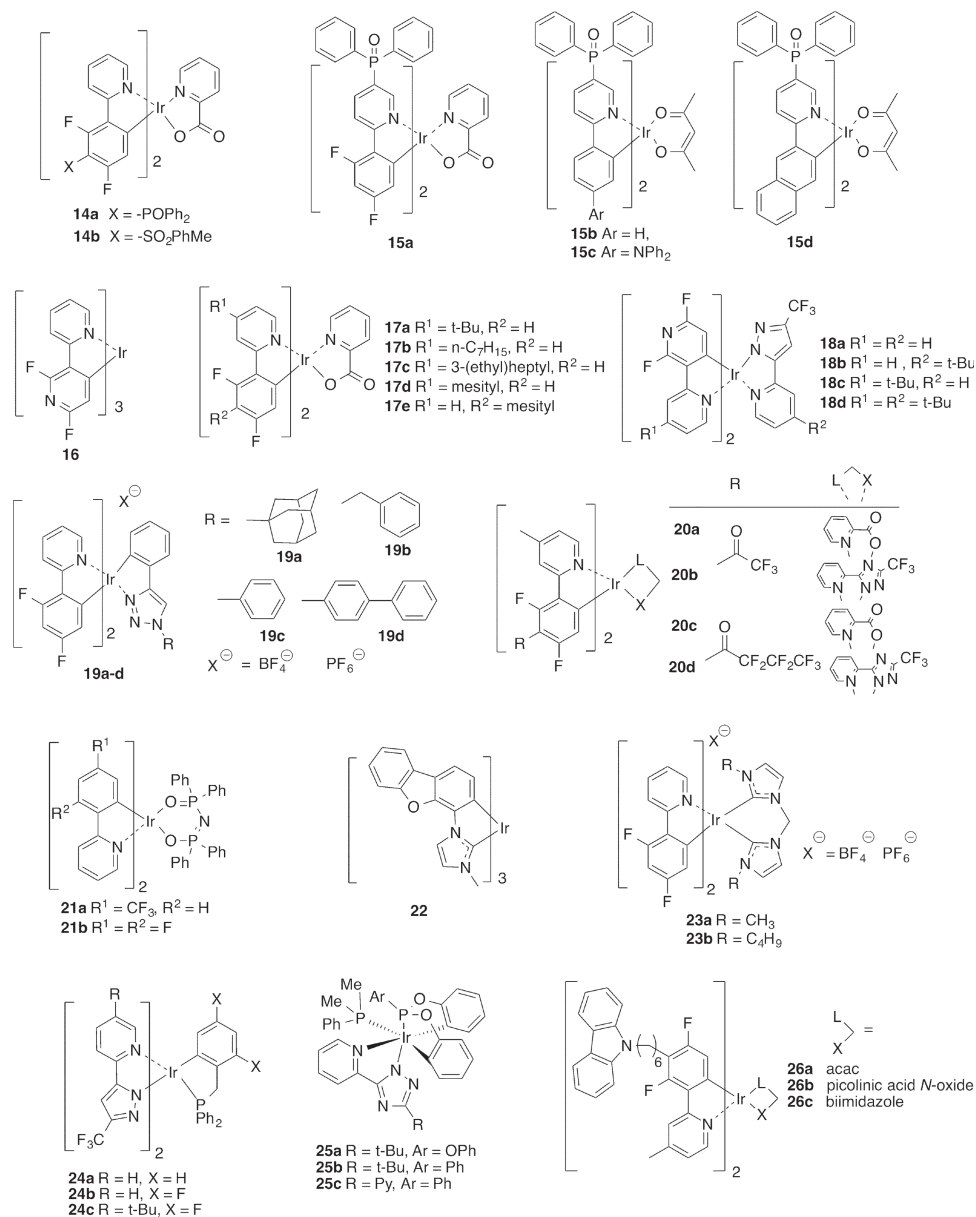
from **17e** demonstrated a CE and PE of 23.7 cd A^{-1} and 12.6 lm W^{-1} (CIE = 0.18, 0.40), respectively.

Modifying the structure of the ancillary ligands could affect the electron density at the metal center. Cyclometalated iridium complexes with ancillary ligands based on N-donor such as pyridyl-pyrazole (**18a–d**) and pyridyl-triazole (**19a–e**) were reported.^[27] For complexes **18a–d**, they exhibited high PL quantum yield in solution and when dispersed in PMMA thin film, and those with bulky groups (**18c–d**) could reduce aggregation effectively, resulting in higher quantum yield (86 and 93% when doped in PMMA). Computation studies showed that there was a strong mixing between the Ir($d(t_2g)$) and π (pyrazole) character, and the excited states were assigned to have MLCT character. OLED based on complex **18d** showed a deep blue emission, with PE measured to be 4.14 lm W^{-1} ($EQE = 7\%$, dopant concentration = 20%, CIE = 0.16, 0.19). For the blue-light-emitting complexes with triazole ancillary ligands (**19a–d**), they are ionic species and were fabricated into electrochemical cells,^[28] which exhibited a longer turn on time than OLED due to the movement of mobile ions in the device.

Kim et al. reported another series of neutral triazole and picolinate complexes **20a–d** in which an additional perfluorocarbonyl unit was introduced to the phenyl ring.^[29] Unlike the pyrazole-based complexes, the lowest triplet excited states have very strong MLCT character. The HOMO level was lowered both by the trifluoromethyl group on the triazole and the perfluorocarbonyl group on the phenyl ring, which resulted in a large bandgap. When doped in mCPPO1, the device from **20a** exhibited a very deep blue color (CIE = 0.14, 0.16) and the maximum PE and EQE measured was 19 lm W^{-1} and 17.1% respectively.

Other than N-donor ancillary ligands, iridium complexes **21a–b** based on tetraphenylimindodiphosphinate (tipi) ligand was reported.^[30] It was suggested that the more polar P=O bond would shorten the lifetime of the excited state, but the emission color was not strongly affected by the ancillary ligand. Complex **21a** and **21b** exhibited emission peak at 525 and 485 nm, with quantum yield of 12.0 and 3.81%, respectively. Interestingly, the emission of these complexes were more intense in solid state, which was attributed to the quenching of the difluoropyridine centered excited state by the ancillary ligand. However, in solid state, there were strong π – π and F– π (py) interactions, resulting in lower triplet metal-ligand-to-ligand charge-transfer (³MLCT) states that suppressed the quenching. Green and bluish-green-light-emitting devices were fabricated from them, and maximum CE and PE of 67.9 cd A^{-1} and 69.9 lm W^{-1} (CIE = 0.28, 0.65) were measured (for complex **21a**).

Nitrogen heterocyclic carbene (NHC) ligands have received tremendous attention in organometallic chemistry in recent years because metal complexes derived from them demonstrate promising potentials in catalysis.^[31] NHCs are strong field ligands with strong σ -donating and π -accepting characters.^[32] The first examples of iridium NHC complexes, Ir(pmb)₃ and Ir(pmi)₃, were reported in 2005.^[33] Compared with O- and N-donor ancillary ligands, cyclometalated iridium complexes with NHC ligands have received relatively fewer attention. It was suggested that the incorporation of strong field ligand could result in a blue shift in emission energy and an increase in blue phosphorescence efficiency.^[34] In recent years, there have been



Scheme 2. Iridium complexes for blue and white light emitting devices.

more examples of light-emitting iridium complexes derived from NHC ligands. Kido et al. reported the use of a heteroleptic *mer*-tris-(dibenzofuranyl-*N'*-methylimidazole)iridium(III) complex **22** in the fabrication of blue OLED. A maximum *EQE* of 18.6% was demonstrated.^[35] White-light OLEDs were fabricated by combining the blue-light-emitting complexes with other red and green phosphors, and highly efficient devices were obtained (*PE* = 55.2 lm W⁻¹; *CE* = 53.7 cd A⁻¹ at 1000 cdm⁻², CIE = 0.40, 0.40). For heteroleptic complexes, De Cola et al. reported a series of ionic iridium complexes **23a–b** with ancillary NHC ligands based on methyl or *n*-butyl substituted methylenediimidazolium salts.^[36] Theoretical computation results showed that both the MLCT and ³LC states have significant contribution to the emissive excited states. The light emitting electrochemical cells fabricated by solution process showed the

deepest blue emission (λ_{max} = 456, 488 nm, CIE = 0.20, 0.34) among other cationic iridium complexes reported.

Although cyclometalated iridium complexes based on N[^]C ligands are one of the most extensively studied emission complexes, the emission properties can also be tuned by using other ligands such as phosphine. Chou et al. reported the synthesis of heteroleptic iridium complexes **24a–c** with benzylphosphine and N[^]N ligands.^[37] The phosphorescence was mainly from the ³ $\pi\pi^*$ excited states with small contribution from the ³MLCT states. Subsequently, further modifications of the P-donor ligands were reported by the same group. Complexes **24a–b** are derived from benzylbis(diphenylphosphine) with or without fluoro substituents.^[38] The phosphine ligand restricts the twisting/torsional motions of the complexes, resulting in an enhancement in the quantum yield. In addition, the triplet emissive states

Table 1. Performance of white- and blue-light-emitting devices fabricated from iridium complexes discussed in this paper.

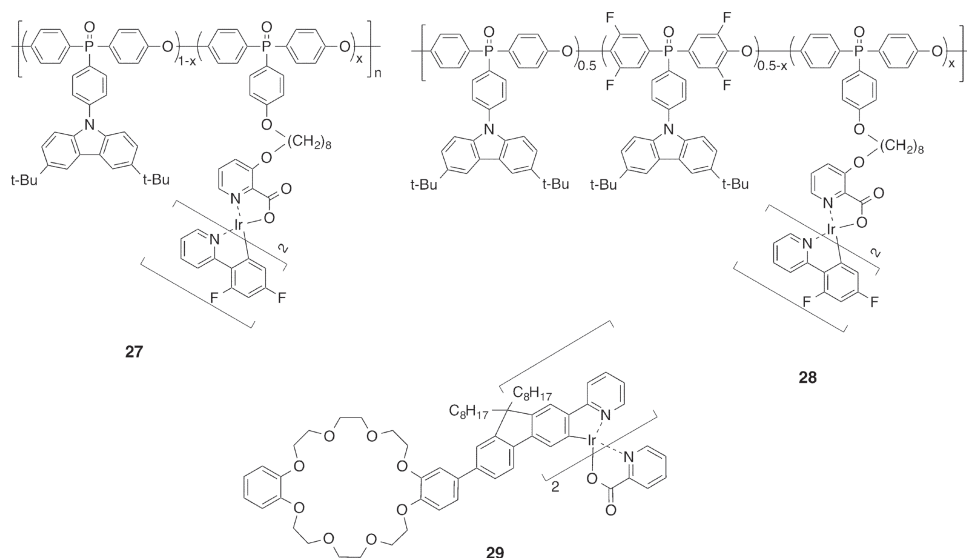
Complex	Device structure	$\lambda_{\text{max, em}}$ [nm]	CE [cd A ⁻¹]	PE [lm W ⁻¹]	EQE [%]	CIE	Ref
14a	ITO/PEDOT:PSS/PVK:OXD-7:Ir(7%)/CsF/Al	460, 489	9.8 ^{a)} 9.2 ^{b)} 5.4 ^{c)}	—	6.3 ^{a)} 5.9 ^{b)} 3.5 ^{c)}	0.17, 0.30	[22]
14b	Same as above	459, 486	7.3 ^{a)} 7.3 ^{b)} 3.8 ^{c)}	—	4.7 ^{a)} 4.7 ^{b)} 2.5 ^{c)}	0.17, 0.29	[22]
14a	ITO/PEDOT:PSS/PVK:OXD-7:Ir(7%):Ir(ppy) ₃ :(piq) ₂ Ir(acac)/CsF/Al	—	25 ^{a)} 24 ^{b)} 16 ^{c)}	—	15 ^{a)} 14 ^{b)} 9.8 ^{c)}	0.36, 0.44	[22]
15d	ITO/NPB/CBP:Ir(3%)/TPBi/LiF/Al	590	27.2 ^{a)}	15.5 ^{a)}	9.7 ^{a)}	0.56, 0.42	[24]
15d	ITO/NPB/CBP:Ir(3%)/CBP:Flrpic/LiF/Al	510, 590	23.9 ^{a)}	13.9 ^{a)}	5.4 ^{a)}	0.29, 0.43	[24]
17e	ITO/PEDOT:PSS/PVK:Ir(20%)/TPBi/LiF/Al	478	23.7 ^{a)}	12.6 ^{a)}	10.4 ^{a)}	0.18, 0.40	[26]
18d	ITO/Plexcore OC/MoO ₃ :DPBIC/DPBIC/Ir(20%): Sim CP/SimCP/P3PyPB/CsF/Al	441, 470	—	4.14 ^{a)}	7.0 ^{a)}	0.16, 0.19	[27]
20a	ITO/ReO ₃ /mCP/mCPPO1:Ir(10%)/TSPO1/LiF/Al	460	21.7 ^{a)} 21.3 ^{b)}	19 ^{a)} 15.2 ^{b)}	16.8 ^{a)} 14.9 ^{b)}	0.14, 0.16	[29]
20c	ITO/ReO ₃ /mCP/mCPPO1:Ir(10%)/TSPO1/LiF/Al	460	16.8 ^{a)} 15.3 ^{b)}	13.5 ^{a)} 10.7 ^{b)}	12.6 ^{a)} 11.5 ^{b)}	0.14, 0.17	[29]
21a	ITO/TPAC/Ir(6%):mCP/TPBi/LiF/Al	526	59.9 ^{b)} 52.7 ^{c)}	69.9 ^{a)}	—	0.28, 0.65	[30]
21b	ITO/TPAC/Ir(10%):mCP/TPBi/LiF/Al	489	25.4 ^{b)} 23.7 ^{c)}	23.5 ^{a)}	—	0.15, 0.50	[30]
22	ITO/TAPC/Ir(10%):PO9/B3PyPB/LiF/Al	445	20.5 ^{b)} 9.4 ^{c)}	19.6 ^{b)} 6.3 ^{c)}	13.3 ^{b)} 6.2 ^{c)}	0.15, 0.19	[35]
22	ITO/TAPC/TCTA/PQ ₂ Ir(dpm):CBP/Ir(ppy) ₃ :CBP/Ir(10%):PO9/ B3PyPB/LiF/Al	—	53.7 ^{b)} 49.6 ^{c)}	55.2 ^{b)} 43.3 ^{c)}	23.3 ^{b)} 21.5 ^{c)}	0.40, 0.40	[35]
24c	ITO/NPD/TCTA/CzSi/Ir(6%):CzSi/comp-lex:UGH2/UGH2/BCP/ Cs ₂ CO ₃ /Ag	428, 455	11.3 ^{a)} 7.7 ^{b)}	8.6 ^{a)} 3.1 ^{b)}	11.7 ^{a)} 8.2 ^{b)}	0.16, 0.11	[38]
25a	ITO/TAPC/TCTA/CzSi/Ir(4%):CzSi/comp-lex: UGH2/UGH2/TmPyPB/LiF/Al	451, 473, 498	22.3 ^{a)} 16.9 ^{b)}	16.7 ^{a)} 8.1 ^{b)}	11 ^{a)} 8.4 ^{b)}	0.22, 0.34	[39]
26a	ITO/PEDOT:PSS/PVK:OXD-7:UGH3:Ir(8%)/OXD-7/Ba/Al	487	20.8 (12 V)	5.8 (12 V)	7.2 (12 V)	0.21, 0.55	[40]
28 (x = 0.05)	ITO/PEDOT:PSS/Ir/TPCz/LiF/Al	470	19.4 ^{a)}	10.0 ^{a)}	9.0 ^{a)}	0.18, 0.33	[46]

^{a)}Maximum value measured; ^{b)}Measured at 100 cd mA⁻²; ^{c)}Measured at 1000 cd mA⁻².

were dominated by the pyridylazole-based intraligand charge-transfer transition with little contribution from the ³MLCT states. Deep blue emissions were observed in the OLEDs fabricated from **24c** showed a peak *PE* of 8.6 lm W⁻¹ (CIE = 0.16, 0.11). In a later report, the efficiency was improved by the use of a phosphite tripod P⁺C⁻C type ligand in complexes **25a–c**.^[39] It was suggested that the tripod ligand could enhance the long term stability of the complex in device operation. In addition, the phosphorus is a strong σ -donor, which could destabilize the metal centered *d-d* excited state that caused the quenching of the radiative states. The emission of the complexes was dominated by the pyridyltriazolate moieties. Devices fabricated from

25a–c (max *PE* = 8.6 lm W⁻¹) generally showed improved efficiencies compared with **24a–b** (max *PE* = 16.7 lm W⁻¹).

In a paper by Kim et al., a different approach was adopted in the design of the C⁺N ligand.^[40] A pendant hexylcarbazolyl moiety was attached to the 3-position of the phenyl ring, which was substituted by two fluoro groups at the 2 and 4 positions. Complexes **26a–c** were obtained by varying the ancillary ligands. It was envisaged that the carbazole unit could improve the blue light emission and charge-transport properties. An intramolecular energy transfer between the carbazole to the iridium core was proposed, which resulted in an increase in luminous intensity without changing the emission color. The



Scheme 3. Structures of some polymeric iridium complexes.

maximum PE measured for **26c**-based device was 7.16 lm W^{-1} at 12 V (CIE = 0.21, 0.55).

2.1.2. Iridium-Complex-Containing Polymers

Compared with molecular iridium complexes, there has been less research work done on phosphorescent iridium-containing polymers. In the process of device fabrication, polymeric materials enjoy the advantages that large area devices can be fabricated at relatively lower cost by solution processes such as spin-coating, casting, or printing techniques. Most of the research done in this area involved the incorporation of the necessary functional units (charge carriers, light emitters) into the polymer main chain and/or side chain. For example, iridium complexes were attached to different saturated or conjugated polymer backbones including poly(styrene-vinyl-carbazole) copolymer,^[41] polystyrene,^[42] polyfluorene,^[43] and poly(fluorenyl-carbazoyl)^[44] copolymers. Dendritic molecules with iridium complexes as the core have also been reported.^[45] In the past few years, there have been several examples of iridium-complex-containing polymers for light emitting applications. Two series of polymers **27–28** (Scheme 3) with fluorinated poly(phenylene ether phosphine oxide) main chains incorporating different proportions of carbazole- and FIrpic-based pendant groups were reported by Ding et al.^[46] The polymer backbones had improved charge-injection properties due to its higher HOMO and lower LUMO levels compared with PVK, while a high triplet energy (2.96 eV) was retained.^[47] The emission of the polymer films was dominated by the FIrpic phosphorescence without contribution from the pendant carbazole, and the intensity was dependent on the iridium complex loading. The EL device demonstrated peak CE and PE of 19.4 cd A^{-1} and 10.0 lm W^{-1} (CIE = 0.18, 0.33), respectively.

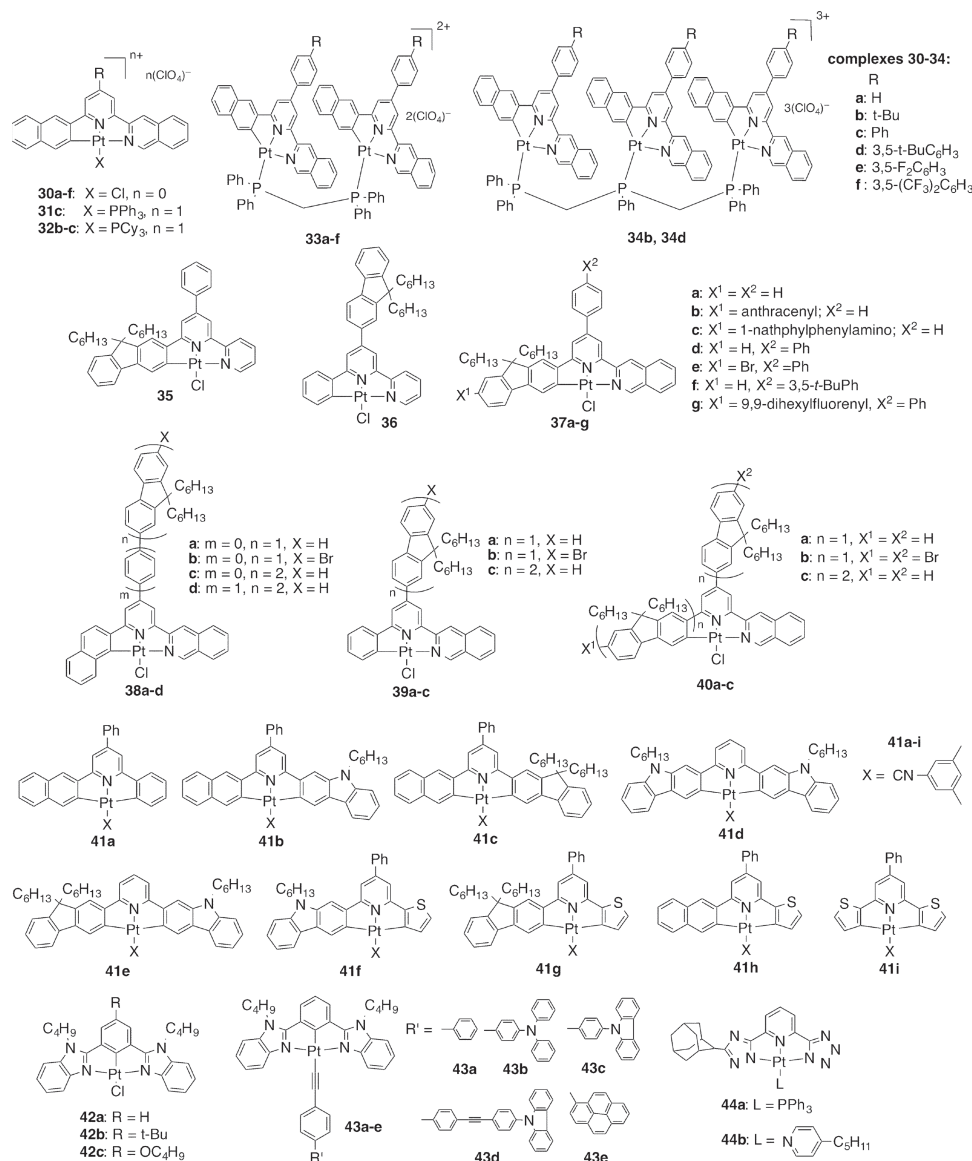
In a more recent paper, Huang et al. synthesized light emitting iridium complex **29** with dibenzo-24-crown-8 end groups, which was used to build supramolecular structures with other

oligofluorene derivatives with dialkylammonium end groups crown ether or alkylammonium end-capped oligofluorene.^[48] The building blocks assembled to each other by the interaction between the crown ether and ammonium moieties beyond a critical concentration (ca. 18 mM). The PL quantum efficiency of the polymer films were in the range between 17–21%, depending on the iridium loading, and was significantly higher than that of the iridium complex monomer (7.7%). An energy transfer from the oligofluorene backbone to the iridium complex was proposed. The EL device exhibited an emission at 562 nm. It was interesting to observe that the CE of the device increased with increasing iridium content, in contrary to other observations that the device performance degraded with higher iridium content due to triplet-triplet annihilation. The reason proposed was that the increasing the iridium complex content could effectively trap holes and the complexes therefore acted as hole carriers.

2.2. Platinum Complexes

Although the first example of organic phosphorescent light emitter was based on platinum porphyrin,^[3] research effort on platinum complexes for OLED applications was relatively few compared with those iridium analogues. In fact, the phosphorescence properties of platinum(II) complexes with d^8 electronic configuration can be tuned by various means due to the unique square planar geometry, and comprehensive reviews have been presented.^[8b,49] In recent years, research on phosphorescent platinum(II) complexes was mainly focused on the development of emitters with high color purity for white-light OLED, and new strategies in structural modification for color tuning.

Square planar cyclometalated platinum(II) complexes have been shown to be promising candidates as alternatives of iridium complexes. These types of complexes exhibit several emissive excited states ligand field (LF), MLCT, LC, and excimeric states due to the strong Pt–Pt interaction. The versatility



Scheme 4. Structures of cyclometalated platinum complexes.

in tuning the structures of the ligands allows us to fine tune the excited states. In this section, cyclometalated platinum complexes based on tridentate ligand of the type C[^]N[^]N, C[^]N[^]C, and N[^]C[^]N for phosphorescent OLED application will be discussed, and the structures of these complexes are shown in **Scheme 4**. Compared with the bidentate C[^]N cyclometalated platinum complexes, complexes with tridentate ligands have a more rigid square planar geometry, which restricts the distortion of the complex that may result in non-radiative decay of the excited states. In addition, modification of the ancillary ligand can also be achieved by replacing the chloride group by other strong σ -donor ligands, resulting in the destabilization of the $d-d^*$ states that can also quench the emission from the triplet states.^[50] In some square planar cyclometalated platinum complexes, strong inter- or intramolecular Pt–Pt interactions were observed.^[51] The interaction between the dz^2 orbitals of the complexes lead to a new $d(\sigma^*-\pi^*)$ transition.^[52] Such a transition

may have lower energy than that of the $\pi-\pi^*$ transition. This opens a new avenue in the color tuning of platinum phosphorescent complexes. Che et al. demonstrated the design of different di- and trinuclear cyclometalated platinum complexes **30–34** with C[^]N[^]N type ligands.^[50] X-ray crystallographic results showed that there were strong $\pi-\pi$ stacking between the aromatic rings, which oriented in pairs and anti to each other. A relatively short Pt–Pt distance (3.165 Å) was observed in dinuclear complex **33a**, while in other dinuclear (**33b–f**) and trinuclear (**34b, d**) complexes, different degrees of intramolecular Pt–Pt interactions were also observed. In the absorption spectra, the dinuclear and trinuclear complexes exhibited absorption bands in the region between 420–525 and 450–550 nm, respectively, which were assigned to be the $d(\sigma^*-\sigma^*)(\pi)$ transition as a result of the Pt–Pt interactions. The corresponding low energy emissions from the triplet metal-metal-to-ligand charge-transfer ³MMLCT [$d\sigma^*-\sigma(\pi^*)$] excited states were observed at

585–637 nm, which showed a red shift when compared with the mononuclear complexes. OLEDs were fabricated from the neutral mononuclear complexes (**30a**, **30f**) with chloride as the ancillary ligand, and these green light emitting devices demonstrated *CE* in the range 12.5–15.4 cd A⁻¹. White-light-emitting OLEDs were fabricated with two emissive layers composed of a blue emitter (9,10-bis-(2-naphthyl)-anthracene) (DNA) and platinum complex **30a** or **30f**.^[53] **30f** demonstrated the best device performance, and the maximum *PE*, *CE*, and *EQE* were measured to be 18.4 lm W⁻¹, 26.4 cd A⁻¹, and 11.8%, respectively (CIE = 0.30, 0.32). **Table 2** summarizes the device performances of different OLEDs fabricated from selected platinum and other transition metal complexes discussed in this paper.

The use of naphthyl and isoquinolinyl ligands in cyclometalated Pt complexes was further explored by the synthesis of different C[∧]C[∧]N- and C[∧]N[∧]N-based complexes. Systematic structure modification on the C[∧]N[∧]N core ligand was done.^[54] Complexes based on 6 ligands with different C-donors including naphthyl (**38a–d**), phenyl (**36**), fluorenyl (**35**, **37a–g**, **40a–c**) and with N-donors including pyridyl (**35**, **36**) and isoquinolinyl (**37–40**) groups were synthesized. The 4-position of the central pyridine ring was modified by phenyl or oligofluorene units. Crystallographic data showed that there existed a substantial π - π overlap between the fluorene-based ligands, but no Pt–Pt interaction was observed. Complexes with fluorenyl and naphthyl peripheral units (**37d**, **37f**) showed very high emission quantum yield in solution (73%). Introduction of a fluorenyl group resulted in significant red shift in the emission spectra, owing to the rise in the d^o(Pt) level and increase in the gap between the MLCT and the non-emission *d–d* states. For the OLED fabricated from complex **37d**, it showed the best device performance with maximum *PE*, *CE* and *EQE* of 9.2 lm W⁻¹, 14.7 cd A⁻¹, and 5.5% respectively (CIE = 0.53, 0.46).

For the Platinum complexes (**41a–i**) with tridentate C[∧]N[∧]C type ligands,^[55] naphthyl, fluorenyl, and thienyl groups were used as the peripheral ligand and the ancillary ligand was based on 2,6-dimethylphenylisocyanide. These neutral complexes exhibited a wide range of emission colors in the green to red regions, originated from the triplet excited states dominated by the mixed ³IL/³MLCT character. Like the C[∧]N[∧]N ligands mentioned above, π - π stacking between ligands was observed (interplanar distance = 3.3–3.5 Å), but there was no Pt–Pt interaction (shortest Pt–Pt distance = 6.967 Å). Complex **41h** with one naphthyl and one fluorenyl unit exhibited the highest emission energy ($\lambda_{\text{max}} \approx 564$ –568 nm), while the one with two phenyl units had the lowest emission energy ($\lambda_{\text{max}} \approx 611$ –619 nm), which were assigned to be originated from the mixed ³MLCT/³IL states. Those complexes with more electron rich ligand (carbazole-**41b**, **41d**, **41f**, **41e**, thiophenyl-**41f–i**) had the HOMO destabilized and showed a red shift in the emission spectra. OLEDs were fabricated by either vacuum deposition (with mCP as the host) or spin-casting (blending with PVK) techniques. Device from **41g** showed the maximum *CE*, *PE*, and *EQE* of 13.9 cd A⁻¹, 10.9 lm W⁻¹, and 12%, respectively (CIE = 0.65, 0.34).

Other than C[∧]N[∧]N type ligands, platinum complex **42a** derived from cyclometalated ligands of N[∧]C[∧]N type were reported by Yam et al.^[56] The central ligand was based on 1,3-bis(*N*-alkylbenzimidazol-2'-yl)benzene and the ancillary

ligand was chloride. The OLED exhibited efficient green light emission with *CE*, *PE*, and *EQE* of 38.9 cd A⁻¹, 27.2 lm W⁻¹, and 11.5%, respectively. In a later report, the complex was modified by introducing different substituents to the phenyl ring (complexes **42b–c**), and by replacing the chloride by various substituted acetylides (complexes **43a–e**).^[57] The presence of a rigid N[∧]C[∧]N type ligand was shown to be able to enhance the molecular rigidity of the complexes, resulting in a lower degree of molecular distortion and suppression of non-radiative decay. In addition, it also reduced the intensity of the vibrational satellite bands in the green light region, giving a higher color purity.^[58] For the complexes with chloride or phenylacetylide ancillary ligands (**42a**, **43a–e**), the triplet excited states were composed of a mixed π - π^* (benzimidazole) and ³MLCT [*d*_π(Pt)- π^* (benzimidazole)] characters. When the ancillary ligands were extended to arylacetylide or pyrenylacetylide (**43d**, **43e**), the lowest triplet excited state had IL [π - π^* (C $\equiv$ C-R')] character. Devices with improved color purity were fabricated by the incorporation of dual emissive layers, to which the complexes were doped into both mCP and TAZ layer. The optimized devices only exhibited pure vibronic-structured emission from the platinum complexes without contribution from BALq. The device based on complex **43e** showed dual emissions in the green and red regions (CIE = 0.35, 0.39), which was very close to pure white light.

The use of N[∧]N[∧]N type cyclometalated Pt complexes in OLED was reported by De Cola et al.^[59] Complexes **44a–b** were derived from an asymmetric ligand with triazole and tetrazole substituted pyridine with phosphine or pyridine ancillary ligands. The bulky adamantyl group was to enhance the solubility/processibility and to prevent axial interactions between molecules. Due to its asymmetric nature, it was interesting to see that the HOMO of the complexes was mainly from the mixed π (triazole) and *d*_{xz}(Pt), with only minor contribution from the π (pyridine) and π (tetrazole). The LUMO was mainly centered at the pyridine moiety. The solutions of these complexes did not show aggregation effect when the PL spectra were measured at high concentration, indicating that the adamantyl group was effective in preventing the interactions between molecules. Solution processed OLED from **44a** and **44b** exhibited *PE* of 3.9 and 4.7 lm W⁻¹, respectively. For devices fabricated by vacuum deposition, **44b** showed a better performance with *CE*, *PE* and *EQE* of 15.5 cd A⁻¹, 16.4 lm W⁻¹, and 5.6%, respectively.

One approach to further rigidify the platinum complex framework is to adopt tetradentate ligands composed of C, N, or O donors. The use of Schiff base or hydroxyphenyl substituted phenanthroline platinum complexes for OLED applications was reported in early 2000s.^[60] A series of O₂N₂ type Schiff base platinum complexes was synthesized and their photophysical and OLED properties were investigated. Various bridging units were used to link the two Schiff base ligands, to which different electron donating or withdrawing groups were also introduced.^[61] These complexes emitted in the yellow to red region with maximum quantum yield of 27%. Temperature-dependent emission lifetime measurements revealed that these complexes have significant triplet MLCT character (zero-field splitting = 14–28 cm⁻¹). The structures of various emissive platinum complexes based on tetradentate ligands are shown in **Scheme 5**.

Table 2. Performance of light emitting devices fabricated from platinum, gold, and other transition metal complexes discussed in this paper.

Complex	Device structure	$\lambda_{\text{max, em}}$ [nm]	CE [cd A ⁻¹]	PE [lm W ⁻¹]	EQE [%]	CIE	Ref
Platinum Complexes							
30a	ITO/NPB/ Pt (5%):CBP/BCP/Alq3/LiF/Al	532, 570	15.4 ^{a)}	15.4 ^{a)}	—	0.37, 0.58	[50]
30d	ITO/NPB/ Pt (3%):CBP/BCP/Alq3/LiF/Al	540, 592	20.2 ^{a)}	12.5 ^{a)}	—	0.38, 0.55	[50]
30a	ITO/NPB/ Pt (5%):CBP/NPB/DNA/BCP/Alq3/LiF/Al	469, 532, 592	—	12.6 ^{a)} 10.1 ^{b)} 6.0 ^{c)}	11 ^{a)} 10.6 ^{b)} 7.3 ^{c)}	0.32, 0.37	[53]
30f	ITO/NPB/ Pt (5%):CBP/NPB/DNA/BCP/Alq3/LiF/Al	440, 552, 591	26.4	18.4 ^{a)} 8.5 ^{b)} 3.7 ^{c)}	11.8 ^{a)} 7.1 ^{b)} 4.2 ^{c)}	0.30, 0.32	[53]
37d	ITO/NPB/ Pt (2%):CBP/BCP/Alq3/LiF/Al	572, 611, 670	14.7 ^{a)}	9.2 ^{a)}	5.5 ^{a)}	0.53, 0.46	[54]
39c	ITO/NPB/ Pt (8%):CBP/BCP/Alq3/LiF/Al	551, 594, 666	13.9 ^{a)}	5.5 ^{a)}	4.2 ^{a)}	0.44, 0.54	[54]
37f	ITO/PEDOT:PSS/ Pt (5%):PVK/BCP/LiF/Al	564, 608, 666	9.2 ^{a)}	3.7 ^{a)}	3.4 ^{a)}	0.52, 0.47	[54]
41g	ITP/PEDOT:PSS/ Pt (5%):PVK/BCP/LiF/Al	608	1.04 ^{a)}	—	—	0.62, 0.35	[55]
41h	ITP/PEDOT:PSS/ Pt (5%):PVK/BCP/LiF/Al	596	1.14 ^{a)}	—	—	0.52, 0.33	[55]
41g	ITO/NPB/TCTA/ Pt (8%):mCP/BAIq/LiF/Al	608	13.9 ^{a)} 5.3 ^{c)}	10.9 ^{a)} 2.2 ^{c)}	12 ^{a)} 4.2 ^{c)}	0.65, 0.34	[55]
41h	ITO/NPB/TCTA/ Pt (6%):mCP/BAIq/LiF/Al	631	13.4 ^{a)} 5.1 ^{c)}	10.5 ^{a)} 2.2 ^{c)}	12.6 ^{a)} 4.2 ^{c)}	0.64, 0.36	[55]
42a	ITO/NPB/CBP/ Pt (6%):CBP/BAIq/LiF/Al	511, 548, 594	17.8 ^{a)}	12.4 ^{a)}	5.7 ^{a)}	0.28, 0.60	[56]
42a	ITO/NPB/TCTA/ Pt (8%):CBP/ Pt (8%):TAZ/BAIq/LiF/Al	513, 551, 603	38.9 ^{a)}	27.2 ^{a)}	11.5 ^{a)}	—	[57]
42b	Same as above	514, 552, 602	40.3 ^{a)}	28.1 ^{a)}	11.8 ^{a)}	—	[57]
42c	Same as above	535, 580, 628	34.7 ^{a)}	26.4 ^{a)}	10.0 ^{a)}	—	[57]
43e	ITO/PEDOT:PSS/ Pt (5%):mCP/TAZ/BAIq/LiF/Al	—	—	—	—	0.35, 0.39	[57]
44a	ITO/PEDOT:PSS/QUPD/OTPD/ Pt (15.6%):PVK:OXD-7/TPBi/CsF/Al	508, 541	13.4 ^{a)}	13.8 ^{a)}	4.9 ^{a)}	—	[59]
44b	ITO/PEDOT:PSS/QUPD/OTPD/ Pt (13.5%):PVK:OXD-7/TPBi/CsF/Al	573	15.5 ^{a)}	16.4 ^{a)}	5.6 ^{a)}	—	[59]
45a	ITO/NPB/ Pt (4%):CPB/BCP/Alq3/LiF/Al	554	31 ^{a)}	—	—	0.48, 0.52	[61]
45b	ITO/NPB/ Pt (1.5%):CPB/BCP/Alq3/LiF/Al	632	10.8 ^{a)}	4.9 ^{a)}	9.4 ^{a)}	0.65, 0.35	[61]
46a	ITO/CFx/NBP/ Pt (4%):CBP/BAIq/Alq3/Mg:Ag	512	50 ^{d)} 37 ^{e)}	—	14.7 ^{d)} 10.6 ^{e)}	0.32, 0.62	[62]
47a	ITO/PEDOT:PSS/NPD/ Pt (6%):Bebq2/TPBi/LiF/Al	620	—	10.7 ^{b)} 6.7 ^{c)}	17.2 ^{b)} 14.4 ^{c)}	0.67, 0.33	[63]
47a	ITO/ND-1501/NPD/ Pt (6%):Bebq2/ETM-143/LiF/Al	620	—	20.7 ^{b)} 11.9 ^{c)}	18.5 ^{b)} 14.4 ^{c)}	0.66, 0.34	[63]
48a	PEDOT:PSS/NPD/TAPC/ Pt (2%):26mCPy/PO15/ LiF/Al	442	—	3.7 ^{b)} 0.25 ^{c)}	4.1 ^{b)} 0.5 ^{c)}	0.15, 0.10	[64]
48b	same as above	452	—	14.3 ^{b)} 6.6 ^{c)}	13.5 ^{b)} 8.35 ^{c)}	0.14, 0.19	[64]
48b	ITO/HATCN/NPD/TAPC/ Pt (6%):26mCPy/DPPS/ LiF/Al	442	—	26.9 ^{a)} 16.8 ^{b)} 10.2 ^{c)}	23.7 ^{a)} 20.4 ^{b)} 15.4 ^{c)}	0.15, 0.14	[64]
48c	Same as above	449	—	20.6 ^{b)} 11.7 ^{c)}	23.3 ^{b)} 16.8 ^{c)}	0.15, 0.13	[64]
49e	ITO/NPB/TCTA/ Pt (6%):mCP/BAIq/LiF/Al	—	71 ^{a)}	55.8 ^{a)}	16.5 ^{a)}	0.33, 0.42	[66]
49e	ITO/PEDOT:PSS/ Pt (16%):PVK:OXD-7/TmPyPb/LiF/Al	—	17 ^{b)}	9.1 ^{b)}	9.7 ^{b)}	0.43, 0.45	[66]
Gold Complexes							
50a	ITO/NPB/Au(4%):CBP/BAIq/LiF/Al	528	37.4 ^{a)}	26.2 ^{a)}	11.5 ^{a)}	—	[67]

Table 2. Continued

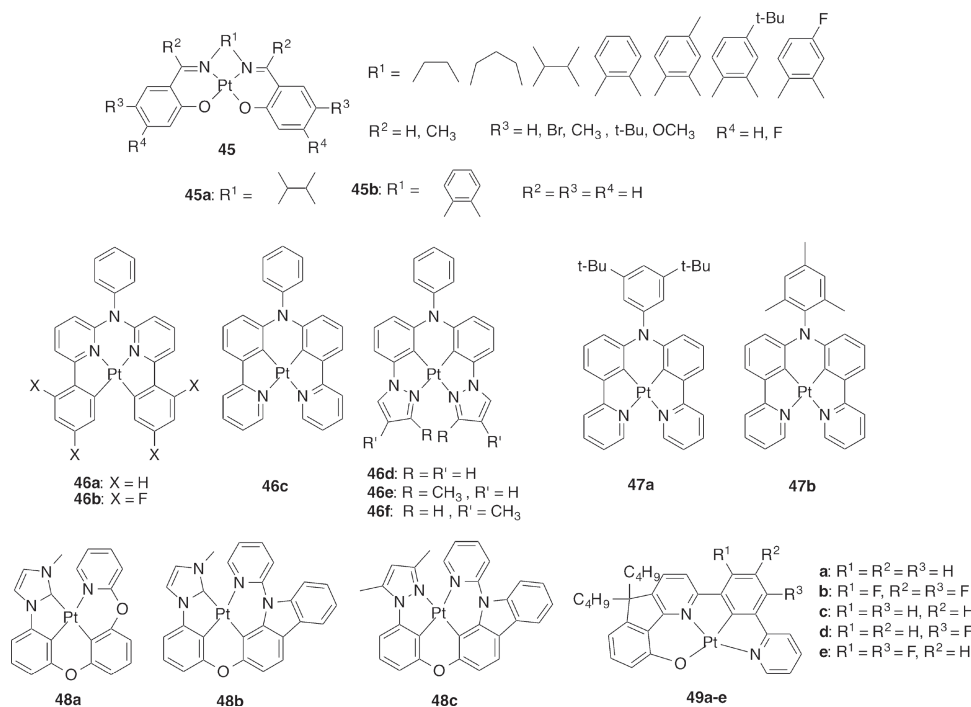
Complex	Device structure	$\lambda_{\text{max, em}}$ [nm]	CE [cd A ⁻¹]	PE [lm W ⁻¹]	EQE [%]	CIE	Ref
50b	ITO/PEDOT:PSS/Au(10%):mCP/3TPYMB/TmPyPB/ LiF/Al	548	22.0 ^{b)} 24.0 ^{f)}	9.0 ^{b)} 14.5 ^{f)}	7.8 ^{f)}	0.50, 0.49	[68]
50c	Same as above	528	21.9 ^{f)}	16.4 ^{f)}	7.0 ^{f)}	0.33, 0.55	[68]
50d	Same as above; dopant concentration = 20%	520	11.4 ^{f)}	9.6 ^{f)}	3.8 ^{f)}	0.30, 0.53	[68]
Osmium Complexes							
51c	ITO/PEDOT:PSS/VB-FNPD/Os(10%):TCTA/TPBi/CsF/Al	582	42.1 ^{a)} 41.0 ^{b)}	47.2 ^{a)} 39.6 ^{b)}	15.7 ^{a)} 15.4 ^{b)}	0.49, 0.48	[69]
51d	same as above	518	48.3 ^{a)} 34.2 ^{b)}	50.9 ^{a)} 22.2 ^{b)}	15.6 ^{a)} 11.0 ^{b)}	0.30, 0.53	[69]
Rhenium Complexes							
52a	ITO/TAPC/Re(2%):mCP/BP4mPy/LiF/Al	527	17.9 ^{a)} 15.8 ^{b)}	12.6 ^{a)} 8.5 ^{b)}	5.9 ^{a)} 5.2 ^{b)}	0.31, 0.54 ^{b)} 0.29, 0.51 ^{c)}	[71]
52b	same as above, dopant concentration = 1%	565	30.3 ^{a)} 29.6 ^{b)}	22.6 ^{a)} 16.3 ^{b)}	10.0 ^{a)} 9.7 ^{b)}	0.43, 0.54 ^{b)} 0.42, 0.54 ^{c)}	[71]

^{a)}Maximum value measured; ^{b)}Measured at 100 cd mA⁻²; ^{c)}Measured at 1000 cd mA⁻²; ^{d)}Measured at 0.01 mA cm⁻²; ^{e)}Measured at 10 mA cm⁻²; ^{f)}Measured at 20 mA cm⁻².

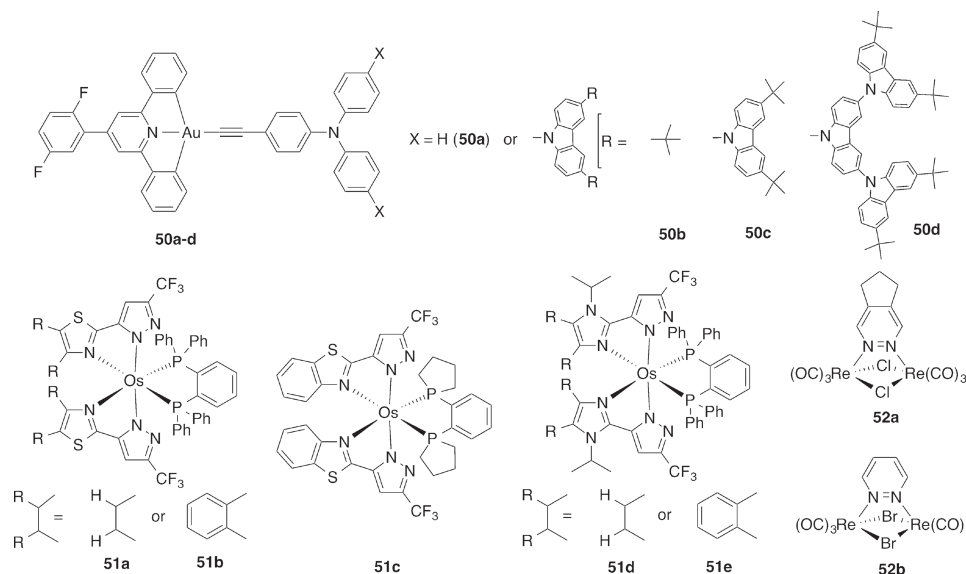
Complex **45b** with rigid phenylene bridge and without peripheral substitution groups showed better OLED performance (PE and $EQE = 4.9 \text{ lm W}^{-1}$ and 9.4%, CIE = 0.65, 0.35) compared with that with bulky but less rigid bridging unit (complex **45a**).

Recently, there have been more examples of tetradentate cyclometalated platinum complexes with N and C donors. Complexes **46a–f** were synthesized from the corresponding

C[^]N[^]N[^]C and N[^]C[^]C[^]N tetradentate ligands that contain a phenylimino bridging unit and pyridine/pyrazole as the N-donor ligands.^[62] From DFT calculations, it was interesting to see that the HOMOs were contributed by the platinum center and the triarylamino bridging unit but with small contribution from the phenyl rings, while the LUMOs were localized at the pyridine or pyrazole moieties. All these complexes showed distorted



Scheme 5. Structures of platinum complexes based on tetradentate ligands.



Scheme 6. Structures of emissive gold, osmium, and rhenium complexes for OLEDs.

square planar geometry in which the two C[∧]N coordinations are twisted. This was in particular significant in complex **46e**, in which the methyl groups on the pyrazole had strong steric repulsion. Their solutions emitted in the range between blue to red region ($\lambda_{\text{max}} \approx 474$ nm for complex **46e** and 613 nm for **46c**), and a significant red shift in emission was observed in the solid states. OLEDs fabricated from **46a** exhibited *CE* and *EQE* of 37 cd A^{−1} and 10.6%, respectively (at 10 mA cm^{−2}). Fukagawa et al. reported the fabrication of OLEDs fabricated from complexes **47a–b** with similar N[∧]C[∧]C[∧]N ligand structures.^[63] Complex **47a** has a more bulky bridging unit, and the energy level of its triplet ³MLCT excited state was lower than those of CBP or Beq₂ hosts, which suppressed any energy transfer from the complex to the hosts. Maximum *EQE* and *PE* of 18.5% and 20.7 lm W^{−1} (CIE = 0.66, 0.34) were measured in the **47a**-based OLED when Beq₂ was the host (at 100 cd m^{−2}).

The bridging unit and the type of C and N donor can be further modified in order to tune the emission color of the complexes. Li et al. reported a series of blue-light-emitting cyclometalated complexes **48a–c** with oxygen bridged tetradentate C[∧]C[∧]C[∧]N and N[∧]C[∧]C[∧]N ligands.^[64] Complexes **48a** and **48b** were derived from the tridentate analogue with two NHC ligands.^[65] They showed less intense vibronically structured emission at room temperature, had much fast radiative decay rate than other platinum or iridium analogues, and did not show excimer emission. OLED from **48b** showed a maximum quantum yield of 23.7% at 2 cd m^{−2}, and it decreased only to 15% at 1000 cd m^{−2} (max *PE* = 26.9 lm W^{−1}, CIE = 0.15, 0.14). The blue color emitted was shown to have higher purity (CIE = 0.15, 0.19) than those of fluorine free iridium complexes.

Structural modification of these tetradentate ligands may be further refined by the introduction of both C, N, and O donors in the same molecule. It was illustrated by a series of cyclometalated O[∧]N[∧]C[∧]N Pt complexes (**49a–e**) synthesized by Che et al.^[66] It was found that the substituents on the phenyl ring could greatly affect the emission properties of the complexes. All of them exhibited high PL quantum yield in solution (ca.

72–93%), and the emission peaks were in the range between 480–520 nm, which were assigned to the triplet emission with mainly ligand character. When the concentration of the solution was increased, low energy emission band centered at ca. 620 nm was observed. This was assigned to the excimer emission. Theoretical calculation results suggested these two emissions originated from two different triplet excited states. Complex **49e** showed the strongest low energy emission, and it was used to fabricate while OLED with only single emitter by doping in mCP host, and the device exhibited very high *CE*, *PE* and *EQE* of 71 cd A^{−1}, 55.8 lm W^{−1}, and 16.5%, respectively, as well as good white color quality (CIE = 0.33, 0.42). Devices fabricated with a PVK host exhibited lower efficiency (max. *PE* = 9.1 lm W^{−1}) and less pure white color (CIE = 0.43, 0.45). The results demonstrated the feasibility in the fabrication of while OLED with only one emissive component, which could greatly simplify the device fabrication process.

2.3. Other Transition Metal Complexes

The use of complexes derived from transition metals other than iridium and platinum for OLED applications has not been extensively explored. Nevertheless, there have been some examples reported in recent years. Some examples of these complexes are shown in **Scheme 6**. Yam et al. reported the synthesis and OLED applications of cyclometalated gold(I) complexes in 2010.^[67] The complex (**50a**) contained a cyclometalated C[∧]N[∧]C type ligand and a substituted acetylide ancillary ligand. Gold is a relatively less expensive metal compared with platinum and iridium, and also has lower toxicity. One of the challenges is to develop emissive gold complexes with good thermal stability for device fabrication process. Complex **50a** had high thermal stability (decomposition temperature > 460 °C). Like other planar cyclometalated complexes, a π - π stacking interaction was observed between the aromatic rings. It showed a broad structureless emission band between 500–800 nm ($\lambda_{\text{max}} \approx 669$ nm),

which was assigned to the $^3\text{LLCT}$ state [$\pi(\text{substituted acetylene}) - \pi^*(\text{C}^*\text{N}^*\text{C} \text{ ligand})$]. In concentrated solution, excimeric emission due to the π stacking was observed. In the OLED, the complex was doped into a CBP layer, and a maximum CE and PE of 37.4 cd A^{-1} and 26.2 lm W^{-1} were measured ($\text{EQE} = 11.5\%$). The structure of this gold(I) complex was further modified in order to optimize the OLED performance.^[68] The ancillary ligand was changed to dendritic carbazole units (complexes **50b–d**). Similar to complex **50a**, both $^3\text{LLCT}$ and excimer emission were observed in concentrated solution. It was interesting to observe that for the ancillary ligand with higher generation of carbazole dendron, the HOMO energy level was lower, which was attributed to the inductive electron withdrawing nature of the carbazole. Therefore, the emission energies of the complexes are in the order **50d** > **50c** > **50b**. The best OLED device performance was observed in **50b** (max $CE = 24 \text{ cd A}^{-1}$, $PE = 14.5 \text{ lm W}^{-1}$, $\text{EQE} = 7.8\%$, $\text{CIE} = 0.50, 0.49$), and the increase in the dendron generation did not result in a significant degradation in performance (CE , PE , and EQE for complex **50c** = 21.9 cd A^{-1} , 16.4 lm W^{-1} , 7.0% , $\text{CIE} = 0.33, 0.55$). Complex **50d** showed the lowest efficiency among these complexes, but the charge-transport properties were improved, as can be seen from the lower device driving voltage.

The synthesis of osmium complexes **51a–e** with various azole chelates and phosphine ligands was reported by Chou et al.^[69] The HOMO and LUMO of these complexes were mainly localized at the osmium center and azole ligands, respectively, and the lowest excited states have mixed MLCT and ILCT characters. The presence of a low-lying triplet metal centered $^3\text{MC } d-d$ state resulted in a non-radiative deactivation in complex **51e**. Such a $d-d$ state was lower in energy than that of the $^3\text{MLCT}/\pi\pi^*$ state. As a result, complex **51e** was not emissive in nature. OLED from complexes with benzothiazole N -donor (**51a–c**) exhibited emission in the orange-red region, while the one with benzimidazole N -donor (complex **51e**) exhibited green emission. Complexes **51c** and **51d** showed the best device performance with max CE/PE of $42/48 \text{ cd A}^{-1}$ and $47.2/50.9 \text{ lm W}^{-1}$ ($\text{CIE} = 0.49, 0.48/0.30, 0.53$), respectively.

De Cola et al. reported the use of two dinuclear rhenium complexes with μ -1,2-diazine ligands for OLED fabrication. The bridging ligands (Cl or Br) have significant effect to the electronic transitions. In toluene solution, **52a** and **52b** exhibited emission originated from the lowest lying $^3\text{MLCT}$ states with peak position at 547 and 620 nm and PL quantum yield of 53 and 0.2%, respectively. The bulky bromide bridging ligand in **52b** resulted in a longer Re-Re distance that is much longer than the optimum coordination by the diazine. As a result, there may exist a reversible bridge opening and fast interchange between bridging and terminal coordination, and the excited state could be rapidly quenched. However, in the solid state or when doped in PMMA film, their photophysical properties are significantly different such that **52a** and **52b** exhibited PL quantum yields of 10 and 49%, respectively ($\lambda_{\text{max}} = 493$ and 560 nm for **52a** and **52b**). The mobility of the ligands in **52b** was restricted, and was suggested to

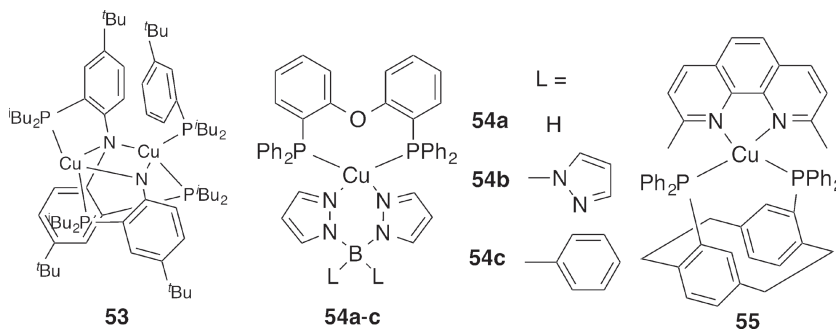
be an example of aggregated induced emission. **52b** was demonstrated to have a better device performance in OLEDs, with maximum CE , PE , and EQE of 30.3 cd A^{-1} , 22.6 lm W^{-1} , and 10%, respectively ($\text{CIE} = 0.43, 0.54$).

2.4. Harvesting of Singlet Excited States in Transition Metal Complexes

Recently, a new concept in designing new type of transition metal complexes from which both singlet and triplet excited states were harvested for light emitting has been proposed. In these complexes, the energy level of the singlet excited states are only slightly higher than those of the triplet states (in the order of 10^2 cm^{-1}). Therefore, efficient thermal population of the singlet states occurs, and all emission could be from the singlet excited states, which have a longer lifetime compared with those from the prompt fluorescence. By this approach, both singlet and triplet excitons can be harvested. Such thermally assisted delayed fluorescence processes have been observed in some copper(I) complexes.^[70] The structures of some of these complexes are shown in Scheme 7. Complex **53** was fabricated into green-light-emitting devices with structure ITO/CFx/NPB/CBP:TAPC/CBP:TAPC:Cu complex(8%)/CBP/BAIq/LiF/Al,^[70a] and a maximum EQE of 16.1% (at 47.5 cd A^{-1}) was observed. Complexes **54**^[70b] and **55**^[70c] are blue and yellow-light-emitting copper complexes with quantum yield in excess of 80%. The emission properties of these copper complexes are found to be strongly dependent on the rigidity of the environment and electronic properties of the ligand. They are promising candidates for the next generation of emissive materials for OLED because of the use of low cost copper.

3. Light-Management Engineering of OLEDs and OSCs

Regarding the light-management engineering of optoelectronic devices, various designs and approaches have been investigated in OLEDs to enhance the light out-coupling efficiency. Through the advances of emission materials and appropriate selections of material systems in active layer, carrier-transport layers and electrodes of the multilayered OLED structure, three important parts of external quantum efficiency including the fraction of



Scheme 7. Structure of copper complexes that exhibit thermally assisted delayed fluorescence properties.

radiative excitons to the total excitons which is related to the used emission materials, the ratio of electrons to holes injected from cathode and anode respectively as well as the intrinsic quantum efficiency of photoluminescence (PL) of emissive organic semiconductor are close to one. The internal quantum efficiency can reach nearly to 100%.^[72] The light out-coupling efficiency (generally around 20%) plays particularly important role nowadays to further improve the external quantum efficiency of OLEDs.

Meanwhile, light trapping scheme is an important topic for OSCs. With the recent progress of new organic materials and the layered device structures (including the optimization of morphology, interface engineering and new device architectures) of OSCs, the power conversion efficiency (PCE) of OSCs has reached over 9% for single-junction polymer-based OSCs^[73,74] and over 10% for tandem OSCs such as 10.6% for polymer-based OSCs^[75] and 12% for small-molecule-based OSCs.^[76] For the typical organic materials of OSCs, since excitons diffusion length is only a few nanometers^[77] and the carrier mobility is typical with the order of magnitude of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^[78,79] the thickness of the active layer of typical OSCs is only a few hundred nanometers, optical trapping becomes an important topic to increase the optical path of light in the device without physically increase the thickness of the active layer of OSCs. Consequently, the schemes to extract light from active layer of OLEDs to outside environment and to trap light into the active layer of OSCs will be reviewed in this article particularly the most recent reports in the last few years.

3.1. Light-Extraction Methods of OLEDs

One of the most serious problems in OLEDs is that the majority, about 82%,^[80] of generated light is trapped in the whole device but not escapes into air due to the induced surface plasmons at the interface of metal and dielectric layers as well as the differences of refractive index between layers of OLED structures including air, glass substrate, transparent electrode as well as organic or inorganic layers as shown in Figure 1. In order to reduce the light couple to substrate mode, substrate modification and microlens array have been investigated. For waveguide guide mode, low-index insertion, and high-refractive-index substrates have been proposed. Regarding the loss to the metal electrode, different schemes have been studied for suppressing surface plasmons. In addition, microcavities and photonic crystals, which will modify the spontaneous emission rate and enhance the light extraction, have been proposed and will also be described.

3.1.1. Substrate Modification

Roughening the substrate is one of the most efficient and simplest ways to enhance light scattering, thus improving out-coupling efficiency of light. One of the recent reports^[81] stated that simply sand-roughening the edge and surface of a glass substrate has contributed to a 20% improvement of luminous efficiency. Meanwhile, microspherically textured substrates have been exploited^[82] to increase light extraction. In the work,

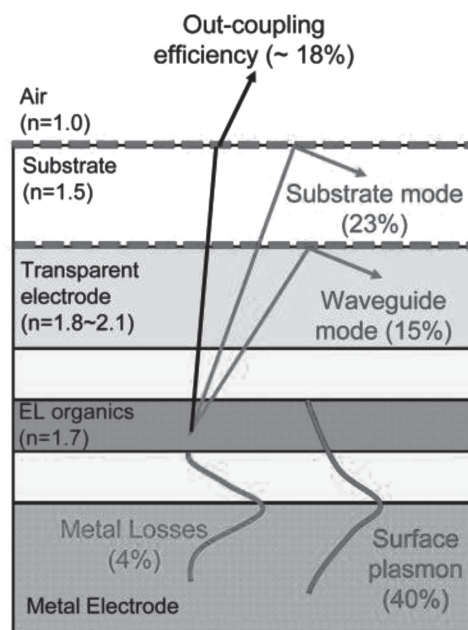


Figure 1. Schematic light loss of conventional OLEDs. Reproduced with permission.^[80] Copyright 2011, Springer.

OLEDs were deposited on single-layer SiO_2 -coated glass substrates, resulting in curved structure of all layers, as shown in Figure 2. This generated curve waveguide was beneficial for light extraction from OLEDs. As a result, the luminous efficiency was improved from 1 lm/W to 3.6 lm/W at 4 V driving voltage (compared with a reference device).

When emitted light reaches the interface of ITO ($n \approx 1.8$) and normal substrate ($n < 1.6$), total internal reflection occurs, resulting in a large amount of light trapped in the device. An efficient way to improve light out-coupling is replacing ITO with an oxide/metal/oxide electrode. When a $\text{Ta}_2\text{O}_5/\text{Au}/\text{MoO}_3$ combined layer was used as the electrode,^[83] a high external quantum efficiency (EQE) of 40% at $10\,000 \text{ cd/m}^2$ was achieved for green OLEDs on plastic. The method not only improves the light out-coupling of OLEDs but also makes it possible to fabricate high-efficiency OLEDs on flexible plastic. By replacing the

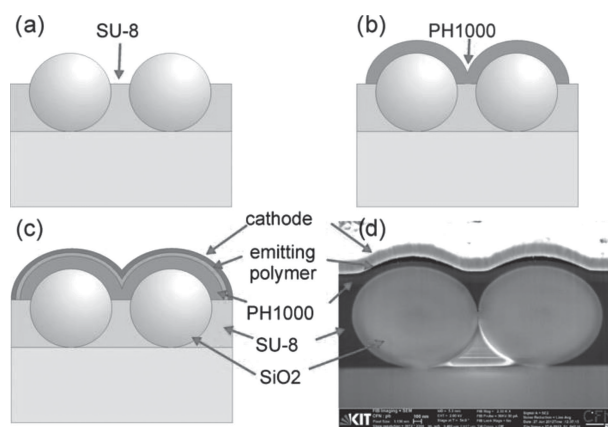


Figure 2. Fabrication scheme of micro-spherically textured OLEDs. Reproduced with permission.^[82] Copyright 2013, Elsevier.

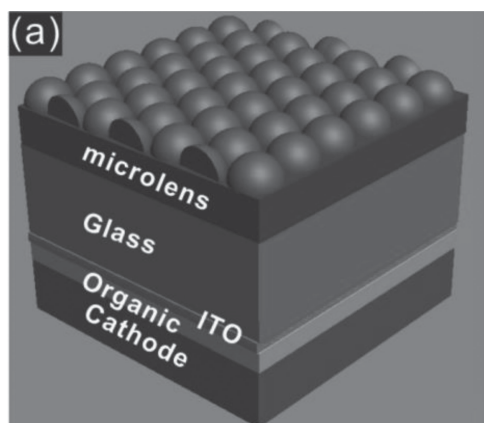


Figure 3. Schematic image of microlens-array-attached OLEDs. Reproduced with permission.^[96] Copyright 2010, AIP Publishing LLC.

ITO electrode with a highly transparent Ta_2O_5 ($n = 2.1$) layer,^[84] light out-coupling was improved. The high-refractive-index layer reduced total internal refraction at the interface of the ITO and the glass substrate. Moreover, the Ta_2O_5 near PEDOT:PSS was etched into a Bragg grating by laser interference lithography for scattering waveguided light. The device with a grating depth of 77 nm exhibited a luminous flux up to four times that of the control devices.

3.1.2. Microlens Arrays

Attaching microlens array on the outermost surface of OLEDs helps to boost out-coupling without altering the luminous spectrum. The EQEs of OLEDs were enhanced^[85] from 29.2% at 1000 cd/m^2 to 54% at 1000 cd/m^2 by simply incorporating a lens on the Cl-ITO device. As shown in **Figure 3**, microlenses have been fabricated through different approaches^[86–89] and the microlens shape would significantly affect light extraction. It was reported^[86] that elliptical microlens arrays improved luminance efficiency (efficiency improvement ratio of 1.60) more than hemispherical microlenses (efficiency improvement ratio of 1.52).

3.1.3. Low-Index Insertion Layer

An ultra-low-index grid embedded between ITO and an organic layer^[90] was used to scatter waveguided light into the substrate. This porous SiO_2 grid was fabricated by glancing-angle deposition with a refraction index (n) of 1.15. Compared with OLEDs without this grid, the ultra-low-index grid-embedded OLEDs achieved three-fold improvement in EQE and luminous efficiency. It was predicted^[91] that using an ultralow-index grid ($n = 1.03$) could obtain up to 50% more light out-coupling based on full-wave electromagnetic simulation.

Recently, a low-index conductive polymer between ITO and the organic layer has been

introduced^[92] to improve the out-coupling efficiency of OLEDs. Because of the similar refractive indices of the organic layers (1.75) and the ITO (1.8), the emitted light will be wave-guided throughout the organic layers and the ITO. However, with the insertion of low-index polymer layer (PEDOT:PSS), as shown in **Figure 4**, the emitted light would change its direction when hitting the PEDOT:PSS layer and would ultimately escape the OLED device with the help of the ITO grid structure. Compared with the control device (no PEDOT:PSS layer nor ITO grid structure), the device structured with an ITO grid and inserted with PEDOT:PSS exhibited a 75% EQE improvement.

3.1.4. High-Refractive-Index Substrate

The total internal reflection at the interface of organic layer ($n = 1.7\text{--}1.9$) and normal glass substrate ($n = 1.51$) hinders large amount of light out-coupling. The use of high-refractive-index substrate can diminish the total internal reflection, thus enhancing light out-coupling from the organic layer. Ordinary glass ($n = 1.52$), sapphire ($n = 1.74$), and high-index glass ($n = 1.80$) were studied^[93] to investigate the light out-coupling. The results exhibited that the device with ordinary glass used as substrate had an EQE of 40%, device with sapphire had higher EQE of 49%, and device with high-index glass had the highest EQE of 51%. Moreover, it was also demonstrated^[94] that high-index glass ($n = 1.78$) substrate contributes to a high EQE.

3.1.5. Suppression of Surface Plasmons

Light trapping due to surface plasmons^[95] at the interface of metal and dielectric materials is detrimental to OLEDs since the emitted light cannot radiate but dissipate as heat in the device. Thus, suppression of surface plasmons is vital for OLEDs to improve its EQE. Recently, buckling structures^[96,97] have been investigated as one of the most efficient approaches to convert the dissipated energy of surface plasmons to useful light as shown in **Figure 5**. The quasi-periodic buckling structure formed spontaneously on elastic materials to successfully improve the current and power efficiency of OLEDs. The difference in thermal expansions of heated polydimethylsiloxane (PDMS) and aluminum (thermally deposited on the PDMS) through cooling resulted in a buckled structure of the PDMS replica, which was put on UV curable resin coated glass

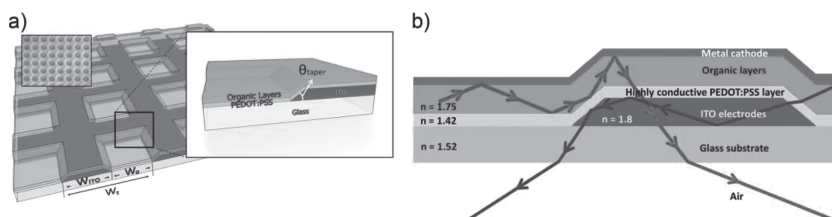


Figure 4. a) Proposed electrode structure consisting of patterned ITO and coated high-conductivity PEDOT:PSS layer. b) Representative cases that converted light trapped in organic/ITO layers into out-coupled mode. Reproduced with permission.^[92] Copyright 2010, John Wiley and Sons.

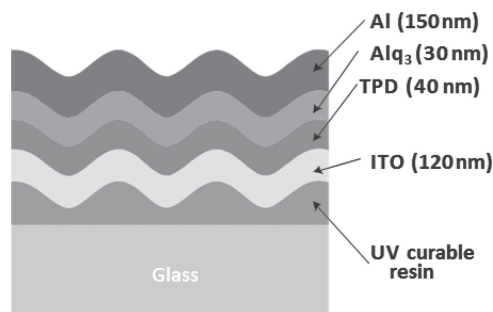


Figure 5. Schematic of buckled structure of OLEDs. Reproduced with permission.^[86] Copyright 2010, Nature Publishing Group.

substrate. After UV/ozone treatment, a buckled-resin-coated substrate formed, followed by deposition of the ITO/organic layer/electrode, generating a corrugated structure all over the layers. Other different approaches^[98,99] have been reported to fabricate this kind of corrugated structure for improving OLED current and power efficiencies.

3.1.6. Microcavities

A microcavity is an optical resonator with coplanar reflectors separated at a distance based on the magnitude of the wavelength.^[100,101] They have been previously applied to inorganic light-emitting diodes for enhancing emission intensity.^[102] After precise cavity design, EQE of 29% was demonstrated on top-emitting OLEDs^[103] as shown in **Figure 6**. Furthermore, by inserting semi-transparent Au layer between ITO and HTL, EQE of 18.8% with almost equal bottom and top emission was achieved.^[104] After structure optimization, the EQE of bi-directional OLEDs reached 24.24%.^[105] Combining diffuser films with microcavity effect in top-emitting organic light-emitting diodes,^[106] improvements not only in EQE but also in more saturated/stable colors were reported.

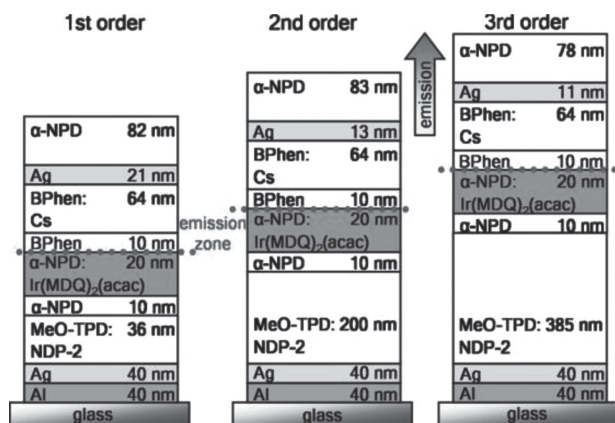


Figure 6. Schematic image of top-emitting OLED with three different cavity structures. The thickness of hole-transport layer was varied in order to avoid surface plasmon. Reproduced with permission.^[103] Copyright 2010, AIP Publishing LLC.

3.1.7. Photonic Crystals

Photonic crystals, structures with a regular repetition of high- and low-refractive-index layers, exhibit significant improvement of light out-coupling in both inorganic LEDs and organic LEDs. Photonic crystals composed of cylindrical air holes within a two-dimensional TiO_2 layer were demonstrated^[107] through the inverse opal method for light out-coupling; they were also theoretically studied through 3D-FDTD simulations. 92% light extraction of the polymer OLED was achieved by inserting a TiO_2 inverse opal structure with a closed top surface between the glass and the anode. Moreover, 1D photonic crystals consisting of high-refractive-index ITO and relatively low-refractive-index antimony-doped tin oxide (ATO) have been reported,^[108] for use in OLED light extraction. Photonic crystals also worked as the anode of the device. The periodically alternative structure was deposited onto a glass substrate by alternatively spin-coating ATO nanoparticles and RF magnetron sputtering ITO films. Recently, 2D gratings simply processed by imprint methods^[109] have been used to fabricate bottom- and top-emitting OLEDs.^[110] With the 2D grating, 13% of EQE enhancement and 42% of luminescence efficiency were reported. Meanwhile, 3D photonic crystal structures of ZnO ^[111] and ZnS ^[112] were also fabricated for OLEDs and showed good light out-coupling properties, as shown in **Figure 7**.

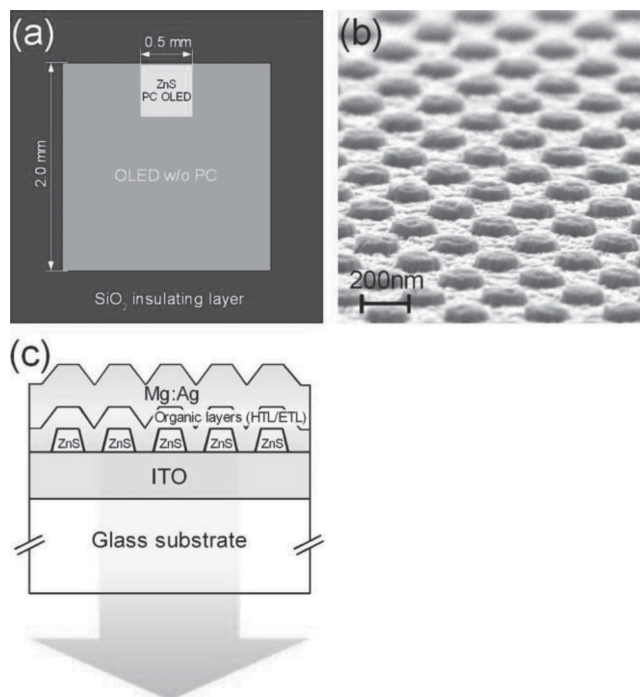


Figure 7. a) Schematic diagram of OLED with ZnS PCs patterned inside the OLED structure. The region outside the OLED was covered with a SiO_2 electrically insulating layer. b) Scanning electron microscopy (SEM) image of the 75-nm-thick ZnS pillars on ITO. c) Schematic side view of the OLED with the embedded ZnS pillars. Reproduced with permission.^[112] Copyright 2009, AIP Publishing LLC.

3.2. Light-Trapping Approaches of OSCs

The typical thickness of OSCs is a few hundred nanometers due to the short exciton diffusion length and low carrier mobility of organic materials.^[113] In order to increase light absorption of OSCs without increasing the thickness of active layer, various metal and non-metal patterns have been incorporated into the devices for improving light trapping of OSCs. Some approaches use periodic patterns, e.g., anti-reflection structures,^[114,115] periodic textures,^[116,117] 2D grating,^[118–121] and 3D grating^[122,123] and random structures, e.g., random microspheres,^[124] random wrinkles^[125] and in OSCs. Moreover, metal nanomaterials (e.g., nanoparticles (NPs), and nanoprisms, nanorods) have been incorporated into carrier-transport layers^[126–138] and active layers^[139–145] for improving OSC performances. Very recently, multiple metal nanostructures and nanomaterials have been simultaneously^[146–150] introduced in OSCs to further enhance the light absorption, electrical properties, and performances of OSCs. Indeed, metal structures in nanoscale have received great amount of attentions due to their extraordinary optical properties from the various electromagnetic modes. While metal nanostructures such as 2D and 3D metal nanogratings can offer strong surface plasmonic resonances (SPRs), metal nanomaterials can support localized surface plasmonics resonances (LPRs). Interestingly, the very strong near field of plasmonic resonances will typically distribute in a region of about a few tens to a few hundred nanometers around the metal nanomaterials and nanostructures which is similar to the thickness of active layer of OSCs, and thus have been considered to be particularly useful for enhancing the light harvesting for organic photovoltaics.^[113,151]

Generally, when sub-wavelength metal nanomaterials (e.g., NPs, nanoprisms and nanorods) are penetrated by an oscillating electromagnetic field (i.e., metal nanomaterials shall be small), the electric field on the nanomaterial surface will exert a restoring force on the driven electrons, leading to a resonance with strong electromagnetic field in and outside the nanomaterials,^[152–155] which is known as LPR. The LPR resonance is a kind of Rayleigh scattering only with a dipole mode. The dipole mode shows different bi-directional scattering distribution for near and far fields. When the size of the metal nanomaterials increases, Mie scattering^[156–159] occurs and multipole (e.g., quadrupole, and octupole) resonances are supported with versatile scattering directions compared with the bi-directional scattering of dipole resonance. The physics is important in understanding the effects of metal nanomaterials incorporated in different regions of OSCs, which will be described in this article.

Importantly, in order to study the improvement of OSCs due to the incorporation of metal nanomaterials and nanostructures, incident photon-to-electron conversion efficiency (IPCE) is one of the key parameters in investigating the performance of OSCs, which depends on both the optical properties and electrical properties such as exciton dissociation, and hole and electron transport and collection at their respective electrodes. In studying the optical effects of metal nanomaterials on the active layer of OSCs, besides IPCE and its enhancement factor (change of IPCE divided by the IPCE of the control OSC), it is important to investigate the light absorption of the active

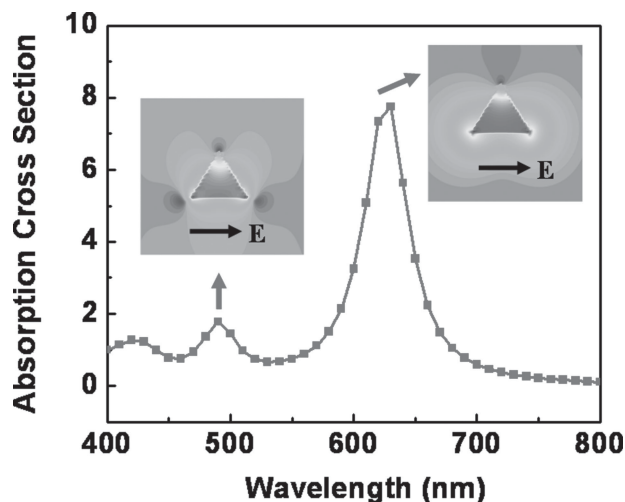


Figure 8. Theoretical absorption of Ag nanoprisms in water. The insets show the E-field distributions at the resonance peaks of 500 and 630 nm with the same polarization direction. Reproduced with permission.^[146] Copyright 2013, John Wiley and Sons.

layer and its enhancement factor. It should be noted that ideally the absorption of the organic materials in the active layer (excluding the absorption of the metal nanomaterials) shall be studied,^[135] which will contribute to the photogenerated current of OSCs. Although, sometimes, it is not easy to directly measure and extract the light absorption of organic materials only in the active layer, particularly for the case where metal nanomaterials are incorporated into the active layer, theoretical modeling^[160,161] can be conducted for calculating the absorption of organic materials only in the active layer and studying the change of the absorption.

3.2.1. Metal Nanomaterials in Carrier-Transport Layers of OSCs

Various metal nanomaterials with different sizes, concentration have been introduced into hole-transport layers such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)^[126–135] and MoO_x^[136] and more recently into electron-transport layers such as TiO₂^[137,138] for improving the power conversion efficiency (PCE) of OSCs. The improvements introduced by metal nanomaterials incorporated in OSCs are considered to be of different origins, such as plasmonic-optical effect, high order resonances effect, scattering effects, plasmonic-electrical (plasmoelectric) effect, charge-storage effect and morphology as described below.

Multipole resonances^[127,147] and light scattering^[132–134,162,163] have been reported for enhancing the light absorption and device performances. For instance, Ag nanoprisms with average side length and thickness of 60 nm and 10 nm respectively supported multipole resonances.^[146] As shown in **Figure 8**, when the incident light was TM polarized, a number of resonances were observed. LPR (low-order) formed with the resonance wavelength of 630 nm. For the LPR, a dipole near field profile was obtained. The small resonance peak associated with the nanoprism in the short wavelength region (<600 nm) was the high-order resonance, which had a more-complex

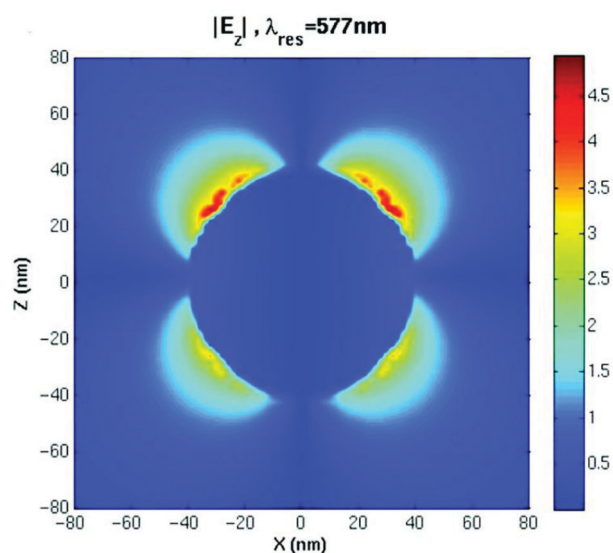


Figure 9. The near-field profile along vertical (E_z) direction around the Au NP with size of 70–80 nm. Reproduced with permission.^[126] Copyright 2011, American Chemical Society.

scattering pattern with different angular momentum, as could be observed from the near-field profile at the resonance peak of 500 nm. Moreover, high-order resonances were also reported in Au NPs with a size of 70–80 nm.^[126] At a resonance wavelength of 577 nm, the near-field profile along the vertical (E_z) direction around the Au NPs had a quadrupole distribution as shown in **Figure 9**.^[126]

Regarding the dipole resonance (i.e., LPR) effect, by using small Au NPs^[135] and Ag NPs,^[136,163] it was reported that although LPR existed in the PEDOT:PSS layer and the PCE improved, the strong electromagnetic (near) field mainly distributed laterally along the PEDOT:PSS layer rather than vertically into the adjacent active layer (see **Figure 10a**), leading to minimal (no clear) enhancement of light absorption in the active layer^[135] as shown in **Figure 10b**. Importantly, the findings could be extended to a typical class of solar cells incorporating

metal NPs in the spacing layers adjacent to the active layer. In this case, the change of the PCE could be explained by the electrical properties and morphology of the OSCs (rather than from optical plasmonic effects).^[135,139–141,146]

It is also important to note that the LPR wavelength of metal nanomaterials will change depending on the optical environment (i.e., the location of the metal nanomaterials in a device structure or the solution where the metal nanomaterials are dispersed). For instance, the LPR peak of the Au NPs in water^[135] was 520 nm, which shifted to 580 nm when the Au NPs were incorporated in PEDOT:PSS of the OLEDs shown in **Figure 10**. To add metal nanomaterials into different materials, various ligands^[135,164,165] were applied to cap the metal nanomaterials. For instance, monofunctional poly(ethylene glycol) (PEG) was coated on Au NPs in ref.,^[135] which did not have discernable effect on the peak position of optical absorption nor exert any significant effect on the device performance. On the other hand, the main role of the ligand was for dispersing the Au NPs well in PEDOT:PSS. The Au NPs without PEG aggregated into clumps of NPs in the PEDOT:PSS film and did not bring any improvement in PCE.^[135] In fact, the surface treatment and modification of metal NPs and nanoclusters formed on electrodes can sometime tune the electrical and physical (mechanical) properties. For instance, some work used plasma-polymerized fluorocarbon (CF_x) to modify Ag NPs on ITO^[165] as a composite anode, the workfunction was adjusted to 5.4 eV, which favored hole extraction and thus improved the performances of ZnPc:C₆₀-based OSCs as compared with a corresponding control device with bare ITO. Similarly, Au NPs modified by UV ozone on ITO were used as a composite anode.^[166] By applying an appropriate time of UV ozone treatment, the workfunction of the composite anode could be adjusted to about 5.1 eV, which again improved the hole extraction and thus the PCE for OSCs with poly(3-hexylthiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PC₆₀BM) as the active layer. The strategy could also be applicable for other electrodes. For instance, by forming a layer of Au nanoclusters with a suitable size on graphene and then treating the composite (graphene/Au NPs) by UV ozone, the workfunction

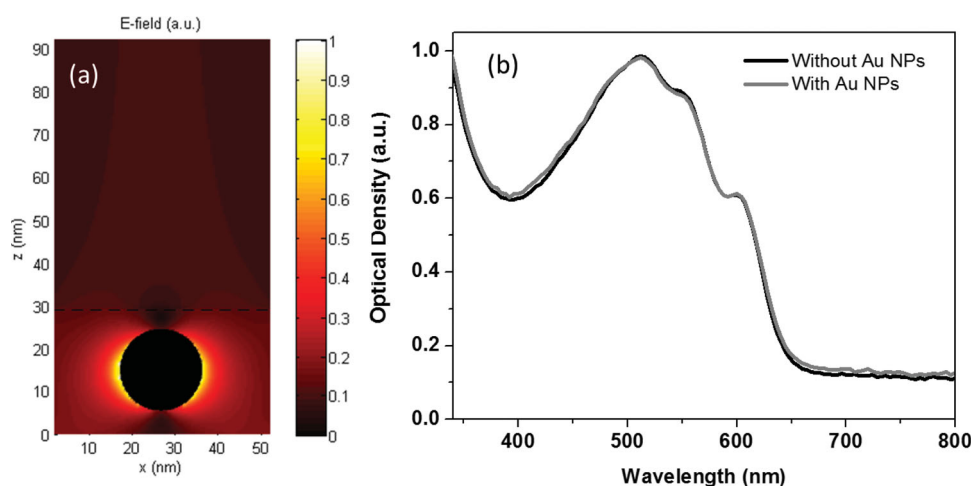


Figure 10. a) Theoretical electric field profile in the PEDOT:PSS/Au NPs/P3HT:PC₆₀BM OSC. b) Optical density of PEDOT:PSS/P3HT:PC₆₀BM film with and without Au NP incorporation (0.32 wt%). Reproduced with permission.^[135] Copyright 2011, The Royal Society of Chemistry.

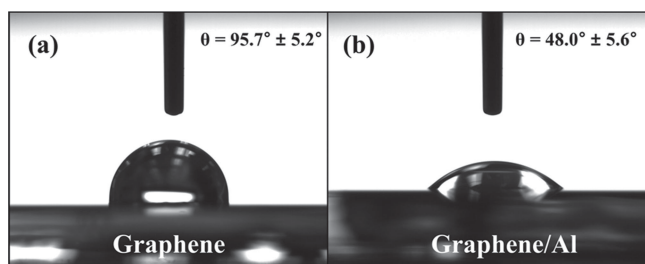


Figure 11. Surface contact angles of: a) single layer graphene and b) single layer graphene/0.5 nm Al nanoclusters. Water was used for the measurement. Reproduced with permission.^[168] Copyright 2013, American Chemical Society.

was adjusted. With an appropriate time (2 min) of UV ozone treatment, the workfunction of the graphene/Au nanocluster composite was adjusted from 4.1 eV to 4.8 eV, favouring hole extraction from P3HT:PC₆₀BM active layer of OSCs and making the composite become an efficient anode.^[167] By introducing 0.5 nm Al nanoclusters on graphene, the composite layer became more energetically favourable as a cathode for electron collection.^[168] This was because the wavefunction significantly reduced from 4.56 eV for pristine single-layer graphene to 1.14 eV for the graphene/0.5 nm Al nanocluster composite, which aligned better with the LUMO of the P3HT of the P3HT:PC₆₀BM active layer. Moreover, the wettability improved significantly. Whereas the contact angle of the pristine single-layer graphene was 95.7° (i.e., very hydrophobic), the angle considerably reduced to only 44.6° as shown in **Figure 11**. In addition, since the Al nanoclusters was very thin, the optical transmission did not have any clear change.^[168]

Very recently, the electrical effects on the carrier generation, carrier extraction, etc. of the carrier-transport layer in OSCs induced by plasmonics,^[138] were studied by incorporating Au NPs in TiO₂ electron-transport layers. The effects are also known as plasmonic-electrical effects or plasmoelectrical effects. The results showed that while typical OSCs using pristine TiO₂ as the electron-transport layer could only normally operate after UV activation with wavelength less than 400 nm, the OSCs using TiO₂ incorporated with the Au NPs can efficiently operate after activation at a plasmonic wavelength

(560–600 nm), far longer than the originally necessary UV light. Otherwise, the J–V characteristics of OSCs will show a poor S-shape. By optimizing the concentration of Au NPs in TiO₂, the performances of the OSCs were improved and an efficiency of 8.74% has been reported.^[138] An integrated optical and electrical model (i.e., a multiphysics model) was also conducted with the consideration of the hot carrier tunneling probability and extraction energy barrier between the TiO₂ and the active layers. Experimental and theoretical studies reported that under plasmonic illumination, the strong charge injection of plasmonically excited electrons from Au NPs into TiO₂, which contributed to the improvement of charge extraction. The mechanism favored trap filling in TiO₂ which could lower the effective energy barrier and facilitate carrier transport in OSCs as shown in **Figure 12**.^[138] The work could contribute to new approaches and knowledge to utilize plasmonically electrical nanostructures in organic optoelectronic devices for enhancing device performance.

Besides the plasmonic-electrical (plasmoelectric) effects, charge-accumulation effects of metal NPs were reported to improved OSC performance^[136] through embedding Au and Ag NPs in a TiO₂ electron-transport layer. The charge-accumulation effects enhanced electron extraction and thus the Au and Ag NPs embedded TiO₂ layer could function as a highly efficient transport layer for improving the performances of inverted organic solar cells (OSCs). The charge-extraction enhancement under solar illumination as shown in **Figure 13** were explained by the transfer of UV-excited electrons from TiO₂ electron-transport layer to metal NPs and the enhanced accumulation of the electrons in metal NPs-TiO₂ composites. The electron accumulation reduced the work function of the electron-transport composite layer after UV illumination as shown in **Figure 14**. The redistribution of charges in the UV-irradiated metal NPs-TiO₂ system assisted the charge extraction in OSCs. A multiphysics study was also conducted to explain the effects of the charge accumulation on device performances (i.e., improving short-circuit current without degrading the open-circuit voltage). The report stated that the NP-TiO₂ transport layer, which was different from the conventional doping effects in semiconductors, exhibited very good charge extraction and collection at electrode for efficient organic optoelectronic devices.^[137] Consequently,

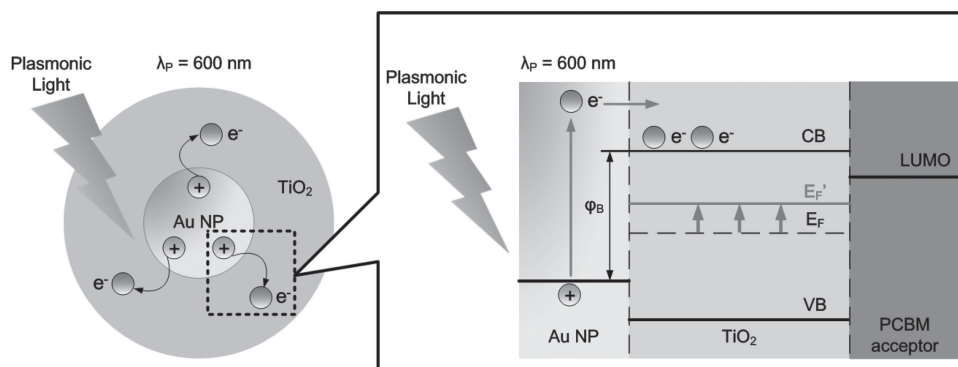


Figure 12. Schematic plasmonic-induced charge-injection process. LUMO denoted the lowest unoccupied molecular orbital of the PC₆₀BM in OSCs. VB denoted valence band and CB denoted conduction band. ϕ_B was the Schottky barrier height between TiO₂ and Au. Electrons were extracted from PC₆₀BM to TiO₂ in OSCs. Reproduced with permission.^[138] Copyright 2013, John Wiley and Sons.

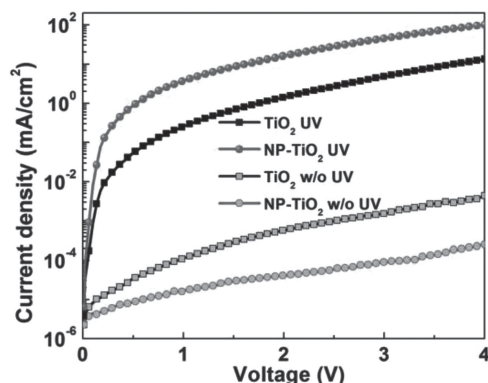


Figure 13. J–V characteristics of electron-only devices using TiO₂ and optimized Au NP-TiO₂ as ETLs measured with and without (w/o) UV excitation. Reproduced with permission.^[137] Copyright 2013, The Royal Society of Chemistry.

by embedding metal NPs in TiO₂ layer, plasmonic-electrical and charge-accumulation effects were reported,^[137,138] both could enhance carrier extraction for better device performances.

3.2.2. Metal Nanomaterials in Active Layers of OSCs

LPRs of metal nanomaterials offer particularly strong electromagnetic (near) field around the nanomaterials. In addition, the incident photons can be scattered for a longer propagation path in the active layer by metal nanomaterials and nanostructures.^[169,170] The later case become strong when the size metal nanomaterials and nanostructures were large. It is therefore considered that adding metal nanomaterials into the active layers of OSCs can enhance the light absorption directly and thus PCE.

By introducing metal NPs in active layers of OSCs, it has been demonstrated that light absorption and PCE were improved.^[139–141,144,171,172] By introducing small metal NPs such as Au NPs with diameter of 18 nm (average) into the active layer, strong LPR near field distributed inside the active layer of poly[2,7-(9,9-dioctylfluorene)-*alt*-2-((4-(diphenylamino)phenyl)-

thiophen-2-yl)malononitrile] (PFSDCN):PC₆₀BM was reported and light absorption enhancement was demonstrated theoretically and experimentally^[144] as shown in **Figure 15**. When larger metal Au NPs (average 70 nm)^[139] and Ag clusters from NPs (40nm)^[140] were introduced in active layer, strong light scattering were obtained which contributed to increase light absorption and PCE similar to the discussion of metal NPs in carrier-transport layers of OSCs. For instance, by embedding 4wt% and 70 nm Au NPs into the polymer blend active layer of P3HT/[6,6]-phenyl C70 butyric acid methyl-ester (PC₇₀BM), the PCE increased from 3.54% to 4.36%; and for poly[[4,4'-bis(2-ethylhexyl)dithieno(3,2-b:2',3'-d)silole]-2,6-diyl-*alt*-[4,7-bis(2-thienyl)-2,1,3-benzothiadiazole]-5,5'-diyl] (Si-PCPDTBT)/PC₇₀BM, the PCE increased from 3.92% to 4.54%.^[140] Besides metal NPs, other metal nanomaterials have also been incorporated in the active layer of OSCs for improving the performances of OSCs such as Au nanodisks,^[173] Ag nanowires,^[141] and Ag nanoprisms.^[142,171] Different NP materials such as Al, Cu, Ag and Au have also been studied.^[174] **Figure 16** showed the absorption of P3HT:PC₆₀BM active layer with different Ag nanomaterials, clear absorption increment of the active layer were obtained.^[141] By introducing a ratio of 0.5 wt% of Ag nanoprism into the blend-polymer active layer of PCDTBT/PC₇₀BM, PCE increased from 5.9% (no nanoprisms) to 6.6%.^[171]

When the metal NPs get close together, couplings between metal NPs will exist. Recently, coupling effects of metal NPs arrays on the active layer of OSCs have also been reported.^[160,175] The coupling effects can be further described as plasmon hybridization of metal NPs. The plasmonic mode in each NP can be hybridized when the NPs approach with each other. The evanescent wave coupling between metal NPs is much stronger than dielectric ones and thus the spectral and spatial features of the plasmonic mode will be strongly modified. The transverse and longitudinal modes in a periodic NP chain were reported for the case that the NPs were embedded into active layer of OSCs.^[160] The versatile plasmonic modes could be supported in interstitial lattice patterned metal NPs to improve the light blocking effect induced by top patterned nanostructures.^[175] It should be noted that there are other kinds of optical enhancement mechanisms through optical couplings in plasmonic nanomaterials and nanostructures including quasi-guided modes (Fano resonances) and plasmonic bandgap and band edge which will be discussed in Section 3.2c.

Besides the optical effects, it has been reported that metal nanomaterials would change the electrical properties of active layer. For example, the embedded Ag NPs in PCDTBT/PC₇₀BM active layer could increase the hole injection barrier which favored the electron transport and thus increased J_{sc} and PCE.^[140] Meanwhile, the incorporation of large Au NPs into P3HT:PC₆₀BM favored hole transport in the active layer^[139] due to the reduction of the hole-injection barrier. It has also been reported that the photon-induced electric conductivity and PCE would be improved by introducing Cu NPs into P3HT due to the increased dissociation rate of the excitons in the presence of Cu NPs.^[176] For the case that Au NPs were embedded into PFSDCN:PC₆₀BM, the hole mobility could be increased by ca. 237% (from $1.26 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $4.25 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and the electron mobility was increased by 28% (from $0.93 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)

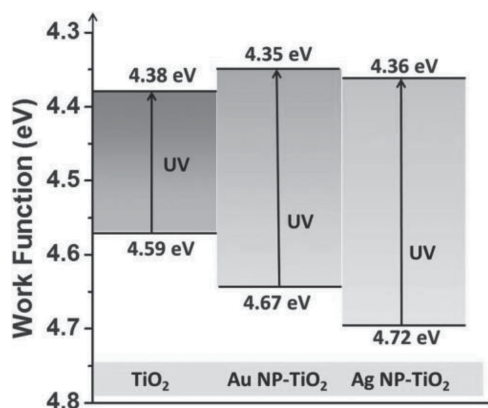


Figure 14. Diagram of workfunction changes of TiO₂ film, Au NP-TiO₂ film and Ag NP-TiO₂ film from the dark condition to under UV illumination (for 15 min), measured by using a Kelvin probe. Reproduced with permission.^[137] Copyright 2013, the Royal Society of Chemistry.

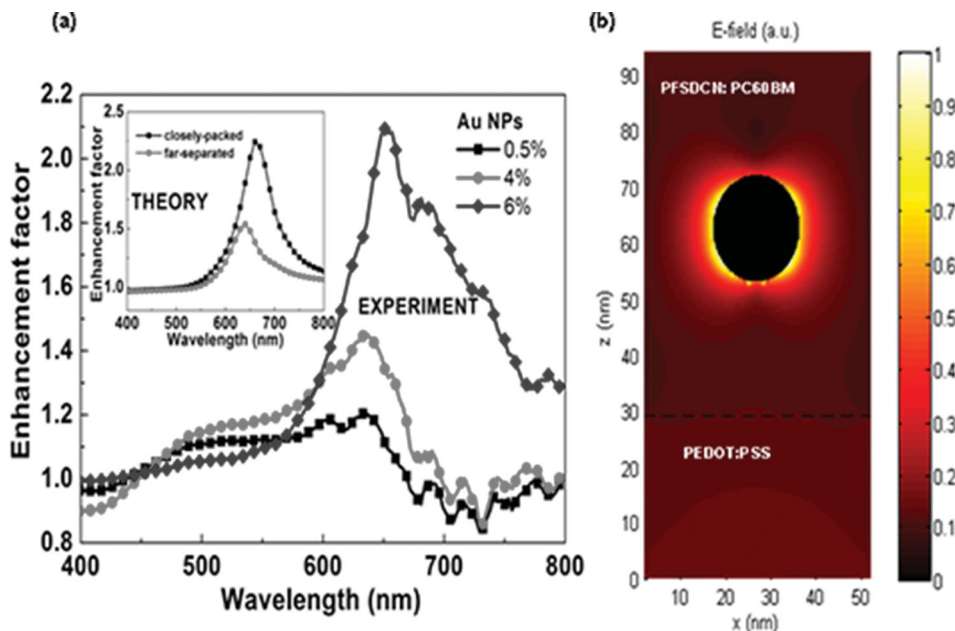


Figure 15. a) Experimental and theoretical (inset) absorbance enhancement factor of the active layer with different amount of Au NPs. b) Theoretical near field distribution around an Au NP in the polymer blend active layer of PFSDCN: PC₆₀BM. Reproduced with permission.^[144] Copyright 2012, The Royal Society of Chemistry.

when 2 wt% Au NPs were used. The increment of carrier mobility and the better balance of the electron and hole mobilities contributed to the performance improvement. However, the maximum PCE was obtained when 0.5% of Au NPs were incorporated into the active layer. The main reasons were the reduction of exciton dissociation at high concentration of Au NPs, the change of morphology and the modification of interfacial charge states at the cathode and even the break down of the Fermi level pinning between the cathode metal and the fullerene reduction potential,^[144] although the light absorption continued to increase at high concentration (i.e., the

increment of light absorption did not imply that PCE of OSCs would improve). It was therefore very important to study both optical and electrical properties of the metal nanomaterial incorporated OSCs for understanding and optimizing the device performances.

3.2.3. OSCs Incorporating Metal Nanostructures

Various 2D gratings have been applied on OSCs for light harvesting applications^[117–120] experimentally and some theoretical studies have also been conducted to understand the physics and introduce different grating anode and cathode design for achieving optical enhancement.^[120,121,177–180] Experimentally, one of the methods was to adopt imprint method to form the pattern on active layer,^[119–121] therefore it would introduce optical effects due to the grating directly on the active layer. In addition, since the carrier-transport layer was very thin about 10 nm, the Ag anode on the active layer would form a metal nanograting pattern.^[120,121] The patterned P3HT: PC₆₀BM was shown in Figure 17a and the diffraction colors at different angles of the completed OSCs anode shown in Figure 17b to 17d confirming Ag grating anode was formed. The IPCE was enhanced as shown in Figure 18. The IPCE increased over the whole wavelength range particularly in the region of 380–550 nm. Moreover, there was a significant enhancement around ca. 715 nm where P3HT did not absorb strongly.^[121] The broadband enhancement in the wavelength range of 380–550 nm was obtained because the light path was elongated or diffracted by the gratings nanostructure,^[181,182] while the enhancement peak at about 715 nm was explained by SPR of the 2D metal grating. For the 2D grating OSCs with P3HT: PC₆₀BM as active layer, PCE increased from 3.09% to 3.68%.^[121] For

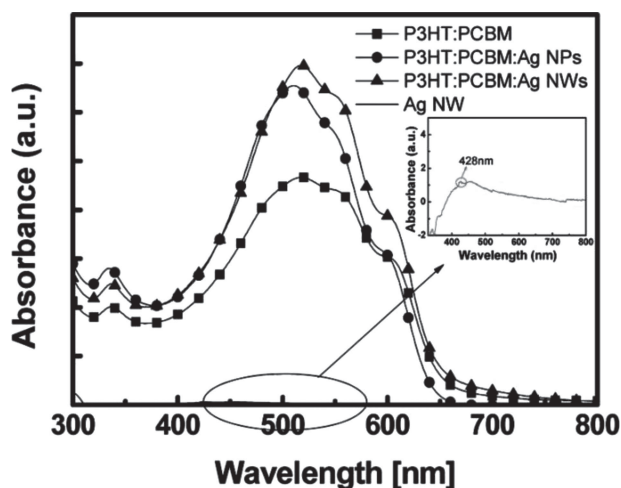


Figure 16. UV-vis absorption spectra of active layers (P3HT: PC₆₀BM, P3HT: PC₆₀BM:Ag NPs, P3HT: PC₆₀BM:Ag NWs, and Ag NWs). Inset: UV-vis absorption spectrum of Ag NWs in solution. Reproduced with permission.^[141] Copyright 2011, American Chemical Society.

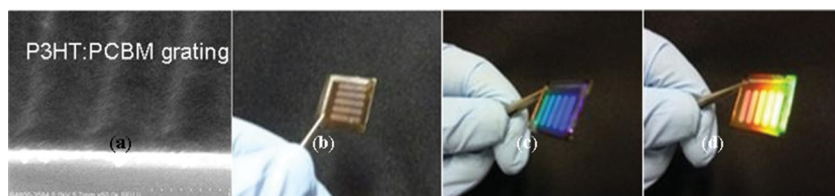


Figure 17. a) The 2D grating patterned P3HT:PC₆₀BM active layer. b–d) Images of OSCs with Ag grating anode at different tilted angles. The diffusion color changes with the angles. Reproduced with permission.^[121] Copyright 2012, American Chemical Society.

small bandgap materials of benzodithiophene polymers (PTB7):PC₇₀BM, PCE increased from 7.20% to 7.73%.^[120]

In Section 3.2c, we discuss the coupling effects of metal NPs. For metal nanostructures, other optical enhancement mechanisms have been recently reported. One of them is the plasmonic bandgap and band edge. Fundamentally different from Bragg scattering by travelling waves in photonic crystals, plasmonic bandgap and band edge could be formed by the interference between surface plasmonic waves. At plasmonic band edges, the SP waves dwell at different spatial locations and show more significant near-field enhancement compared with photonic band edge. The slow wave enhancement at photonic band edge^[183] could not be extended to very loss metal materials.^[180] At the plasmonic bandgap, the near-field enhancement is quite weak due to the destructive interference of SP waves; but a high reflectance can be achieved for elongating the optical path. This can be explored for enhancing optical absorption of thin-film OSCs. Although several groups found relevant physical phenomena indeed improved absorption of thin-film OSCs,^[184,185] these physical phenomena could be attributed to plasmonic band edge enhancement mechanism.^[121]

The other one of optical enhancement mechanisms is quasi-guided mode or Fano resonance. Space harmonics (floquet modes) supported in periodic structures enable the guided mode excited with a radiation (leaky) loss. Arising from the interference between a narrow discrete guided mode and a broad continuum (incident light), the quasi-guided mode^[186]

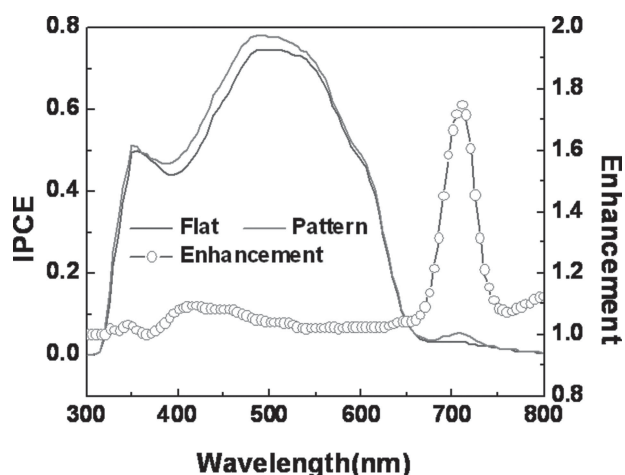


Figure 18. IPCE of flat (control) P3HT:PC₆₀BM OSC and 2D grating patterned P3HT:PC₆₀BM OSC and the IPCE enhancement ratio. Reproduced with permission.^[121] Copyright 2012, American Chemical Society.

with an asymmetric and narrow Fano line shape^[187] has extraordinary transmittance and reflectance also called resonant Wood's anomaly.^[188] The quasi-guided mode can elongate the optical path or enhance the optical near-field. Recently, the novel super-lambertian effect in the angular response of OSCs incorporated with back metallic gratings was reported where quasi-guided mode played an important role at both polarizations which will be described in more detail later.^[179] Polman's group studied how to control the Fano lineshape to potentially enhance optical absorption of thin-film solar cells.^[189]

Typically, 2D gratings have polarization-dependent optical properties. In order to achieve polarization-independent optical enhancement in OSCs, 3D grating^[119,122,190–193] and randomly patterned nanostructures have been reported.^[124,194,195] By using 3D grating nanostructures as shown in **Figure 19**,^[123] the PCE of P3HT:PC₆₀BM OSCs increased from control 3.09% to 3.63% (2D grating) and then to 3.85% (3D grating with the same periodicity).^[123] The further improvement though replacing 2D grating to 3D grating could be explained by the polarization-independent optical enhancement and increase in effective interfacial area for hole collection to anode and decreased R_s .^[123] The hexagonal 3D grating pattern (as shown in **Figure 20**) also make PCDTBT/PC₇₀BM OSCs increase PCE from 3.0% to 3.9%.^[122] Recently, random 3D metal nanostructures were reported for the polarization-independent optical enhancement in OSCs.^[124] The fabrication steps were described in **Figure 21**. The PCE of the P3HT: indene-C60 bis-adduct (ICBA) OSCs increased from 5.12% to 5.47%. In the work, the LPR of this electrode was tuned to the red absorption tail of the active layer. The absorption of active layer was mainly enhanced by the strong light scattering. The efficiency enhancement due to the plasmonic effects demonstrated in the work could be generally adopted to thin film solar cells, as the LPR of the electrode could be adjusted to coincide with the absorption edge of semiconductors within the visible and near-infrared regions of the spectrum. The report also showed that the hole-mask colloidal lithography technique was compatible with organic semiconductor systems and the nanostructured electrode could also be produced by other high-throughput methods such as nanoimprint lithography.^[124]

Angular response is also an important optical property of photovoltaics devices. A theoretical study reported that triangular grating structures showed the particular opportunities to obtain a good angular performance.^[196] In the work, the angular behavior of the excited modes for P3HT:PCBM OSCs on triangular nanograting with different periodicity and depth was examined. It was found that the depth of the metallic grating was crucial for a good wide-angle response for the case of normal triangular gratings. On the other hand, copper phthalocyanine (CuPc)/fullerene (C60)-based OSCs with periodically rectangular nanostructures as electrode were also theoretically investigated.^[179] The theoretical results showed that with metal strips nanostructure at the back of OSCs, the light absorption was higher than that of the planar OSCs for the cases of s and p polarizations. The enhancement could be explained by the SPRs and Wood's anomalies. The results also showed that when the

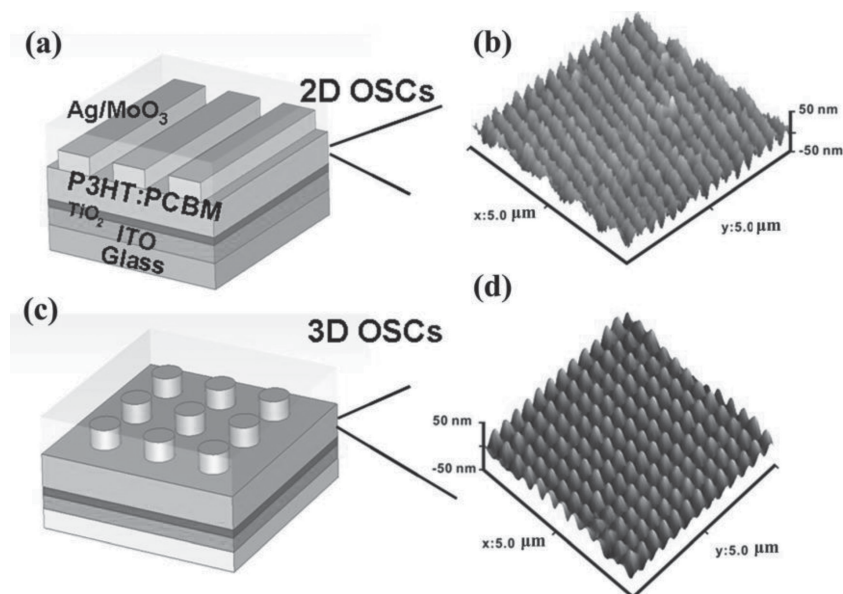


Figure 19. The schematics of: a) 2D P3HT:PC₆₀BM OSCs and c) 3D P3HT:PC₆₀BM OSCs; the atomic force microscopy (AFM) images of active layer with: b) 2D nanograting and d) 3D nanopattern. Reproduced with permission.^[123] Copyright 2013, AIP Publishing LLC.

angle of incident light increased, the absorption of s-polarized light decayed faster than that of the p-polarized light. The faster decay of the s-polarized absorption is not sensitive to the device structure. As a result, for the s-polarized light, the absorption enhancement was mainly in the small angle (i.e., nearly normal incident). When the angle increased, the absorption of the

s-polarized light in the striped OSCs would be similar that in the planar structures. For the case of p-polarized light, as the (optical) electric field propagated across the interface of the multilayered device structure, the p-polarized light had better optical confinement. The enhanced light absorption could achieve super-Lambertian (i.e., the p-polarized absorption enhancement is over the generalized Lambert's cosine law). It should be noted that since the absorption enhancement of Wood's anomalies was narrow in wavelength regime, the contribution on the total absorption was rather limited. Consequently, the wide-angle and broadband absorption improvements due to the SPRs would contribute to the evolution of high-efficiency photovoltaic cells.

3.2.4. Metal Nanostructures and Nanomaterials for Large and Broadband Enhancement in OSCs

So far, symmetric and one type of metal nanomaterials and nanostructures at one time have been incorporated in different layers and regions of OSCs for improving the performance. Indeed, multiple metal nanostructures and nanomaterials have been simultaneously introduced in OSCs^[146–150] to further enhance the light absorption and performances of OSCs. For instance, different sizes of Au NPs have been embedded into both the hole-transport layer of PEDOT:PSS and the active layer of P3HT:PC₆₀BM layers of one single OSC.^[197,198] 18 nm Au NPs and 35 nm Au NPs were used for the PEDOT:PSS and P3HT:PC₆₀BM respectively. While the Au NPs in PEDOT:PSS change the morphology and thus improve the hole collection and conduction properties, the Au NPs in P3HT:PC₆₀BM enhanced both light absorption and electrical properties particularly the electron and hole mobilities of the active layer and the better balanced electron and hole mobilities. The PCE of OSCs finally increased from 3.16% (control) to 3.85% (Au NPs in all polymer layers).^[197] In another report of using 30 nm Au NPs in PEDOT:PSS and 80 nm Au NPs in P3HT:PC₆₀BM, PCE increased from 1.7% (control) to 3.7% (Au NPs in all polymer layers).^[198]

While plasmonic resonances which induces regionally-concentrated optical near-field around the metal nanomaterials and nanostructures can be used to enhance the light absorption particularly around the resonance wavelength regions, multiple plasmonic resonances at different wavelength regions were proposed for wideband optical enhancement including the multiple LPRs using metal nanorods,^[147] metal NPs from different metal materials,^[147] metal NPs and metal nanoprisms, multiple SPRs using two different metal nanograting systems simultaneously^[178] and complicated nanograting structure,^[199] as well as combining LPRs and SPRs using metal NPs and metal nanograting simultaneously in one single OSCs. The simple approach is to use metal nanorods.^[147,200] Since a nanorod has longitudinal and transverse axes with different lengths, two SPRs at different resonance wavelengths can be obtained. By

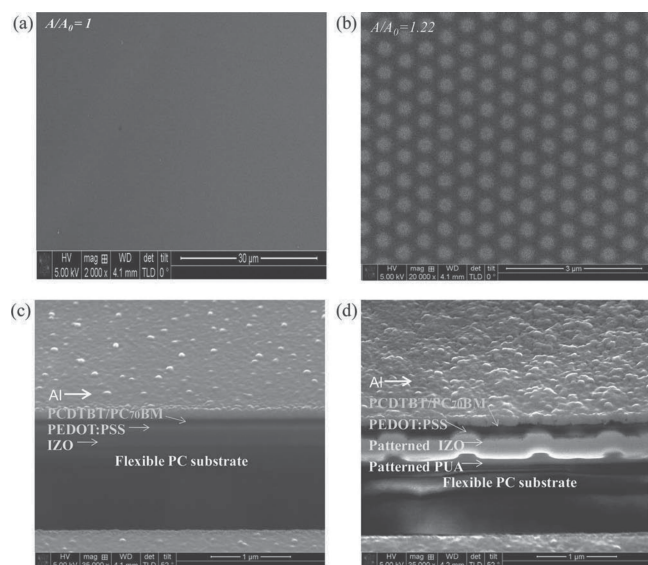


Figure 20. FIB (focused ion beam) fabricated cross sectional image: a) 52° tilted images and c) device sequential inner structure of a flat IZO (without nano pattern), spin coated with PEDOT:PSS and an active layer (PCDTBT:PC₇₀BM) on a flexible PC substrate. The images (b) and (d) show device sequential inner structure of nano-patterned IZO (50 nm-height), spin coated with PEDOT:PSS and an active layer (PCDTBT:PC₇₀BM) on a flexible PC substrate. Reproduced with permission.^[122] Copyright 2012, John Wiley and Sons.

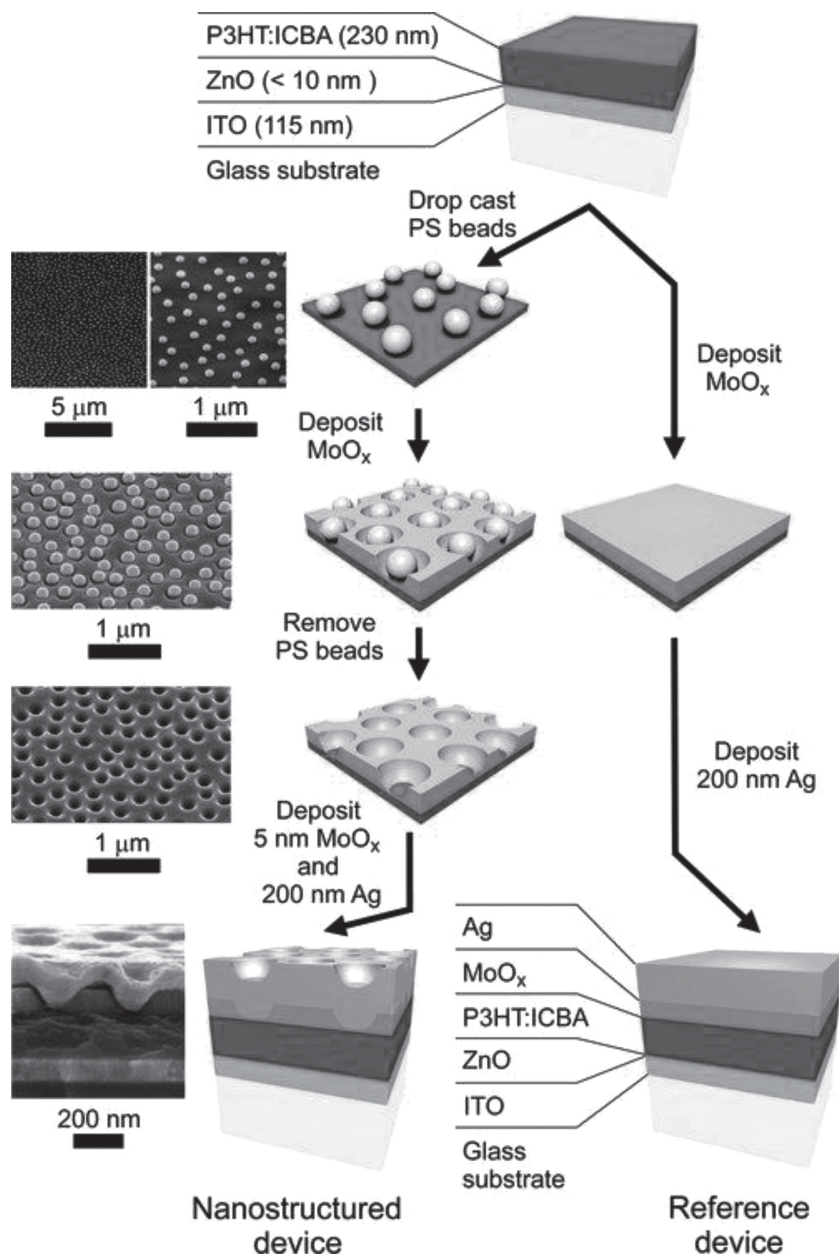


Figure 21. Fabrication process flow for an organic solar cell including a nanostructured rear electrode (left) and a reference device with a flat electrode (right). The scanning electron micrographs presented the nanostructured sample at different stages during the fabrication process. The fabrication of both types of devices started with the deposition of an electron collecting ZnO layer on a glass/ITO substrate, followed by the deposition of the P3HT:ICBA active layer by spin coating. Then, a non-closed-packed layer of PS beads without long range order was applied by drop casting from an aqueous dispersion on the active layer surface of the nanostructured device. These PS beads acted as a shadow mask during the deposition of the MoO_x hole transport layer by thermal evaporation. After the removal of PS beads by a residue-free adhesive tape, an additional 5 nm thick MoO_x layer was deposited to separate the active layer from the direct contact of metal electrode. The device was finalized by thermal evaporation of 200 nm Ag. The MoO_x/Ag anode of the flat reference device is deposited directly on the active layer. Reproduced with permission.^[124] Copyright 2013, John Wiley and Sons.

embedding Au nanorods with diameter of 15 nm and length of 40 to 50 nm into the active layer of PTB7:PC₇₀BM, PCE of 8.41% (8.52% the best) was reported while the control PCE

is 7.25% as shown in Figure 22. Since SPR wavelength depended on the metal material, combined Ag NPs and Au NPs were also proposed for wide absorption band enhancement.^[147] As shown in Figure 23, by adding a suitable amount of mixed Au NPs and Ag NPs, both with sizes of about 40–50 nm, into the PEDOT:PSS layer, the absorption and EQE improved and PCE reached 8.67%.^[147]

Since the wavelength of plasmonic resonances depended on the geometry of metal nanomaterials, combined Ag NP and Ag nanoprism system was proposed to realize wideband absorption improvement as shown in Figure 24.^[146] The experimental and theoretical studies showed the observed PCE enhancement was originated from the simultaneous excitation of various plasmonic low- and high-order resonances modes which depend on the size and shape of the metal nanomaterials as well as the polarization of light. Particularly for the Ag nanoprisms, the high-order resonances resulted in a larger contribution than low-order resonances to the absorption enhancement of OSCs through a better overlap with the active material absorption spectrum. With wideband absorption improvement, J_{sc} was improved by 17.91% for P3HT:PC₆₀BM-based OSCs. Finally, PCE enhanced from 3.6% (control) to 4.3% (incorporated mixed Ag NPs and Ag nanoprisms) by about 20% as compared with the pre-optimized control OSCs.

OSCs with combined front and back Ag nanogratings were theoretically studied.^[178] This combination provided multiple and semi-independent enhancement mechanisms to achieve a broadband absorption. The theoretically optimized top and back gratings had periodicity of 490 nm, with front grating elements of 60 by 10 nm and back elements of 60 by 30 nm. Under TM polarized light, absorption increased from 48% to 65%. In addition, OSCs with combined gratings were much less sensitive to the angle of incident light than the single grating cases when there were no obvious influence on the TE polarized light absorption. Recently, a more sophisticated grating structure incorporating nanovoids into conventional rectangular backplane gratings has been theoretically proposed.^[199] Hybridization of Fabry–Perot cavity modes originated from surface plasmon reflection at the grating elements with strongly localized plasmonic modes of the nanovoids was demonstrated to significantly enhance performance in the long wavelength regime, while at the same time, the absorption improvements induced by conventional grating structures

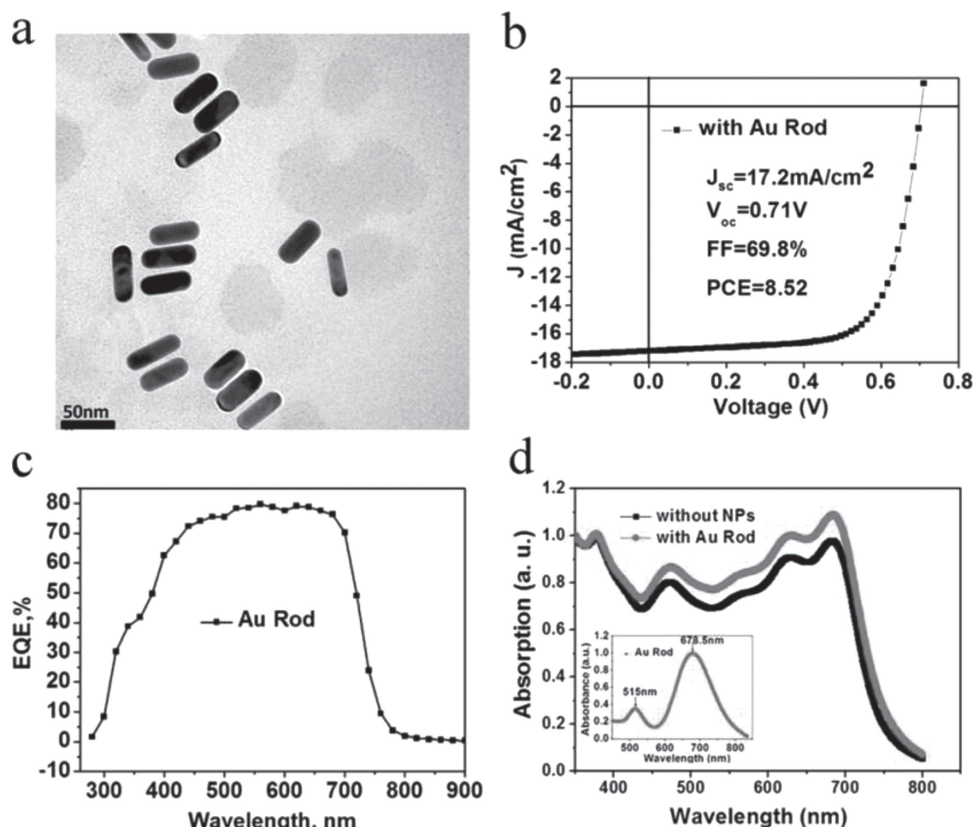


Figure 22. a) TEM images of Au Rod in water. b) J–V curve of PTB7/PC₇₀BM with Au Rod. c) EQE spectra of PTB7/PC₇₀BM with Au Rod. d) UV–vis absorption spectrum of PTB7/PC₇₀BM with and without Au Rod. Inset: UV–vis absorption spectrum of Au Rod in water. Reproduced with permission.^[147] Copyright 2013, American Chemical Society.

in the short wavelength regime were preserved. The absorption could achieve up to 41% enhancement compared with the OSCs without any grating.

Dual metal nanostructures in one unit of inverted OSCs composed of Au NPs (i.e., LPR) embedded in the active layer and an Ag nanograting electrode (i.e., SPR) as the back reflectors were experimentally demonstrated as shown in Figure 25.^[150] The inverted OSC device structure was ITO/ TiO₂ (20 nm)/ poly{[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl]-*alt*-[2-(2'-ethyl-hexanoyl)-thieno[3,4-b] thiophen-4,6-diyl]} (PBDTTT-C-T):PC₇₀BM + Au NPs (100 nm thick)/MoO₃ (10 nm)/Ag nanograting electrode. Various Ag nanogratings with the mask grating periodicities of 750 nm and 350 nm as well as concentration of Au NPs with diameters of 20 nm and 50 nm were individually optimized for the best OSC performances before integrating together to form the dual plasmonic OSCs. By theoretical studies of the fundamental physics behind various intriguing optical phenomena, the results showed that the collective excitation of Floquet modes, SPR, LPR and their hybridizations would enable broadband absorption enhancement. In addition, the devices achieved positive electrical effects simultaneously. The positive electrical effects included the improved hole and electron mobilities and better balance of the mobilities. The presence of positive electrical effects was important because the improvement

of light trapping and optical absorption was not the sole target in a practical optical design. A correspondingly critical requirement in designing device structures is how to design practical optical device structures for realizing both improved optical absorption and positive electrical effects. With the comprehensive studies, the best performed OSCs with the dual plasmonic metal nanostructures achieved PCE of 8.8% (average)^[150] and 9.2% (best) as shown in Figure 25. By replacing the 2D nanograting with the 3D metal nanograting pattern demonstrated by the same group,^[123] further performance enhancement and polarization-independent optical response could be achieved in dual plasmonic OSCs.

4. Conclusions

We have summarized the recent development of new phosphorescent metal complexes that are mainly based on iridium, platinum, and few other transition metals. The emission energy is strongly affected by the structure of the ligand, as it may affect the relatively energy level of different excited states. In addition, the rigidity of the complexes formed has also been demonstrated to be an important factor in the improvement in device efficiency and emission color purity. Other electronic properties such as charge-carrier mobilities can also be

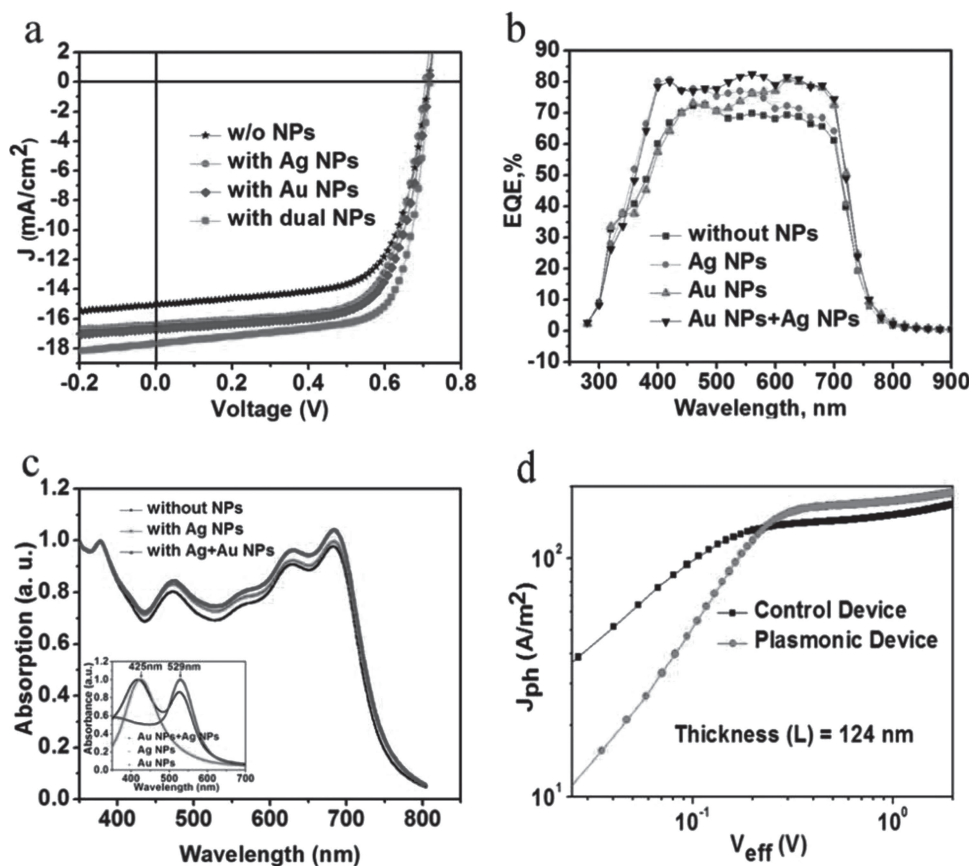


Figure 23. a) Current–voltage characteristics of solar cells with and without NPs. b) EQE spectra of PTB7/PC₇₀BM with and without NPs. c) UV–vis absorption spectra of PTB7/PC₇₀BM without NPs, with Ag NPs and with dual NPs. Inset: UV–vis absorption spectrum of NPs in water. d) Photocurrent density (J_{ph}) versus effective voltage (V_{eff}) characteristics of the control and dual NPs devices. Reproduced with permission.^[147] Copyright 2013, American Chemical Society.

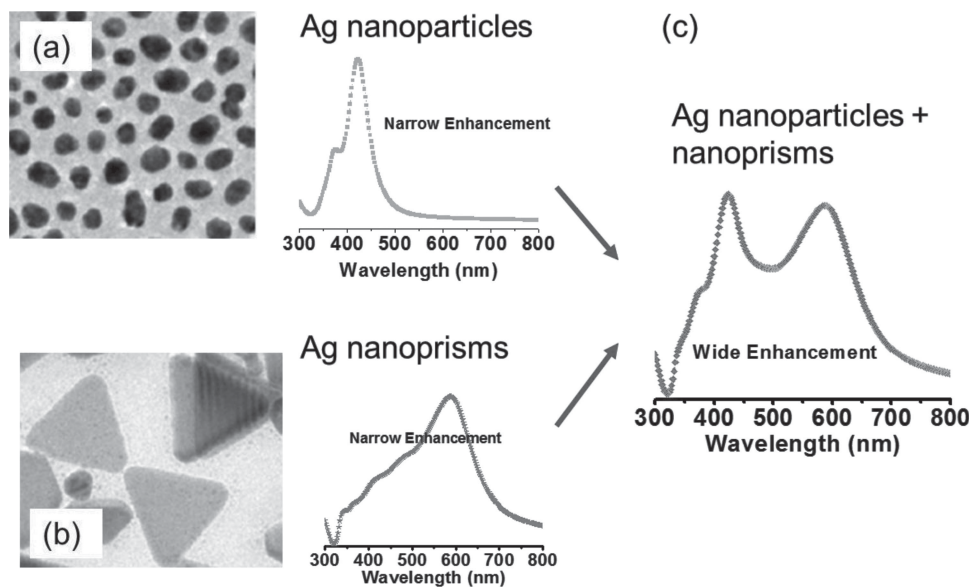


Figure 24. Schematic diagram showing the 20 nm Ag NPs and 60 nm Ag nanoprisms with different extinction peaks in ethanol. The combined Ag nanomaterials solution show widened enhancement spectrum. Reproduced with permission.^[146] Copyright 2013, John Wiley and Sons.

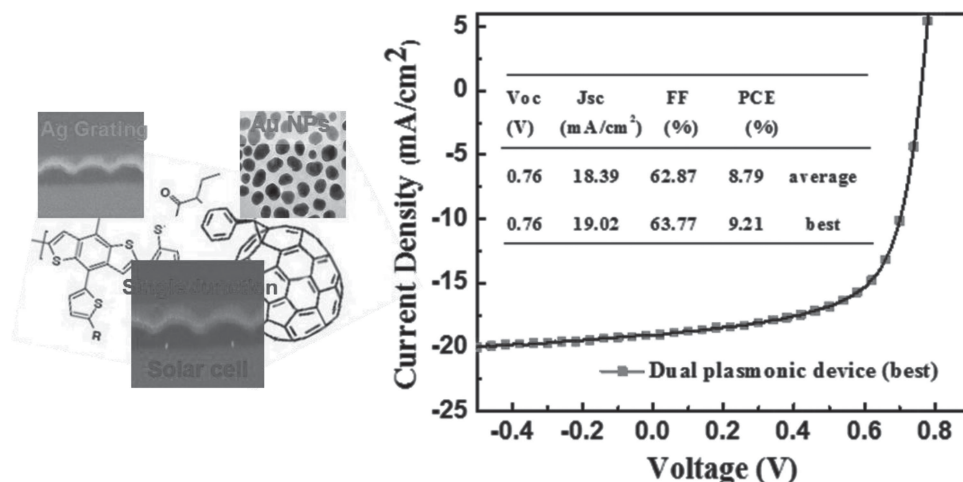


Figure 25. The left hand figure shows the SEM pictures of the Ag nanograting, Au NPs and the cross-section SEM picture of integrated Ag nanograting and Au NPs on the background chemical structures of PDBTTT-C-T and PC₇₀BM. The right hand figure shows the J–V characteristics of the best performed dual plasmonic OSCs with PCE of 9.2%. Inset was a table showed the device parameters of the dual plasmonic OSCs. Reproduced with permission.^[150] Copyright 2012, John Wiley and Sons.

improved by the insertion of charge-transport units into the ligand. In addition, most phosphorescent-light-emitting molecules reported to date are based on expensive transition metals, which clearly limits their practical application in commercial products. The use of relatively low cost transition metal complexes based on zinc, copper etc. and the harvesting of both triplet and singlet emissive excited states may be a possible direction of the development of phosphorescent metal complexes. Although organic materials have already been applied in commercial devices, there is still room for improvement in device lifetime/efficiency, and for lighting applications. Regarding the light extraction of OLEDs, through intensive investigation and novel approaches (e.g., photonic crystals, array patterns, and substrate patterning), architectures (e.g., microcavity structure) and material systems (low-index insertion layer and high-index substrate), ideal light extraction has been significantly improved. The future development of simple and practical light-extraction schemes will contribute the new evolution of high-performance OLEDs. For the light trapping of OSCs, various remarkable and new methods based on metal nanomaterials and nanostructures, that can enhance the light absorption within a very thin active layer of a few hundred nanometers, and their optical and electrical physics have been described. The PCE of OSCs incorporating metal nanostructures has reached about 9%. With further advances of wide-band and polarization-independent light-trapping schemes, which increase not only the optical absorption but also the electrical properties, will make OSCs become practical alternatives for photovoltaics.

Acknowledgements

This work was supported by the Research Grants Council (RGC) of the Hong Kong Special Administrative Region, China through the Theme Based Research Scheme T23–713/11, the General Research Fund (HKU711813, HKU700311P and HKU711612E), the RGC-NSFC grant

(N_HKU 705/10 and N_HKU709/12), and the collaborative research fund of CUHK1/CRF/12G. W.C.H.C. would like to acknowledge technical help from Wei. E. I. Sha, Jian Mao, and Xingang Ren in preparing the manuscript.

Received: December 16, 2013

Revised: May 21, 2014

Published online: July 10, 2014

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