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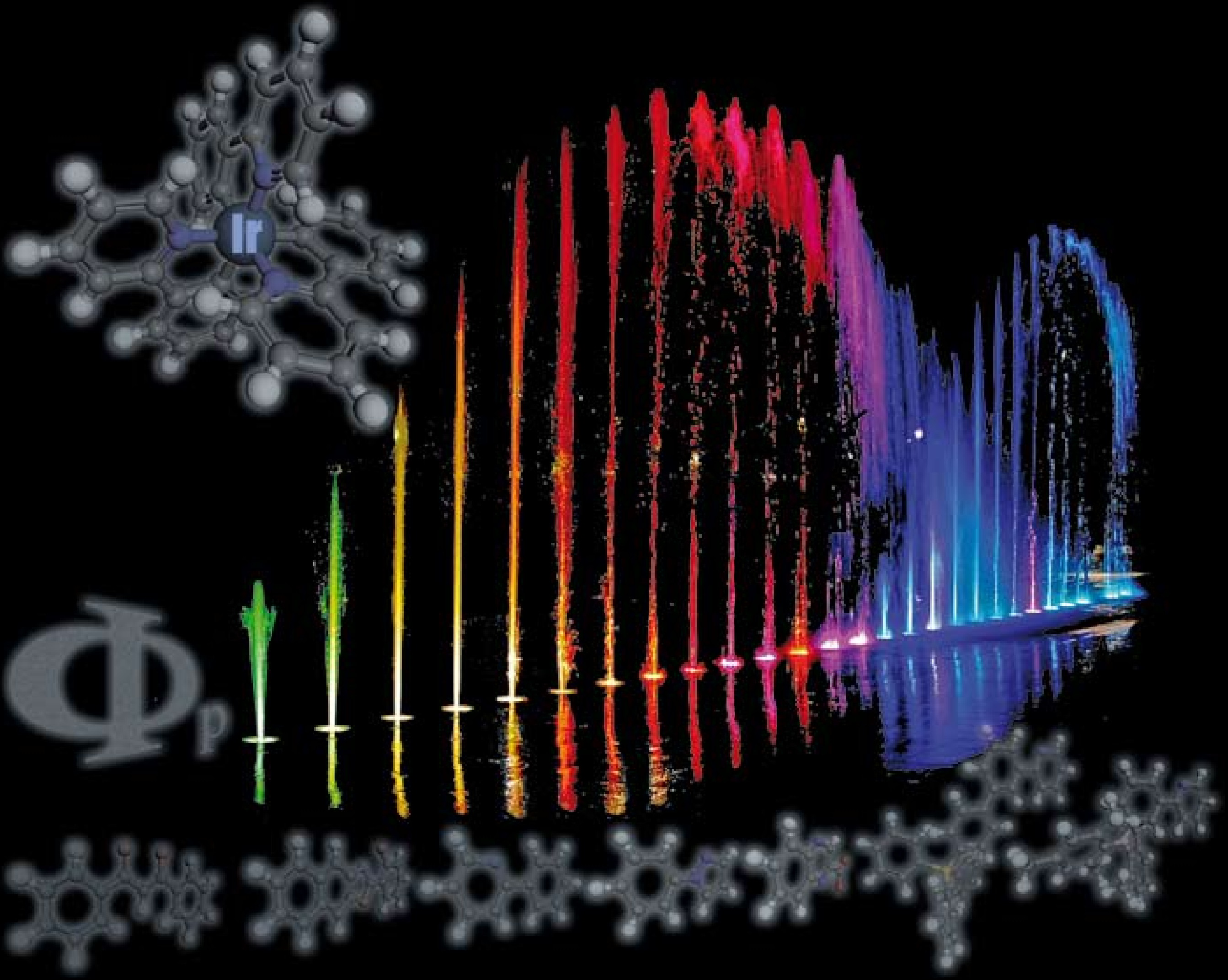

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Phosphorescent iridium(III) complexes: toward high phosphorescence quantum efficiency through ligand control

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Phosphorescent Ir(III) complexes attract enormous attention because they allow highly efficient electrophosphorescence. In pursuing the development of Ir(III) complexes during the last decade, significant progress has been made in terms of the colour-tunability, thermal- and photo-stability, phase homogeneity, and phosphorescence efficiency. By far, extensive synthetic efforts have been focused on the molecular design of ligands to achieve a wide range of phosphorescence colour that is compatible with organic light-emitting device (OLED) applications. In contrast, less has been known about a collective structure–property relationship for phosphorescence quantum efficiency. In fact, a few rule-of-thumbs for high phosphorescence quantum efficiency have been occasionally reported, but a collective rationale is yet to be investigated. In this article, we provide a comprehensive review of 8 different methods reported so far to achieve high phosphorescence quantum efficiency from Ir(III) complexes. The methods included herein are limited to the cases of intramolecular controls, and thus are discussed in terms of variations in ligand structures: (1) geometric isomer control, (2) rigid structure and restricted intramolecular motion, (3) larger mixing of ^{1}MLCT and ^{3}LC states, (4) de-stabilizing a thermally accessible non-emissive state, (5) introducing dendrimer structures, (6) control in substituents of ligands, (7) confining the phosphorescent region of a mixed ligand Ir(III) complex and (8) sensitized phosphorescence by using attached energy donors. Each method is closely related to intramolecular excited state interactions, which strongly affect radiative or non-radiative transitions. A comprehensive understanding of these methods leads us to conclude that the modulation in ligand structures has a profound effect on both the phosphorescence colour and phosphorescence quantum efficiency. Thus, the judicious selection of ligand structures and their chelate disposition should be considered before synthesis. We expect that the guidelines for attaining a high phosphorescence efficiency, summarized in this Perspective, would be helpful in developing highly phosphorescent Ir(III) complexes.

Introduction

Transition metal complexes are drawing great interest as they offer highly efficient room-temperature phosphorescence. In particular, Ir(III) complexes are considered to be the most promising since

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Soo Young Park earned his PhD degree from Seoul National University (SNU) on plasma polymerization (1988). He was a senior researcher in the Korea Institute of Science and Technology 1985–1995 and a frontier researcher at the Institute of Physical and Chemical Research, Japan, 1992–1993. He joined the SNU faculty in 1995 and was tenured to full professor. Since 2004 he has been Professor in Materials Science and Engineering at SNU and a director of the 'Organic Nanophotonics' National Research Laboratory of Korea.

they exhibit: (1) good photo- and thermal stabilities, (2) high phosphorescence quantum efficiency (Φ_p), (3) relatively short phosphorescence lifetimes (τ_p), (4) facile colour tuning through ligand structure control and (5) large cross-section for the exciton formation.[1] Such characteristic features of Ir(III) complexes are attributed to the efficient spin–orbit coupling provided by the Ir metal as well as the strong structural/electronic interactions between the Ir metal and ligands.

Phosphorescent Ir(III) complexes are promising for various applications such as biological labelling agents[2–4] and phosphorescent sensors.[5–22] Facile generation of triplet states then enables encouraging applications as sensitizers for charge-transfer reactions in DNA,[23–25] photocatalysts for CO_2 reduction[26–27] and singlet oxygen sensitizers.[28–30] Above all, the most important projected use of the Ir(III) complexes is electrophosphorescence including light-emitting electrochemical cells (LECs)[31–36] and organic light-emitting devices (OLEDs).[37–39] This is due to the above mentioned characteristics of Ir(III) complexes, which enable both nearly 100% internal device quantum efficiency and versatile colour tuning. Such promising features prompted the development of a number of novel phosphorescent Ir(III) complexes and valuable reviews were recently published.[34,40–42]

The use of phosphorescent emitters is particularly attractive in developing polymer-based OLEDs, not to mention standard vacuum evaporation-based OLEDs. For the large-area display or illumination, solution processes utilizing polymeric materials, such as spin-coating or inkjet printing are indispensible. However, a relatively low device efficiency of fluorescent polymer-emitting layers unfortunately retards their aggressive use in polymer OLEDs although luminance is already acceptable for commercial application. Hence, it is widely recognized that phosphorescent polymer-emitting layers will provide a significant breakthrough in obtaining both the large active area and high device efficiency. In this regard, much effort has been devoted to give successful demonstrations of high efficiency electrophosphorescence from polymer systems comprising Ir(III) complexes.[43–56]

In pursuing Ir(III) complexes for the successful electrophosphorescence, the key requirement is to attain high Φ_p. Many novel highly phosphorescent Ir(III) complexes have been reported so far, but the study on collective structure–property relationships for obtaining large Φ_p is rather rare in the literature and still not fully established. Even though quantum chemical methods such as density functional theory (DFT) and time-dependent density functional theory (TD-DFT) are very successful in predicting phosphorescent emission energy ($\lambda_{\text{phosphorescence}}$) and related electronic states, they fail to afford quantitative information on Φ_p due to their deficiency in taking spin–orbit coupling effect. Therefore, it is highly desirable to establish general guidelines and methods to obtain high Φ_p Ir(III) complexes. This prompted us to collect reported examples of controlled Φ_p and find correlation of them with ligand structures. In this Perspective, we overview the structural parameters affecting Φ_p and then summarize the methods to attain high Φ_p from phosphorescent Ir(III) complexes. The methods covered herein include: (1) geometric isomer control, (2) rigid structure and restricted intramolecular motion, (3) larger mixing of ^{1}MLCT and ^{3}LC states, (4) de-stabilizing a thermally accessible non-emissive state, (5) introducing dendrimer structures, (6) control in substituents of ligands and (7) confining the phosphorescent region of a mixed-ligands Ir(III) complex.

In addition to these methods, this Perspective introduces a widely used tactic to achieve high phosphorescence brightness utilizing (8) sensitized phosphorescence by using attached energy donors.

Before starting the discussion, it would be helpful to introduce the concise basics of the general structure and photophysical processes of phosphorescent Ir(III) complexes, and to define relevant terminology.

Basic structure of phosphorescent Ir(III) complexes and ligand control

The general structure of a phosphorescent Ir(III) complex includes one core Ir atom and three monoanionic bidentate ligands. Usually, the atoms in the ligand, which are bonded to the Ir are C and N, where C has a formal negative charge. The coordinative disposition around the Ir atom involves the formation of a 5- or 6-membered metallacycle, and the most popular ligand is 2-phenylpyridine (ppy). These C∧N ligands and the resulting complexes are named cyclometalating ligands and cyclometalated complexes, respectively. Other ligands are called ancillary ligands if their ligand structure is different from that of the cyclometalating ligand. Representative examples of such ancillary ligands are picolinate and acetylacetonate.

The standard synthesis of an Ir(III) complex is accomplished through a two-step process in which the first step is known as the Nonoyama reaction that yields a chloride-bridged dinuclear Ir(III) dimer.[57,58] The Ir(III) dimer contains four cyclometalating ligands. To this Ir(III) dimer, substitution of the third ligand for the chlorides results in the final phosphorescent complex. The third ligand can be either a cyclometalating ligand or an ancillary ligand. If it is identical with the two cyclometalating ligands, which have been already incorporated in the dimer, the resulting complex is designated homoleptic, and otherwise, heteroleptic. In addition, since the coordination arrangement of an Ir(III) complex is octahedral, the homoleptic Ir(III) complex could have geometric isomers of either facial (*fac*-) or meridional (*mer*-) form (Fig. 1). In contrast to the meridional form, the facial form principally has a C_3 axis of symmetry and this induces different photophysical properties in terms of Φ_p, τ_p and absorption or phosphorescence spectral shape.[59]

Although many different ligand structures have been reported, most of the cyclometalating ligands have one neutral coordinating part and one anionic part. The ppy is a typical ligand structure in which the phenyl ring plays the role of the anionic part. Some of congeneric examples are benzo[*h*]quinone, 2-phenyloxazole, 2-phenylbenzo[*d*]thiazole and 2-(2-pyridyl)thiophene. The Ir–C bond between the Ir(III) metal and these ppy-based ligands is very strong enough to be comparable to covalent bonds. Thus, the structure of the complex is characterized as a multiply bonded and compact framework, which brings both extremely good thermal stability and extensive electronic interactions between the d-orbital of Ir and π-orbital of the ligands. Additionally, since the Ir atom is known to have a large spin–orbit coupling effect, the Ir(III) complexes have more chances to exhibit efficient room-temperature phosphorescence.

Similar to many phosphorescent as well as fluorescent chromophores, multiple optical excitation paths are available in

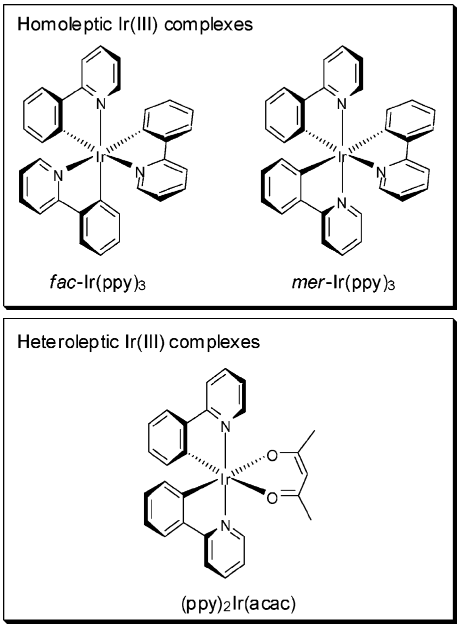

Fig. 1 Structure of Ir(III) complexes containing 2-phenylpyridine (ppy) cyclometalating ligands.

an Ir(III) complex particularly because of: (1) the delocalized highest occupied molecular orbital (HOMO) that spans over the Ir atom and anionic phenyl rings of ligands, (2) the lowest unoccupied molecular orbital (LUMO) preferentially localized at ligands and (3) efficient spin–orbit coupling. Thus, in principle, at least four transitions, singlet and triplet metal-to-ligand charge-transfer (^{1}MLCT and ^{3}MLCT) transitions and singlet and triplet ligand-centered (^{1}LC and ^{3}LC) transitions, should be considered. Generally, the ^{1}LC transition energy is higher than the ^{1}MLCT transition energy. However, since the exchange energy (E(singlet excited state) $-E$(triplet state)) of the MLCT transition state is smaller than that of the LC state,[60] the ^{3}MLCT transition state energy is higher than the ^{3}LC transition state energy. Hence, the general energetic order of these transitions is ^{1}LC > ^{1}MLCT > ^{3}MLCT ≥ ^{3}LC. Usually, the ^{3}MLCT and ^{3}LC absorption bands are seldom distinguished due to their small molar absorbances and featureless band shapes.

The lowest triplet state, which is responsible for phosphorescence emission according to Kasha's rule,[61] is either ^{3}MLCT transition state or ^{3}LC transition state. Generally, phosphorescence originating from the LC transition state can be distinguished from that of the MLCT transition state in terms of spectral shape, τ_p, rigidochromic and solvatochromic behaviours:[57] (1) LC phosphorescence comprises prominent vibronic structures whereas a MLCT phosphorescence spectrum is structureless, (2) τ_p of LC phosphorescence is longer than that of MLCT phosphorescence, which reflects reduced metal contribution in the LC transition, (3) MLCT phosphorescence exhibits a hypsochromic shift when the medium becomes rigid (*e.g.* when solvent freezes or polymer hosts are left below T_g),[62] and (4) MLCT phosphorescence also exhibits a similar hypsochromic shift in non-polar media.[2,63–65] Both (3) and (4) indicate a charge-transfer (CT) character involved in the MLCT phosphorescence because the CT state energy is strongly affected by the arrangement of electric dipoles of surrounding media.[66,67] Apart from precisely judging which transition (MLCT or LC) state is more responsible for the observed phosphorescence, it is generally accepted to describe that the phosphorescent state is a mixed state of MLCT and LC transition states.[60] There are several literature examples discussing the nature of the phosphorescent state based on the perturbation theory.[68–74] According to this theory, the phosphorescent state is generated between ^{1}MLCT and ^{3}LC transition states through a spin–orbit Hamiltonian. Although, unfortunately, a ligand structure-based relationship that predicts dominance of LC or MLCT character in the phosphorescence is still un-established, it is certain that the LUMO of most Ir(III) complexes resides on the cyclometalating ligands. This allows facile and efficient phosphorescence colour tuning through the cyclometalating ligand structure controls. Many variations of cyclometalating ligand structures and resulting emission controls have been established and easily found in the literature.[57,59,75–98]

The working principle of ancillary ligands on affecting phosphorescence emission is somewhat different from that of cyclometalating ligands. Li *et al.* synthesized heteroleptic Ir(III) complexes by using ancillary ligands of various field strength, such as pyrazolyl, pyrazolemethane, pyrazolylborate, isocyanide, and diphenylphosphine-containing borate.[60] These ancillary ligands controlled the Ir-centered d-(t$_{2g}$) orbital energy, *i.e.* metal-centered HOMO energy, to different extents enabling the authors to manipulate the MLCT transition state energy without altering LC transition state. This manipulation, in turn, resulted in tuning the degree of mixing between the ^{1}MLCT and ^{3}LC transition states. Much similar but earlier results were also reported by Nazeeruddin *et al.*[99] In their study, systematic tuning of the t$_{2g}$ orbital energy was carried out by means of using cyanide, thiocyanate and isocyanate ancillary ligands whose field strength are cyanide > thiocyanate > isocyanate. The resulting Ir(III) complexes were found to emanate blue, green and yellow phosphorescence, respectively. A tendency of this kind of variation of the triplet state can be predicted through the spectrochemical series,[100–102] and more examples of using this strategy were published by Chen *et al.*[103] and Mak *et al.*[84]

In contrast to above studies using non-chromophoric ancillary ligands, chromophoric ancillary ligands were also investigated. Hay conducted quantum chemical calculations based on TD-DFT and DFT in order to envisage a relationship between the structure and the global position of LUMO in molecules.[104] In a series of heteroleptic Ir(III) complexes containing ppy cyclometalating ligands but with variable ancillary ligands, it was specifically observed that the π^* orbital of the benzoylacetonate ancillary ligand (bza) is the global LUMO and constitutes the lowest triplet state, whereas the acetylacetonate ancillary ligand (acac) does not. The relatively small Φ_p of the benzoylacetonate containing Ir(III) complex compared to that of acetylacetonated one was explained based on this LUMO difference. Syntheses and optical characterization of Ir(III) complexes with such chromophoric β-diketonate such as acac, bza and dibenzoylmethane (dbm) ancillary ligands were carried out by Lamansky *et al.*[57] In this work, they found that Φ_p was strongly dependent upon changing the ancillary ligand structures (Fig. 2).

Very recently, it was found that the use of specific low band gap ancillary ligands enabled efficient phosphorescence colour tuning. For example, the introduction of the quinolinecarboxylate ancillary ligand into an Ir(III)–phenylpyrazole system brought about the shift in the location of global LUMO from the

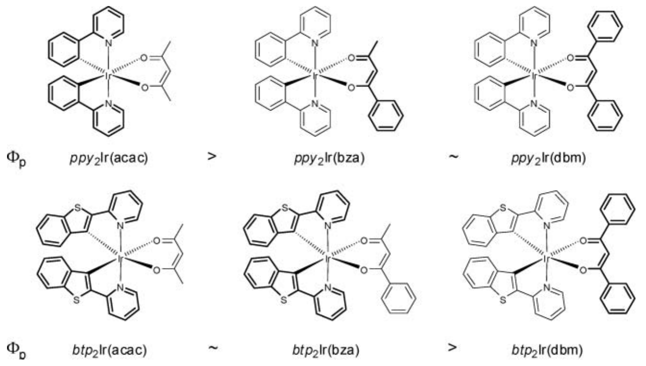

Fig. 2 Change in Φ_p by shifting the LUMO position in heteroleptic Ir(III) complexes. Thick fragments indicate ligands having global LUMO.

phenylpyrazole to the quinolinecarboxylate, thus resulting in colour-tuned phosphorescence in a range of yellow to orange.[105] Our group has also concentrated on colour tuning using chromophoric ancillary ligands.[106–108] By utilizing 2-(2,4-difluorophenyl)pyridine cyclometalating ligand, which is used to obtain blue phosphorescence when coordinated into Ir(III) complexes, a series of lower band gap ancillary ligands were incorporated to give high efficiency ancillary ligand-centered phosphorescence emission. For this phosphorescence tuning, we proposed and observed interligand energy flow from the high energy 2-(2,4-difluorophenyl)pyridine ligand to the low energy ancillary ligand. More detailed discussions and intramolecular energy harvesting phosphorescence by using this interligand photophysics are described in this Perspective.

Methods to achieve high phosphorescence quantum efficiency (Φ_p)

In principle, phosphorescence quantum efficiency (Φ_p) is determined in relation to the radiative rate constant for phosphorescence (k_r) and the non-radiative rate constant (k_{nr}): $\Phi_p = k_r/(k_r + k_{nr})$. Thus, high Φ_p can be attainable either by reducing k_{nr} or increasing k_r. For the case of k_{nr}, well-known band gap (energy gap) law predicts that $\ln(k_{nr})$ is inversely proportional to the emission energy.[109] This implies that higher Φ_p can be observed for higher energy phosphorescence. However, due to additional non-radiative transition processes, such as an energy transfer involving thermal activation, the Φ_p does not strictly obey the band gap law.[110] Meanwhile, phosphorescent k_r is strongly related to spin–orbit coupling in the excited states since k_r has a mathematical formalism including transition probability between singlet ground state and triplet excited state. In a widely recognized expression for this spin–orbit coupling effect, aforementioned perturbation theory is applied to draw a relationship that k_r is proportional to the square of the phosphorescence emission energy but inversely proportional to the energy difference between two perturbing excited states (*e.g.* ^{1}MLCT and ^{3}LC transition states).[60] Thus, in order to describe Φ_p, it is required to consider the nature of the ground state and involved excited states and relevant photophysical interactions among them.

1. Geometric isomer control

As mentioned above, there are two different geometric isomers (*fac*- and *mer*-) for a homoleptic Ir(III) complex. It is known that, principally, the *fac*-isomer is a thermodynamic product and generally yields high Φ_p, whereas the *mer*-isomer is a kinetic product and has low Φ_p. Thus, it is quite preferred to obtain *fac*-forms. A systematic study on synthetic control and optical characterization of *fac*- and *mer*-Ir(III) complexes was performed by Tamayo *et al.*[59] They prepared a series of homoleptic Ir(III) complexes from two different cyclometalating ligands of ppy and 1-phenylpyrazole (ppz) derivatives. Among three different methods employed for the synthesis, a two-step process employing the Nonoyama reaction[58] followed by substitution of an identical cyclometalating ligand for the chlorides gave the best result. During this final step, mixtures of *fac*- and *mer*-forms were inevitably obtained. However, temperature control improved selectivity in these isomers: high temperature (>200 °C) gave the *fac*-Ir(III) complex as a major product but relatively low temperature (<150 °C) preferentially furnished the *mer*-Ir(III) complex. In addition, they were also successful in transforming *mer*-Ir(III) complexes to *fac*-forms by refluxing in glycerol. More importantly, different optical behaviours of *fac*- and *mer*-isomers were testified by observing that *mer*-forms have broad and bathochromically shifted phosphorescence spectra compared to those of *fac*-forms. In contrast, *fac*-Ir(III) complexes exhibited higher electrochemical stability and higher Φ_p. The smaller Φ_p (less than 1/10 of that of *fac*-form) of *mer*-isomers was ascribed to: (1) the bond dissociation in the excited state to yield the more stable *fac*-isomer, which quenches the excited state energy and (2) relatively long *trans* Ir–C distances. However, since heteroleptic Ir(III) complexes containing identical cyclometalating ligands can be easily synthesized under milder reaction conditions to give high Φ_p and controlled phosphorescence colours, it is not always necessary to synthesize *fac*-homoleptic Ir(III) complexes at such high reaction temperatures.

2. Rigid structure and restricted intramolecular motion

In some cases, it has been observed that Φ_p of Ir(III) complexes in solid states such as frozen solutions, doped polymer films or powdery states is higher than that in fluidic solution states. Apart from the temperature effect on phosphorescence in the frozen solution, higher Φ_p in immobilized states is very much beneficial because many applications are based on the solid state uses. For instance, Harding *et al.* reported such behaviour from a series of Ir(III) complexes comprising dendronic ligands, which showed enhanced brightness in doped poly(methylmathacrylate) films (6 wt%).[111] A similar observation was reported earlier by Sajoto *et al.*[112] When *fac*-tris(1-[(9,9-dimethyl-2-fluorenyl)]pyrazolyl-$N,C^{2'}$)iridium(III) (*fac*-Ir(flz)$_3$) or Ir(III) complexes with *N*-heterocyclic carbene ligands were dispersed in poly(styrene) films, Φ_p increased by more than one order compared to that in solution. These observations indicate that motional relaxations imposed on the specific part of the molecular structure are responsible for hazardous non-radiative transitions, thus resulting in low Φ_p in mobile states. For the structural origin of these behaviours, Ir–ligand stretching vibrations[110,111], C–C ring deformation[60] and C–H vibration in aryl rings[98] were suggested. These vibrational motions aid strong coupling between vibronic levels in the potential energy surface of ground state and isoenergetic levels in the potential energy surface of excited states, thus facilitating faster non-radiative transitions.[111] Li *et al.* commented in their publication that a longer C–Ir bond influences the Ir–ligand stretching to increase vibronic coupling (Herzberg–Teller coupling).[1,60]

The degree of the vibrational non-radiative decay can be estimated by the Huang–Rhys factor (*S*), which is roughly a ratio of the amplitude of (0–1) band over the amplitude of (0–0) band of a phosphorescence spectrum for single mode approximation.[113] Since non-radiative transition probability is proportional to the displacement in the excited state, the magnitude of the Huang–Rhys factor, which is proportional to the square of the displacement in the excited state, allows us to estimate the degree of non-radiative coupling. That is, a large Huang–Rhys factor indicates increased vibrational non-radiative decay and small Φ_p. For example, Lo *et al.* observed an apparent tendency of decreased Φ_p with increasing temperature in a series of blue phosphorescent Ir(III) complexes containing phenyltriazolate ligands.[87] Such a phenomenon could not be explained by the simple band gap law. Instead, they proposed a deactivation mechanism describing a vibrationally activated non-radiative decay based on identified strong-coupling limit (Huang–Rhys factor > 1).

Similar examples were also found for a class of heteroleptic Ir(III) complexes. Zhao *et al.*[114] and our group[115] recently reported highly enhanced phosphorescence in the solid state for a series of Ir(III) complexes containing imine-based chromophoric ancillary ligands (Fig. 3). The compounds were nearly non-phosphorescent ($\Phi_p < 0.002$, quinine sulfate standard[116]) in various solution states, whilst frozen solution, doped polymer films and powders of them (absolute PLQY[117]) showed very bright phosphorescence (Table 1). The corresponding Φ_p enhancement in the solid state was larger than that in solution by two orders. Based on a series of absorption and photoluminescence experiments for various temperature-controlled samples, crystal structure determination and the predicted triplet state geometry, we were able to propose that restricted intramolecular motions in the solid state are responsible for such behaviour. In other words, it was considered that increased motional freedom imposed on the imine fragment of the chromophoric ancillary ligand attributed to the very low Φ_p in the solution state.

Table 1 Photophysical and electrochemical data of the Ir(III) complexes in Fig. 3

	PL λ_{max}/nm	Φ_{solid} [a]	$\Phi_{solution}$ [b]
1	563	0.53	0.0020
2	596	0.24	0.0013
3	581	0.20	0.0011
4	604	0.18	0.0019

[a] Absolute PLQY. [b] Quinine sulfate reference.

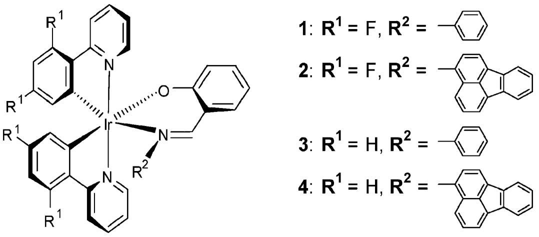

Fig. 3 Heteroleptic Ir(III) complexes exhibiting highly enhanced phosphorescence in the solid state.

Based on these results, it could be concluded that a plausible design rule of the ligand structure for higher Φ_p is to minimize hazardous intramolecular motions. This strategy is particularly important for deep red phosphorescence since poor brightness is expected by the band gap law. One of such approaches is to employ rigid and compact ligand frameworks. In fact, Duan *et al.* achieved high Φ_p (~0.5) red phosphorescence from Ir(III) complexes containing dibenzo[*f*,*h*]quinoxaline ligands (Fig. 4a).[75] Compared with ppy-based ligands, the dibenzo[*f*,*h*]quinoxaline ligands are conformationally more rigid due to the additional fused benzene ring. Hwang *et al.* also aimed at achieving highly efficient red phosphorescence by utilizing 2,3-diphenylquinoxaline ligands in which the quinoxaline moiety is believed to provide enhanced rigidity of the ligand framework (Fig. 4b).[82] Likewise, Ono *et al.* reported a notable result that smaller Φ_p was observed for the ppy ligands tethering conformationally free substituents such as diphenylamine or phenoxazine, while a conformationally rigid carbazole substituent gave a relatively larger Φ_p (Fig. 5).[88]

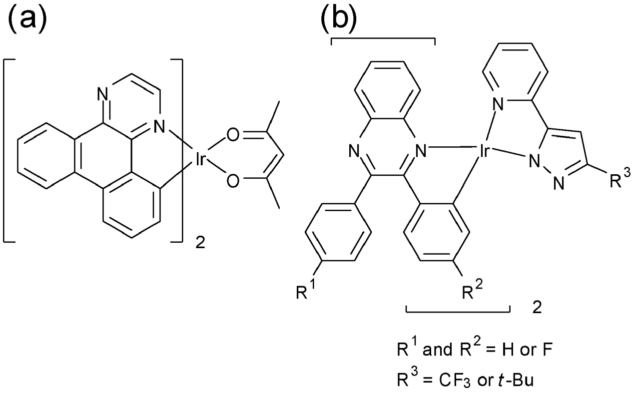

Fig. 4 Highly phosphorescent Ir(III) complexes containing rigid ligands.

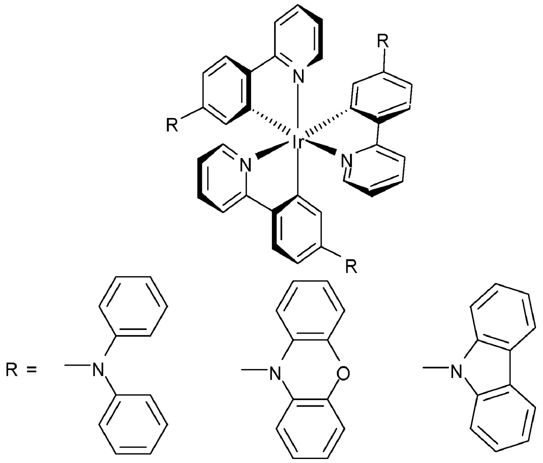

Fig. 5 Phosphorescent Ir(III) complexes comprising ligands of controlled rigidity.

3. Larger mixing of ^{1}MLCT and ^{3}LC states

As mentioned before, the lowest triplet state for phosphorescence is considered as a mixed state between the ^{3}LC transition and ^{1}MLCT transition states through spin–orbit coupling. This mixed state can carry MLCT character in various degrees depending on the structure of ligands[62,70,118] or, more precisely, an energy gap between the ^{1}MLCT and ^{3}LC transition states. Since a faster phosphorescent transition rate, thus high Φ_p can be obtained by larger participation of the MLCT state, it is very important to secure the strong contribution of MLCT character in the triplet state. A successful control of this method has been achieved by Li *et al.*[60] They tuned the ^{1}MLCT transition state energy by introducing various ancillary ligands of different degrees of electrochemical effect (ligand field effect) without altering the cyclometalating ligand-centered LC transition state energy. The structural fragment of the Ir(III) core and 2-*p*-tolylpyridine-based cyclometalating ligands was fixed, and acac, bis(pyrazolyl)borate, diphosphine chelates or *tert*-butylisocyanide ancillary ligands were introduced (Fig. 6). As a result, while the reduction potential of the Ir(III) complexes was relatively intact, the oxidation potential of them showed a large dependence upon varying the ancillary ligands. Since oxidation process in the Ir(III) complexes occurs mostly at the Ir(III) center, this observation indicates that the MLCT transition state energy was selectively controlled. That is, energetic position of the ^{1}MLCT transition state energy could be varied relative to that of ^{3}LC transition state energy. Regarding spin–orbit coupling between them as the first order perturbation, we can expect that more MLCT contribution to the lowest triplet state would be achieved if the energy difference (ΔE) of the ^{1}MLCT and ^{3}LC states is smaller. Thus, enhanced spin–orbit coupling, and consequent a larger phosphorescent transition rate can be attainable to induce a large Φ_p (see Fig. 7). As a result, it is concluded that lowering ΔE of ^{1}MLCT and ^{3}LC can be an effective method in achieving high Φ_p if the Φ_p is solely governed by the radiative transition rate. Practically, reducing the ΔE of the ^{1}MLCT and ^{3}LC transition state energy could be achieved through lowering the ^{1}MLCT transition state energy by using electron-donating ligands which de-stabilize the t_{2g} orbital of the Ir atom. Hence, before applying newly synthesized ligands, it is necessary to consider their electrochemical effect on MLCT transition energy.

The relative dominance of MLCT or LC character in the phosphorescence state and resulting photophysical behaviours

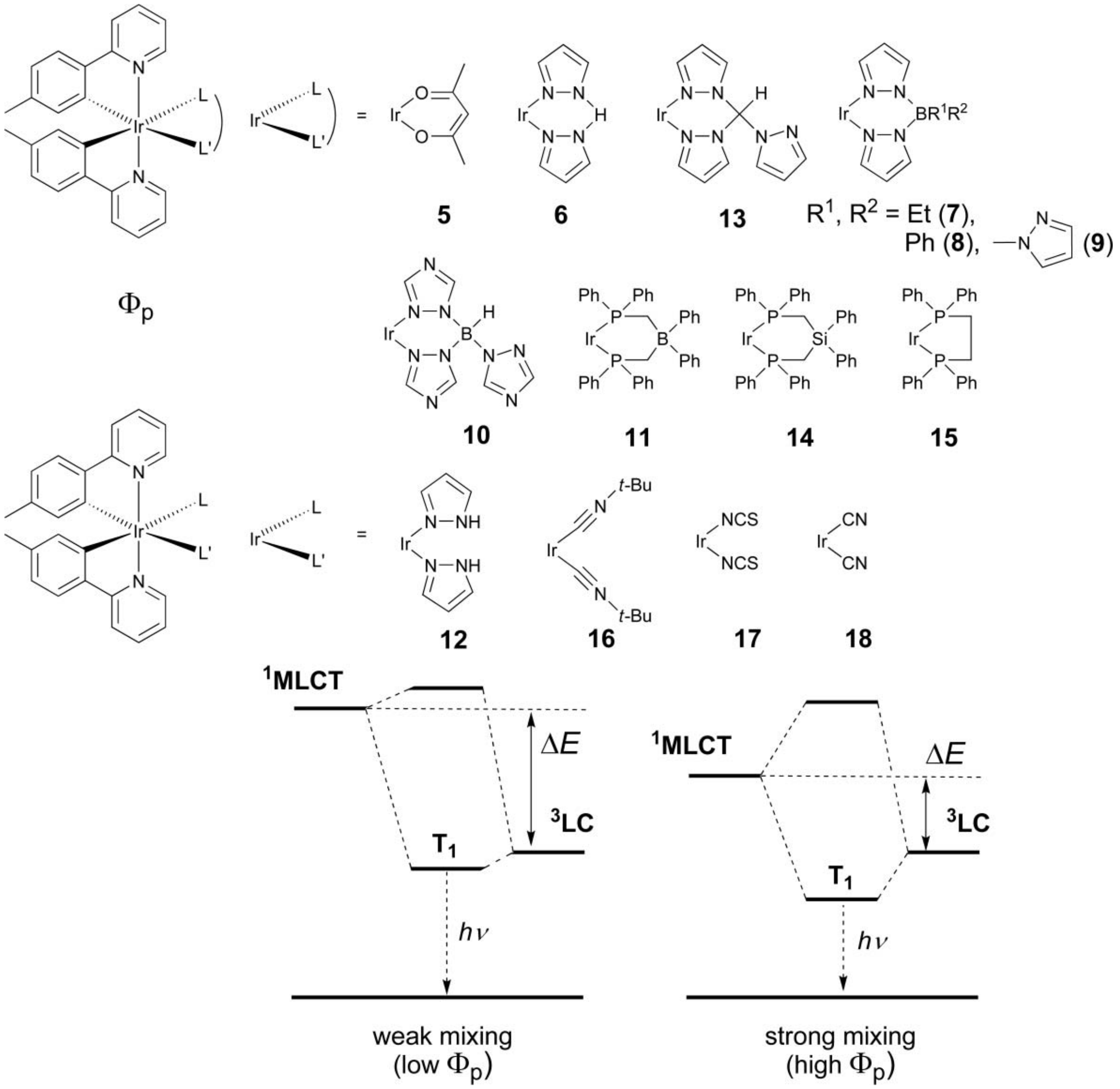

Fig. 6 Heteroleptic Ir(III) complexes showing a controlled ^{1}MLCT transition state energy.

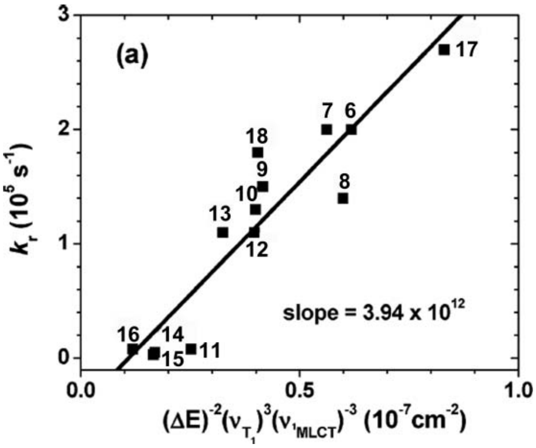

Fig. 7 Plot of radiative decay rate (k_r) *vs.* $(1/\Delta E)^2(\nu_{T1}/\nu_{1MLCT})^3$ for (tpy)$_2$Ir(LL′) complexes. Refer to Fig. 6 for the structures of complexes and the used notations. Reprinted with permission from *Inorg. Chem.* 2005, **44**, 1713–1727. Copyright 2005 American Chemical Society.

have been well described by Tsuboyama *et al.*[62] They synthesized red phosphorescent Ir(III) complexes by coordinating low band gap cyclometalating ligands, such as 2-thiophene-2-ylpyridine, 2,5-dithiophene-2-ylpyridine, 2-(benzo[*b*]-thiophen-2-yl)pyridine, 2-(9*H*-fluoren-2-yl)pyridine, 1-phenylisoquinoline, 1-(thiophen-2-yl)isoquinoline and 1-(9*H*-fluoren-2-yl)isoquinoline. Then they classified the resulting Ir(III) complexes into MLCT or LC groups based on their photophysical behaviours. Their finding was that the Φ_p of the MLCT group is larger than that of the LC group, given that the emission energy is the same. It was also found that the MLCT group shows greater radiative transition rates. These phenomena were explained based upon the radiative transition rate, which is proportional to the square of the transition dipole moment for phosphorescence. In this relationship, the dipole moment is again a function of the spin–orbit coupling product of the ^{1}MLCT transition state and the ^{3}LC transition state. Consequently, it is to be noted that the larger mixing through a close energetic positioning of the ^{1}MLCT and ^{3}LC states affords larger Φ_p.

However, this approach implies that high efficiency blue phosphorescent Ir(III) complexes are not easy to obtain because lowering the ^{1}MLCT transition state energy through raising (de-stabilizing) the HOMO energy, aiming at achieving high Φ_p, inevitably results in bathochromically shifted emission. Dedeian *et al.* concluded in their recent publication that stabilization of the HOMO finally leads to smaller Φ_p.[63] Their photophysical and electrochemical data on a series of heteroleptic Ir(III) complexes manifested that stabilization of the HOMO energy by introducing cyanide or isocyanide ancillary ligands gives rise to high energy ^{1}MLCT transition state (*i.e.* blue emission), but this induces smaller mixing between ^{1}MLCT and ^{3}LC transition states, which finally results in smaller radiative transition rate. This explanation is in accordance with the above-mentioned discussion by Li *et al.*[60]

In contrast, there is a recent report that mere increases in MLCT character may lead to concomitant enhancement in both k_r and k_{nr}. This means that Φ_p can be decreased although MLCT character increases. Through extensive investigation on isoelectronic blue phosphorescent Os(II) complexes containing 5-(2-pyridyl)azolate, 5-(2-pyridyl)-1,2,4-triazolate, trifluoroacetate or carbonyl ligands, Cheng *et al.* found that greater MLCT contribution adversely resulted in smaller Φ_p.[119] This ironical result was explained to happen when both k_r and k_{nr} are attributed to the identical wave functions of the triplet state and ground state, which implies that non-radiative transition is subject to the same MLCT contribution as radiative transition is. Thus, together with large MLCT contribution, it might be important to provide a deep potential energy surface of the triplet excited state in order to prevent facile vibrational coupling with a potential energy surface of ground state. This could be achieved by using ligands of rigid structure. All together, it is important to have rigid ligands and to implement more MLCT character into excited state for realizing high Φ_p.

4. De-stabilizing a thermally accessible non-emissive state

It has been recognized that one of the advantageous features of Ir(III) complexes over other phosphorescent transition metal complexes is their high energy metal-centered d–d transition.[63] Since this d–d transition (*e.g.* t_{2g}–e_g) is generally a non-phosphorescent process, such a large d–d transition energy effectively suppresses an exothermic energy transfer from an emissive state to the d–d transition state, thus allowing efficient phosphorescence. In contrast, isoelectric Rh(III) complexes exhibit poor phosphorescence efficiency due to quenching by the proximal non-radiative d–d transition state. However, if we aim at deep blue phosphorescent Ir(III) complexes, this d–d transition state could be a serious problem. That is, as the deeper blue phosphorescence is sought by virtue of wide band gap cyclometalating ligands, the corresponding high-lying triplet state gets to approach the d–d transition state. In this case, thermal energy can facilitate an excited state energy transfer to the d–d transition state to bring about non-radiative transition. For example, it has been demonstrated that such a thermally supported transition to the non-radiative excited state could be really problematic as the triplet state energy of ligands increase. Sajoto *et al.* observed that a homoleptic Ir(III) complex containing 1-phenylpyrazole ligands (Ir(ppz)$_3$) exhibited very low phosphorescence efficiency in solution at room temperature, whereas a relatively low energy-phosphorescent Ir(III) complex of similar structure containing 1-[(9,9-dimethyl-2-fluorenyl)]pyrazole ligands (Ir(flz)$_3$) showed much better efficiency (Fig. 8a).[112] This was due to the thermal propagation of a non-radiative excited state of Ir(ppz)$_3$, which was considered to be either a metal-localized ligand field state (d–d transition state) or a ligand-localized n–π^* state. In order to overcome this problem, they proposed use of *N*-heterocyclic carbene (NHC) ligands (Fig. 8b). The NHC ligand has two short C–Ir bonds and possesses very high ligand field strength. Due to these effects, the NHC ligands strongly de-stabilize the Ir–L anti-bond to effectively shift the non-radiative excited state upward. As a result, thermodynamic probability to populate this proposed non-emissive state at the expense of cyclometalating ligand's triplet state energy is reduced.

The use of high-field ligands was already reported for the study of blue phosphorescence.[63] As mentioned earlier, Nazeeruddin *et al.* demonstrated phosphorescence colour tuning through controlling metal-centered HOMO energy by using cyanide, thiocyanate and isocyanate ancillary ligands.[99] Similarly, Lee *et al.* reported blue-shifted phosphorescence from ppy-based

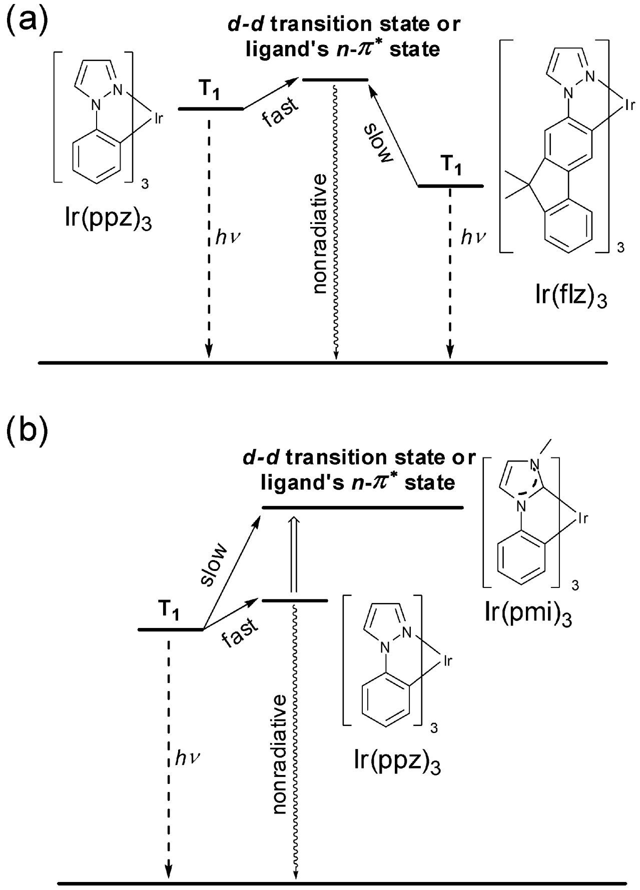

Fig. 8 (a) Energetics of Ir(III) complexes involving non-radiative transitions. (b) Tuning of the non-emissive state (either metal-centered ligand field state (d–d transition state) or ligand-localized n–π* state) to control Φ_p of the Ir(III) complexes.

heteroleptic Ir(III) complexes containing cyanide or tributylphosphine ancillary ligands.[120] In these approaches, de-stabilizing both the phosphorescent MLCT transition state and the d–d transition state was induced by back-bonding of the π-acidic (high-field) ancillary ligands (*e.g.* cyanide and tributylphosphine). From these demonstrations, it can be concluded that both wide band gap cyclometalating ligands and high-field ancillary ligands are required to achieve efficient blue phosphorescence. In contrast, as mentioned in a previous section, simply using high-field ligands would give rise to the increased ΔE between ^{1}MLCT and ^{3}LC transition state energy to reduce the degree of mixing of them. This, subsequently, leading to a low Φ_p.

5. Introducing dendrimer structures

Incorporation of sterically hindering dendrons at the periphery of an emitting core is a widely recognized method for achieving high solid state photoluminescence quantum efficiency. Additional benefits by using dendrimer structures are high thermal stability, enhanced solubility in solvents and polymer matrices, better compatibility in solution processes, and colour tunability. Many helpful reviews were published for the case of fluorescent dendrimers.[121–123] Although, in principle, inherent Φ_p of the emission center is seldom affected by attachment of common dendrons, solid state photoluminescence quantum efficiency is largely controllable by such dendrons. The prime objective in using the dendritic structures is to suppress hazardous non-luminescent ground-state and excited-state interactions, such as aggregates and excimer formations, respectively. This shielding (or site-isolation) strategy is more important for the phosphorescent materials because excited-state lifetime of them is generally much longer than that of fluorescent materials.[21,124–126]

Burn and Samuel's group has carried out pioneering work on phosphorescent Ir(III) complexes with dendronic ligand structures.[111,127–145] They achieved very high device efficiencies from a series of dendrimer Ir(III) complexes tethering 2-ethylhexyloxy terphenyl dendrons. The dendrimers exhibited an efficient site-isolation effect to yield high solid state photoluminescence quantum efficiency. Importantly, their remarkably high efficiency blue (a maximum external device quantum efficiency of 10.4%),[137] green (a maximum emission efficiency of 55 cd A^{-1})[127] and red (a maximum external device quantum efficiency of 5.7%)[131] electrophosphorescence indicate a beneficial role of the dendrons. They also proved the effectiveness of this site-isolation by measuring phosphorescence lifetimes in the solid state; their conclusion was that increased generation of dendrimer structures resulted in less reduction of the phosphorescence lifetime (thus unaltered solid state photoluminescence quantum efficiency).[134,135] This indicates that efficient site-isolation of the phosphorescent center can be attributed to the dendrimer structures. In addition to this, a recent study of them revealed that the dendritic structures are able to efficiently confine electrically generated triplet excitons inside the structure of dendrimer Ir(III) complexes.[144,145] This is a very advantageous feature for high efficiency electrophosphorescence because exciton diffusion generally induces hazardous exciton–exciton annihilations.

However, several disadvantageous aspects of the alkyl-terminated dendrons were pointed out, such as an electrically insulating property and a low T_g of the material. In order to overcome these drawbacks, the use of arylated dendrons has been proposed. Cumpstey *et al.* employed an all aromatic 'Müllen dendron', which was synthesized through a Diels–Alder reaction of 2,3,4,5-tetraphenylcyclopentadiene and acetyl-terminated ppy ligand followed by dehydration to yield a four-phenylated core (Fig. 9a).[146] From a similar point of view, our group reported dendritic Ir(III) complexes containing *p*-triphenylsilylphenyl dendrons (Fig. 9b and c). A noticeably high solid-state photoluminescence quantum efficiency (74 ± 3%) was recorded for the neat film of the Ir(III) complex, with which highly efficient polymer electrophosphorescence devices (32.8 cd A^{-1}) were also fabricated.[117] An electronic effect of this *p*-triphenylsilylphenyl dendron was

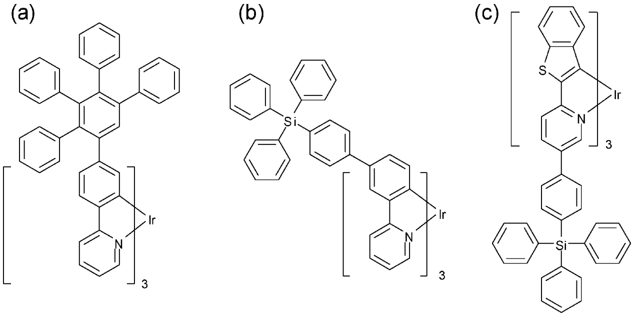

Fig. 9 Dendritic Ir(III) complexes comprising all-aromatic dendrons.

also investigated by attaching it at a pyridylbenzo[*b*]thiophene cyclometalating ligand, which was known to yield red phosphorescence (625 nm) (Fig. 9c).[147] In both photoluminescence and electrophosphorescence spectra, additional bathochromic shifts (646 nm) were observed. This observation, together with DFT calculation results, indicated that introduction of the dendrons preferentially stabilizes the LUMO of the Ir(III) complex to give deep red phosphorescence. This feature is beneficial for red-emitting polymer electrophosphorescence because both deep red phosphorescence and improved phase homogeneity of the doped Ir(III) complex–polymer film can be achieved.

Recent progress in dendrimer Ir(III) complexes is using functional dendrons, such as energy-donating fluorescent moieties or charge-transporting moieties. In fact, these approaches are not directly related to the control in Φ_p. Nevertheless, implementing bright phosphorescence from high Φ_p Ir(III) complexes evidently requires such approaches. In particular, the use of charge-transporting dendrons is expected to overcome the problem of an electrically insulating shell of previous dendrimer Ir(III) complexes. From this viewpoint, hole-transporting carbazole derivatives were encouragingly employed. Lo *et al.* reported the synthesis of a series of Ir(III) complexes containing carbazole dendrons, which showed enhanced hole-transporting properties compared with the alkylated terphenyl dendrimer Ir(III) complex (Fig. 10a).[140] Such an improved charge-transporting behaviour was explained based on delocalized HOMO distribution over carbazole dendrons. Tsuzuki *et al.* also synthesized dendrimer Ir(III) complexes with ppy ligands tethering three or nine 9-phenylcarbazole groups (Fig. 10b).[148] Ding *et al.* adopted the similar strategy of introducing bis(*tert*-butylcarbazole) dendrons into a 1,2-diphenylbenzo[*d*]imidazole cyclometalating ligand (Fig. 9c).[149] Likewise, Li *et al.* synthesized carbazole-end-capped dendritic Ir(III) complexes (Fig. 9d).[150] In addition to carbazole, a hole-transporting bulky triphenylamine moiety was also incorporated into dendrimer Ir(III) complexes, where the number of triphenylamine functionality was varied by adopting it as a dendritic branching structure (Fig. 11).[151] In this

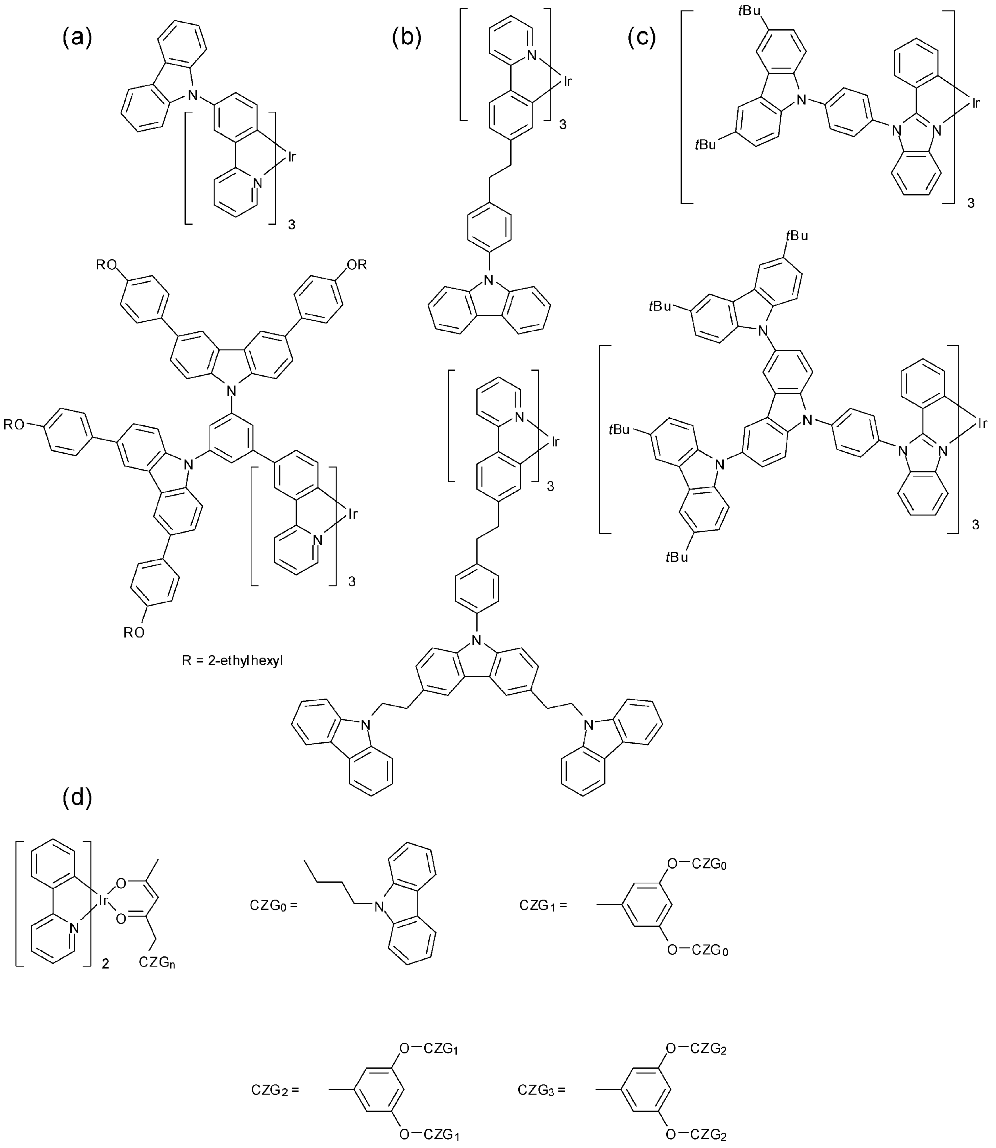

Fig. 10 Dendrimer Ir(III) complexes containing hole-transporting dendrons.

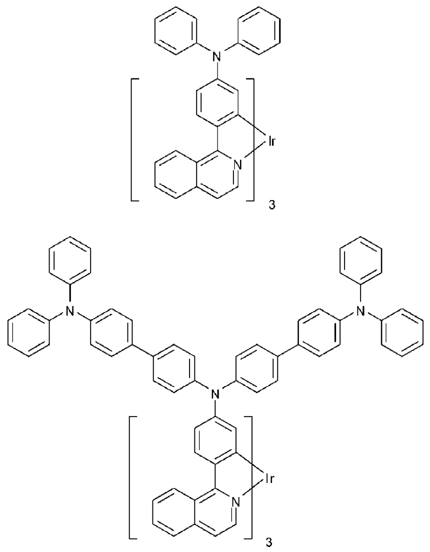

Fig. 11 Dendrimer Ir(III) complexes containing hole-transporting triphenylamine moieties.

study, performed by Zhou *et al.*, a very high external device quantum efficiency (11.65%) was recorded from a multilayer electrophosphorescence device. Unfortunately, however, it was found that the increased generation of the dendrimer structure led to a decreased device efficiency.

It is to be considered that the energetic interactions between dendrons and an emitting center can also be used to increase photoluminescence quantum efficiency. In a very recent publication by Harding *et al.*, it was reported that multiphenylated dendrons were energetically in equilibrium with the emitting center of their dendronized phosphorescent Ir(III) complex, thus providing a stable excitation energy.[111] In this system, the dendrons play the role of an excitation energy reservoir for the phosphorescent center. The author explained that this energetic relationship is similar to the case of CBP (4,4′-bis(carbazol-9-yl)biphenyl) and FIrpic (iridium(III) bis[(4,6-difluorophenyl)-pyridinato-*N*,$C^{2\prime}$]picolinate) in which CBP is energetically in thermally assisted equilibrium with FIrpic and thus, provides continuous excitation energy to FIrpic after photoexcitation. Consequently, the phosphorescent complex could exhibit enhanced and prolonged emission to give high solution state photoluminescence quantum efficiency. More examples are introduced in section (8) in more detail. However, this tactic (*i.e.* electronic interactions between a phosphorescent center and dendrons) should be used with great caution because Φ_p might be rather reduced due to the inevitably increased degree of vibrational motions imposed on the elongated chromophoric region.

6. Control in substituents of ligands

It has been well known that introduction of electron-donating and electron-withdrawing substituents or change in their positions at the ligand greatly affect phosphorescent colour of resulting Ir(III) complexes. This substituent control also accompanies changes in τ_p and thus to some extent, Φ_p. Although it is considered that further studies are required to understand and predict such substituent effects on Φ_p, some reports on Φ_p control by using substituents are occasionally found in literature. For example, Ir(III) complexes containing mono- or difluorophenylisoquinoline ligands showed different τ_p behaviour depending on the linking position of the phenyl ring at the isoquinoline.[83] When the phenyl ring was introduced at the 1-position of isoquinoline, variation of the position and number of the fluoro substituents at the phenyl ring did not affect τ_p of their Ir(III) complexes. In contrast, the introduction of a phenyl ring at 3-position greatly increased τ_p if the fluoro substitution was made at the phenyl ring. Deep explanations for the origin were not discussed in detail, but the author mentioned that this observation might be understood based on electronic effect induced by the substituents within the ligand structure. A helpful example was reported by Zhu *et al.* for the case of an Ir(III) complex with aza-aromatic cyclometalating ligands.[86] Despite that the ligand has a tight and compact structure, low Φ_p was observed in the solution state. They explained that this was due to the bipolar character originated from the electron-rich nitrogen atom and the electron-deficient metal center. More interestingly, Coppo *et al.* commented influence of fluorine groups on Φ_p in their publication[77]; although a fluorine substituent meta to Ir–C bond was successful in achieving blue phosphorescence, it inevitably resulted in low Φ_p. This can be attributed to the weakening of the Ir–C bond due to the electronegative fluorine substituents.

The introduction of electron-donating substituents such as dimethylamino group at the neutral ring of ligands is a promising method to bring phosphorescence emission to blue region because LUMO of an Ir(III) complex is effectively destabilized. This control was reported by Di Censo *et al.*, in which 4-dimethylaminopyridine or difluorinated phenyl fragments constituted cyclometalating ligands of Ir(III) complexes that further had two nitrile ancillary ligands.[152] In this work, they found an apparent reduction of Φ_p for the amino-Ir(III) complexes. The amino-Ir(III) complexes exhibited a several-fold larger k_{nr} value in comparison with that of amine-absent Ir(III) complexes. The presence of low-frequency vibrational motion imposed on the dimethylamino group was suggested to be responsible for this larger k_{nr} value. Nevertheless, a rash conclusion should not be drawn from this result since band gap law predicts smaller k_{nr} the amino-Ir(III) complexes exhibiting wider band gap.[109] Actually, this group reported in their another publication that electron-donating 4,4′-bisdimethylamino groups at bipyridine ligand resulted in 34-fold-decreased k_{nr} for the cyclometalated cationic Ir(III) complexes compared to the complex containing 4,4′-bis(*tert*-butyl)bypyridine.[153] The corresponding Φ_p increased by roughly about 4-fold.

Although heteroaromatic ligands enable us to effectively control phosphorescence colour,[57,62,82] the presence of certain heteroatoms in the ligands severely deteriorates Φ_p of their Ir(III) complexes. For example, as noted by Hwang *et al.*, sulfur-containing compounds, such as 2-(thiophen-2-yl)pyridine, 2-(benzo[*b*]thiophen-2-yl)pyridine and 2-phenylbenzo[*d*]thiazole are fairly good ligands for red phosphorescence due to the high polarizability and basicity of the sulfur atom. However, Ir(III) complexes containing these ligands exhibited relatively lower Φ_p in comparison with those of Ir(III) complexes containing sulfur-free ligands.[82] As a potential reason for their low Φ_p, thermal population of a poorly luminescent n–π* transition state embedded in the sulfur-containing ligands was considered. Thus, according to this result, use of thio-ligands needs to be avoided at least when the high Φ_p is mainly pursued. However this conclusion is ambiguous since an adverse tendency was found for the case of Ir(III) complexes containing 2-phenylbenzo[*d*]thiazole ($\Phi_p = 0.44$), 2-phenylbenzo[*d*]oxazole ($\Phi_p = 0.38$), 2-(4-fluorophenyl)benzo[*d*]thiazole ($\Phi_p = 0.54$) or 2-(4-fluorophenyl)benzo[*d*]oxazole ($\Phi_p = 0.38$).[154] In addition, a similar finding was recently reported for a series of Ir(III) complexes having Coumarin-based ligands differing heteroatom of the benzoxazole fragment.[155] In this work carried out Borisov *et al.*, the Ir(III) complex of the benzothiazolated Coumarin ligands exhibited improved Φ_p (0.54) in comparison with that ($\Phi_p = 0.34$) of the native (sulfur-free) Coumarin complex.

Meanwhile, pyrazole-derivatives were substituted for pyridine of ppy-type ligands in an effort to achieve hypsochromic shift in phosphorescence. However, recent work carried out by Dedeian *et al.* shows that this pyrazole introduction significantly lowered down Φ_p of resulting complexes.[156] Particularly, simultaneous use of both pyrazole and difluorophenyl ring fragments for cyclometalating ligands induced significant reduction in Φ_p. In contrast, either fluoro-absent 1-phenylpyrazole ligand or fluorinated 2-phenylpyridine ligand did not show such decrease. The pronounced k_{nr} increase with the introduction of the pyrazole ring attributed for this observed Φ_p. The authors proposed that potential Ir–$N_{pyrazole}$ bond breakage or pyrazole ring distortion could result in such k_{nr} effect. This explanation was supported by the finding that the pyrazolated Ir(III) complexes were more unstable in the mass spectrometry condition.

The examples introduced in this part reveal that substituent effects on Φ_p are not easy to be predicted. Nevertheless, some rule-of-thumbs can be drawn: (1) avoiding intraligand charge-transfer character, (2) avoiding substituents, which induce weak Ir–ligand bonds and (3) avoiding substituents of many vibrational freedom.

7. Confining the phosphorescent region within a mixed ligand Ir(III) complex

As mentioned in the introductory part, typical Ir(III) complexes principally have a multitude of concurrent electronic transitions (^{1}MLCT, ^{3}MLCT, ^{1}LC, and ^{3}LC). This is due to the fact that the Ir(III) complexes have delocalized molecular orbitals for the transition despite of their compact structure. In addition, if coordinated ligands allow additional intraligand or interligand transitions, such as intraligand charge-transfer (ILCT) or ligand-to-ligand charge-transfer (LLCT) transition,[94] we should take account of more orbitals in order to properly describe the phosphorescence behaviour. For example, considerably different Φ_p was observed for different ancillary ligands in a series of heteroleptic Ir(III) complexes comprising 1-(2,4-difluorophenyl)pyrazole cyclometalating ligand.[157] While use of 3-trifluoromethyl-5-pyridylpyrazole ancillary ligand resulted in low Φ_p (0.0067), much higher Φ_p (0.06–1) was recorded for congeneric ancillary ligands such as 3-*tert*-butyl-5-pyridylpyrazole, 3-*tert*-butyl-5-pyrazylpyrazole and 3-*tert*-butyl-5-isoquinolinylpyrazole. The low Φ_p of the 3-trifluoromethyl-5-pyridylpyrazole ancillary ligand's complex was attributed to characteristically delocalized LUMO in its Ir(III) complex, which subsequently led to mixing with various electronic states including a LLCT transition state. This provoked weakening of Ir–ligand bonds, thus finally facilitating faster non-radiative transitions. Hence, in order to avoid such complexity and hazardous photophysics, it is proposed to confine the global LUMO of a Ir(III) complex within a good ligand that can result in high Φ_p.

Confining the global LUMO at a certain ligand of a mixed-ligands Ir(III) complex then allowing phosphorescence from it requires an spatial energy transfer (flow) between ligands whose energy difference is large enough to suppress back energy transfer. For this, one single ligand (chromophoric ligand) should confine the global LUMO within its structure and thus be responsible for phosphorescence even though all of the ligands can be excited. In such cases, the excited state energy is spontaneously transferred to the low energy chromophoric ligand. This is a kind of energy harvesting which takes place intramolecularly. Although this intramolecular energy flow might be regarded as *internal conversion* in a strict photophysical sense, the expression of '*energy transfer*' would be preferred in order to underscore its nature of spatial energy flow. This kind of intramolecular energy transfer for the case of a phosphorescent Ir(III) complex was mentioned by Pawlowski *et al.*[158] They synthesized an Ir(III) complex containing a chromophoric naphthylalaniate ancillary ligand and ppy cyclometalating ligands and observed a large degree of control in phosphorescence spectra. The author proposed an intramolecular energy transfer to the ancillary ligand, which was expected to be responsible for the phosphorescence colour change. Also, Kappaun *et al.* reported similar phosphorescence controls from a series of Ir(III) complexes having energetically anisotropic ligands (ppy and 8-hydroxyquinoline-based ancillary ligands).[159]

Recently, our group was successful in demonstrating high Φ_p phosphorescence colour tuning and energy-harvesting phosphorescence by virtue of this intramolecular interligand energy transfer (ILET). Based on the framework of a heteroleptic Ir(III) complex containing high energy 2-(2,4-difluorophenyl)pyridine cyclometalating ligands, low energy ancillary ligands of various picolinate derivatives were introduced.[106] When the relatively higher energy ancillary ligands such as picolinate or 6-methylpicolinate were incorporated, inherent blue phosphorescence of the cyclometalating ligand was observed. In contrast, efficient colour-tuned phosphorescence ($\Phi_p \sim 0.4$) was recorded when relatively lower energy ancillary ligands such as quinaldinate, picolinamide, isoquinolinate, pyrazinate, pyrazinamide and quinoxalinate were used (Fig. 12). Based on photophysical and electrochemical experiments and DFT calculations, we proposed that ILET process took place between the ligands to give efficient phosphorescence from the low energy ancillary ligand. In fact, we have directly observed the ILET process through transient photoluminescence experiments and determined the very high ILET efficiency ($\Phi_{ILET} > 99\%$).[107] Our experimental data led us to conclude that cyclometalating ligands are preferentially excited, then the low energy ancillary ligands accept the excited-state energy through spontaneous energy flow (ILET), eventually giving rise to the ancillary ligand-centered phosphorescence. This process has great implication in obtaining high Φ_p from the material design point of view since the chromophoric ancillary ligand can be introduced into the complexes with high synthetic versatility.

One of the interesting results from this ILET-mediated phosphorescence is the characteristic multi-level photophysics as depicted in Fig. 12. Because of this, the ancillary ligand-centered phosphorescence exhibits a large Stoke's shift. This unique

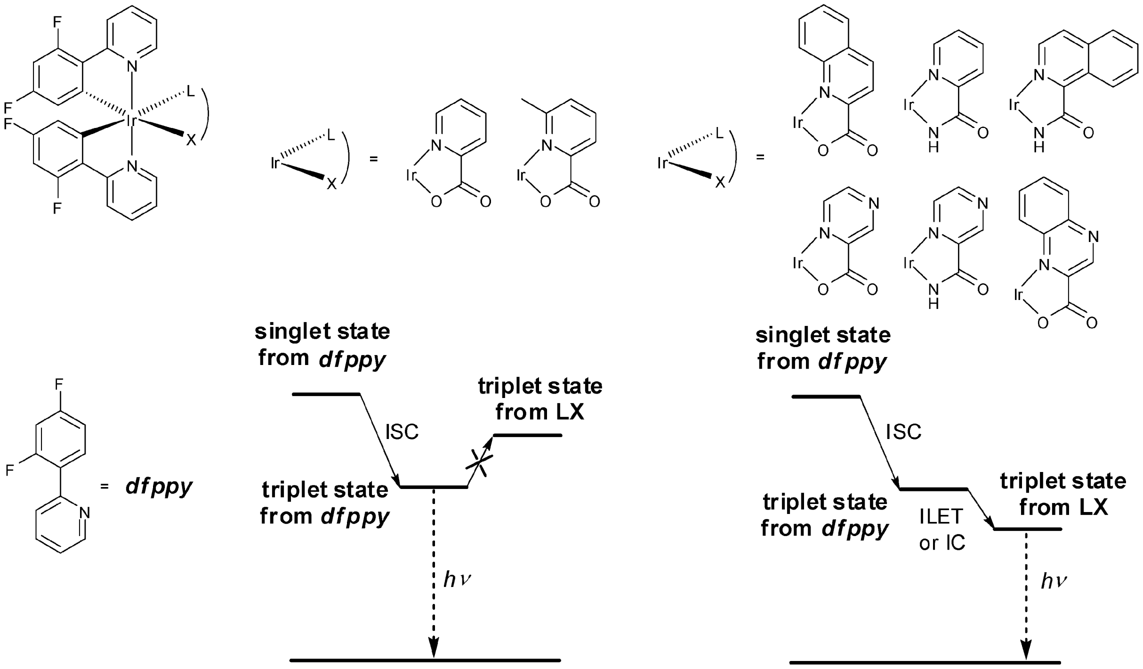

Fig. 12 Interligand energy transfer within heteroleptic Ir(III) complexes.

feature of ILET process enabled us to generate efficient white phosphorescence since Förster-type energy transfer through the spectral overlap can be avoided when we mix a blue phosphorescent complex and the ILET-mediated red phosphorescent Ir(III) complex.[107] Actually, we observed stable white phosphorescence even when a large amount of the ILET-mediated red phosphorescent Ir(III) complex was blended with a blue phosphorescent material in poly(methylmethacrylate) films.

In addition, we developed another class of Ir(III) complexes exhibiting a different working mode of phosphorescence.[108] In this study, we carried out systematic control of the number of fused phenyl rings in the hydroxyphenyloxazole-based low energy chromophoric ancillary ligands (Fig. 13). In contrast to the previous Ir(III) complexes described above, the ancillary ligands in this series of Ir(III) complexes participated in optical excitation transition to a large extent to give broad absorption bands together with cyclometalating ligand-centered absorptions. Here again, however, we observed an exclusive ancillary ligand-centered phosphorescence emission, which strongly indicates the existence of excited-state energy confinement at the ancillary ligand. Thus, it could be concluded that although both the cyclometalating ligands and the chromophoric ancillary ligand all together contributed to the excitation process, characteristic energy flow between them (ILET) afforded the ancillary ligand-centered phosphorescence. This class of Ir(III) complexes can have an additional excitation process to potentially contribute improved phosphorescence brightness, which can be described as energy-harvesting phosphorescence. As for the practical applications, multilayer electrophosphorescence devices with ILET-Ir(III) complexes were fabricated to demonstrate that this energy-harvesting phosphorescence involving ILET also operated under electrical excitation. Overall, it is worth mentioning that intramolecular energy transfer can be encouragingly used to attain high Φ_p.

8. Sensitized phosphorescence by using attached energy donors

Although sensitization does not improve the inherent Φ_p of an emission center, sensitization of phosphorescence by using high energy (usually fluorescent) donors is a broadly used method to accomplish high photoluminescence intensity. For instance, this method was employed as a successful working principle of phosphorescent biosensor. Based on their earlier study on sensitized blue phosphorescence,[160] Kwon *et al.* recently reported amplified phosphorescent emission from a biotin responsive tripodal sensor.[161] This tripodal system comprises a blue phosphorescent Ir(III) complex, an energy-donating fluorophore and avidin at each end. The strong binding interaction between avidin and biotin exerted close contact between the energy donor and the energy accepting Ir(III) complex to facilitate improved intermolecular energy transfer. Consequently, 4-fold-enhanced phosphorescence emission was observed and its high energy transfer efficiency (Φ_{ET} = 74%) was determined. Actually, this sensitized phosphorescence has been widely adopted for polymer systems, which have both an energy-donating host part and phosphorescent Ir(III) complex dopants.[43–56,162–170] In particular, there are many reports on polymer systems in which a covalent bond was used to bind the energy-donating polymeric host and Ir(III) complexes.[53–55,171–186] For example, Wang *et al.* synthesized poly(*N*-vinylcabazole)-co-poly(styrene) systems containing covalently bonded Ir(III) complexes at the styrene part. In their work, either Click reaction[54] or condensation between a formyl group and an amine[55] was employed in order to attach Ir(III) complexes. In these systems, the carbazole or excimeric carbazoles are regarded as energy donors to guarantee high Φ_p of the Ir(III) complexes.

In order to facilitate sensitized phosphorescence, a relatively high energy donor is required for an exothermic energy transfer. This would be a difficult requirement in case of blue phosphorescence, especially for polymeric energy donors. For example,

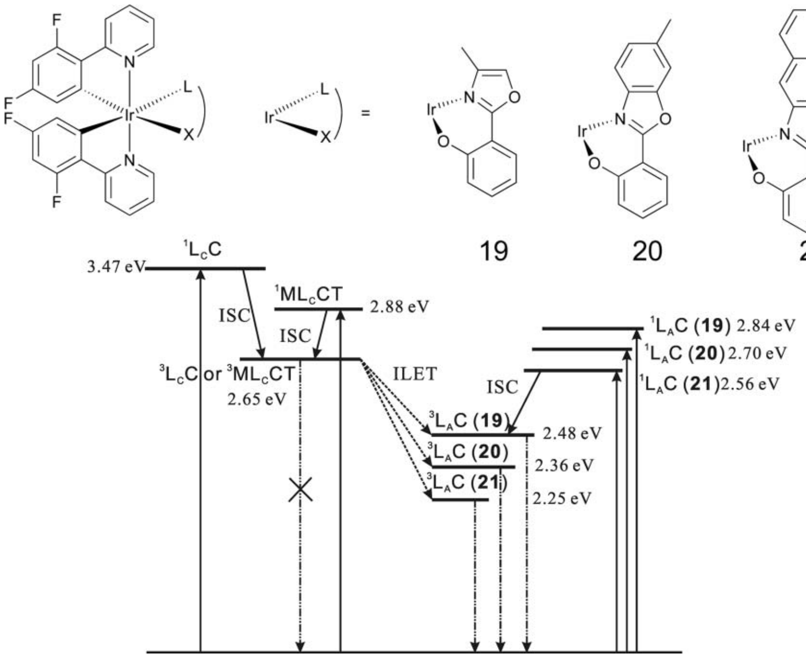

Fig. 13 Energy-harvesting phosphorescence through interligand energy transfer.

even a non-conjugated poly(*N*-vinylcarbazole) cannot guarantee exothermic energy transfer process for sensitized blue phosphorescence because of its lower energy carbazole excimers.[187,188] In this regard, our group modified structure of the energy donating poly(*N*-vinylcarbazole) into poly(3-vinylcarbazole) in order to suppress face-to-face overlaps between carbazole planes (Fig. 14).[171] This modification resulted in higher triplet state energy of the hosting polymer, thus ensuring the exothermic energy transfer from the modified polymer to an Ir(III) complex to give highly efficient sensitized blue phosphorescence.

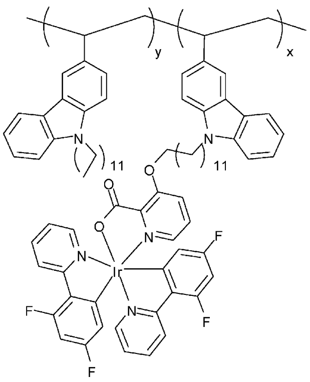

Fig. 14 Polymers containing an Ir(III) complex to attain sensitized blue phosphorescence.

Meanwhile, partial energy transfer from fluorescent polymeric parts to the phosphorescent emitters was used as a method to achieve multi-colour emission. One of particularly interesting applications of this is white emission which is constructed from blue fluorescence and green and red phosphorescence. A representative example is the work performed by Jiang *et al.*[53] In this work, blue emitting fluorene and green emitting benzothiadiazole were used for the fluorescent units in a main-chained co-polymer, while red phosphorescent Ir(III) complexes consisting of 3-phenylquinoline ligands was covalently linked to the polymer chain. Efficient white emission was demonstrated through the control in feed ratio of those units.

Outlook

Phosphorescent Ir(III) complexes are particularly promising for innovative applications such as electrophosphorescence for OLEDs. One of prime advantages of phosphorescent Ir(III) complexes is versatility in their ligand structure. By manipulating the framework, constituent atoms and substituent of ligands, it is feasible to attain various phosphorescence colours. This control is also valid for phosphorescence quantum efficiency. However, in contrast to the phosphorescence colour tuning, influence of ligand structure on the phosphorescence quantum efficiency requires further understanding. This prompted us to collect and overview methods for achieving high phosphorescence quantum efficiency. In this article, we have summarized 8 methods particularly from a material design point of view. Based on the methods described here, it could be envisaged that ligand controls strongly affect phosphorescence quantum efficiency.

The remaining challenges in developing phosphorescent Ir(III) complexes are to realize: (i) high efficiency deep blue phosphorescence,[189,190] (ii) multi-functionalities and their controls and (iii) supramolecular structures. These topics inevitably require modulation in the ligand structures. Thus, reliable principles for 'ligand controls and their effect on phosphorescence quantum efficiency' would be greatly helpful for these challenges. We hope that the methods for high phosphorescence quantum efficiency summarized in this Perspective will serve as an guideline in developing highly efficient phosphorescent Ir(III) complexes.

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References

1 W. J. Finkenzeller and H. Yersin, *Chem. Phys. Lett.*, 2003, **377**, 299–305.
2 K. K.-W. Lo, C.-K. Chung, T. K.-M. Lee, L.-K. Lui, K. H.-K. Tsang and N. Zhu, *Inorg. Chem.*, 2003, **42**, 6886–6897.
3 K. K.-W. Lo, C.-K. Chung and N. Zhu, *Chem.–Eur. J.*, 2003, **9**, 475–483.
4 J.-M. Hsieh, M.-L. Ho, P.-W. Wu, P.-T. Chou, T.-T. Tsai and Y. Chi, *Chem. Commun.*, 2006, 615–617.
5 E. Vanderdonckt, B. Camerman, F. Hendrick, R. Herne and R. Vandeloise, *Bull. Soc. Chim. Belg.*, 1994, **103**, 207–211.
6 G. Di Marco, M. Lanza, M. Pieruccini and S. Campagna, *Adv. Mater. (Weinheim, Ger.)*, 1996, **8**, 576–580.
7 G. Di Marco, M. Lanza, A. Mamo, I. Stefio, C. Di Pietro, G. Romeo and S. Campagna, *Anal. Chem.*, 1998, **70**, 5019–5023.
8 W. Goodall and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, **17**, 2893–2895.
9 Y. Amao, Y. Ishikawa and I. Okura, *Anal. Chim. Acta*, 2001, **445**, 177–182.
10 M. C. DeRosa, P. J. Mosher, G. P. A. Yap, K.-S. Focsaneanu, R. J. Crutchley and C. E. B. Evans, *Inorg. Chem.*, 2003, **42**, 4864–4872.
11 M. C. DeRosa, D. J. Hodgson, G. D. Enright, B. Dawson, C. E. B. Evans and R. J. Crutchley, *J. Am. Chem. Soc.*, 2004, **126**, 7619–7626.
12 C. Schaffner-Hamann, A. V. Zelewsky, A. Barbieri, F. Barigelletti, G. Muller, J. P. Riehl and A. Neels, *J. Am. Chem. Soc.*, 2004, **126**, 9339–9348.
13 L. Huynh, Z. Wang, J. Yang, V. Stoeva, A. Lough, I. Manners and M. A. Winnik, *Chem. Mater.*, 2005, **17**, 4765–4773.
14 M. E. Köse, R. J. Crutchley, M. C. DeRosa, N. Ananthakrishnan, J. R. Reynolds and K. S. Schanze, *Langmuir*, 2005, **21**, 8255–8262.
15 M.-L. Ho, F.-M. Hwang, P.-N. Chen, Y.-H. Hu, Y.-M. Cheng, K.-S. Chen, G.-H. Lee, Y. Chi and P.-T. Chou, *Org. Biomol. Chem.*, 2006, **4**, 98–103.
16 Q. Zhao, T. Cao, F. Li, X. Li, H. Jing, T. Yi and C. Huang, *Organometallics*, 2007, **26**, 2077–2081.
17 A. L. Medina-Castillo, J. F. Fernandez-Sanchez, C. Klein, M. K. Nazeeruddin, A. Segura-Carretero, A. Fernandez-Gutierrez, M. Grätzel and U. E. Spichiger-Keller, *Analyst*, 2007, **132**, 929–936.
18 M. Schmittel and H. Lin, *Inorg. Chem.*, 2007, **46**, 9139–9145.
19 T.-H. Kwon, J. Kwon and J.-I. Hong, *J. Am. Chem. Soc.*, 2008, **130**, 3726–3727.
20 H. Chen, Q. Zhao, Y. Wu, F. Li, H. Yang, T. Yi and C. Huang, *Inorg. Chem.*, 2007, **46**, 11075–11081.
21 K. K.-W. Lo, K. Y. Zhang, S.-K. Leung and M.-C. Tang, *Angew. Chem., Int. Ed.*, 2008, **47**, 2213–2216.
22 Y. You and S. Y. Park, *Adv. Mater. (Weinheim, Ger.)*, 2008, **20**, 3820–3826.
23 F. Shao, B. Elias, W. Lu and J. K. Barton, *Inorg. Chem.*, 2007, **46**, 100187–110199.
24 F. Shao and J. K. Barton, *J. Am. Chem. Soc.*, 2007, **129**, 14733–14738.
25 B. Elias, F. Shao and J. K. Barton, *J. Am. Chem. Soc.*, 2008, **130**, 1152–1153.
26 K. A. Belmore, R. A. Vanderpool, J. C. Tsai, M. A. Khan and K. M. Nicholas, *J. Am. Chem. Soc.*, 1988, **110**, 2004–2005.
27 N. D. Silavwe, A. S. Goldman, R. Ritter and D. R. Tyler, *Inorg. Chem.*, 1989, **28**, 1231–1236.
28 J. N. Demas, E. W. Harris, C. M. Flynn and J. D. Diemente, *J. Am. Chem. Soc.*, 1975, **97**, 3838–3839.
29 J. N. Demas, E. W. Harris and R. P. McBride, *J. Am. Chem. Soc.*, 1977, **99**, 3547–3551.
30 R. Gao, D. G. Ho, B. Hernandez, M. Selke, D. Murphy, P. I. Djurovich and M. E. Thompson, *J. Am. Chem. Soc.*, 2002, **124**, 14828–14829.
31 S. T. Parker, J. D. Slinker, M. S. Lowry, M. P. Cox, S. Bernhard and G. G. Malliaras, *Chem. Mater.*, 2005, **17**, 3187–3190.
32 H. J. Bolink, L. Capelli, E. Coronado, A. Parham and P. Stössel, *Chem. Mater.*, 2006, **18**, 2778–2780.
33 M. K. Nazeeruddin, R. T. Wegh, Z. Zhou, C. Klein, Q. Wang, F. De Angelis, S. Fantacci and M. Grätzel, *Inorg. Chem.*, 2006, **45**, 9245–9250.
34 M. S. Lowry and S. Bernhard, *Chem.–Eur. J.*, 2006, **12**, 7970–7977.
35 H.-C. Su, F.-C. Fang, T.-Y. Hwu, H.-H. Hseih, H.-F. Chen, G.-H. Lee, S.-M. Peng, K.-T. Wong and C.-C. Wu, *Adv. Funct. Mater.*, 2007, **17**, 1019–1027.
36 H.-C. Su, H.-F. Chen, F.-C. Fang, C.-C. Liu, C.-C. Wu, K.-T. Wong, Y.-H. Liu and S.-M. Peng, *J. Am. Chem. Soc.*, 2008, **130**, 3413–3419.
37 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151–154.
38 M. A. Baldo, C. Adachi and S. R. Forrest, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **62**, 10967–10977.
39 C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, *J. Appl. Phys.*, 2001, **90**, 5048–5051.
40 V. Marin, E. Holder, R. Hoogenboom and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 618–635.
41 P. -T. Chou and Y. Chi, *Chem.–Eur. J.*, 2007, **13**, 380–395.
42 *Highly Efficient OLEDs with Phosphorescent Materials*, ed. H. Yersin, Wiley-VCH, Weinheim, 2008.
43 R. C. Kwong, S. Lamansky and M. E. Thompson, *Adv. Mater. (Weinheim, Ger.)*, 2000, **12**, 1134–1138.
44 C.-L. Lee, K. B. Lee and J.-J. Kim, *Appl. Phys. Lett.*, 2000, **77**, 2280–2282.
45 P. A. Lane, L. C. Palilis, D. F. O'Brien, C. Giebeler, A. J. Cadby, D. G. Lidzey, A. J. Campbell, W. Blau and D. D. C. Bradley, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **63**, 235206–235213.
46 F.-C. Chen, Y. Yang, M. E. Thompson and J. Kido, *Appl. Phys. Lett.*, 2002, **80**, 2308–2310.
47 X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater. (Weinheim, Ger.)*, 2002, **14**, 581–585.
48 S. Lamansky, P. I. Djurovich, F. Abdel-Razzaq, S. Garon, D. L. Murphy and M. E. Thompson, *J. Appl. Phys.*, 2002, **92**, 1570–1575.
49 W. Zhu, Y. Mo, M. Yuan, W. Yang and Y. Cao, *Appl. Phys. Lett.*, 2002, **80**, 2045–2047.
50 X. H. Yang, D. Neher, U. Scherf and S. A. Bagnich, *J. Appl. Phys.*, 2003, **93**, 4413–4419.
51 X. Yang, D. Neher, D. Hertel and T. K. Däubler, *Adv. Mater. (Weinheim, Ger.)*, 2004, **16**, 161–165.
52 X. H. Yang and D. Neher, *Appl. Phys. Lett.*, 2004, **84**, 2476–2478.
53 J. X. Jiang, Y. H. Xu, W. Yang, R. Guan, Z. Q. Liu, H. Y. Zhen and Y. Cao, *Adv. Mater. (Weinheim, Ger.)*, 2006, **18**, 1769–1773.
54 X.-Y. Wang, A. Kimyonok and M. Weck, *Chem. Commun.*, 2006, 3933–3935.
55 X.-Y. Wang, R. N. Prabhu, R. H. Schmehl and M. Weck, *Macromolecules*, 2006, **39**, 3140–3146.
56 Y. Xu, R. Guan, J. Jiang, W. Yang, H. Zhen, J. Peng and Y. Cao, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 453–463.
57 S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304–4312.
58 M. Nonoyama, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 767–768.
59 A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, *J. Am. Chem. Soc.*, 2003, **125**, 7377–7387.
60 J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2005, **44**, 1713–1727.
61 T. Tsuboi and N. Aljaroudi, *Jpn. J. Appl. Phys., Part 1*, 2008, **47**, 1266–1270.
62 A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino and K. Ueno, *J. Am. Chem. Soc.*, 2003, **125**, 12971–12979.
63 K. Dedeian, J. Shi, E. Forsythe, D. C. Morton and P. Y. Zavalij, *Inorg. Chem.*, 2007, **46**, 1603–1611.
64 A. R. Hosseini, C. Y. Koh, J. D. Slinker, S. Flores-Torres, H. D. Abruña and G. G. Malliaras, *Chem. Mater.*, 2005, **17**, 6114–6116.
65 D. Di Censo, S. Fantacci, F. De Angelis, C. Klein, N. Evans, K. Kalyanasundaram, H. J. Bolink, M. Grätzel and M. K. Nazeeruddin, *Inorg. Chem.*, 2008, **47**, 980–989.
66 P.-T. Chou, Y.-I. Liu, H.-W. Liu and W.-S. Yu, *J. Am. Chem. Soc.*, 2001, **123**, 12119–12120.

67 J. W. Seo, S. Kim and S. Y. Park, *J. Am. Chem. Soc.*, 2004, **126**, 11154–11155.
68 M. G. Colombo and H. U. Güdel, *Inorg. Chem.*, 1993, **32**, 3081–3087.
69 M. G. Colombo, A. Hauser and H. U. Güdel, *Inorg. Chem.*, 1993, **32**, 3088–3092.
70 M. G. Colombo, T. C. Brunold, T. Riedener, H. U. Güdel, M. Förtsch and H.-B. Bürgi, *Inorg. Chem.*, 1994, **33**, 545–550.
71 G. F. Strouse, H. U. Güdel, V. Bertolasi and V. Ferretti, *Inorg. Chem.*, 1995, **34**, 5578–5587.
72 H. Wiedenhofer, S. Schuetzenmeier, A. V. Zelewsky and H. Yersin, *J. Phys. Chem.*, 1995, **99**, 13385–13391.
73 F. W. M. Vanhelmont, H. U. Güdel, M. Förtsch and H.-B. Bürgi, *Inorg. Chem.*, 1997, **36**, 5512–5517.
74 H. Yersin and D. Donges, *Top. Curr. Chem.*, 2001, **36**, 81–186.
75 J. P. Duan, P. P. Sun and C. H. Cheng, *Adv. Mater. (Weinheim, Ger.)*, 2003, **15**, 224–228.
76 W.-C. Chang, A. T. Hu, J.-P. Duan, D. K. Rayabarapu and C.-H. Cheng, *J. Organomet. Chem.*, 2004, **689**, 4882–4888.
77 P. Coppo, E. A. Plummer and L. De Cola, *Chem. Commun.*, 2004, 1774–1775.
78 W.-S. Huang, J. T. Lin, C. H. Chien, Y.-T. Tao, S.-S. Sun and Y.-S. Wen, *Chem. Mater.*, 2004, **16**, 2480–2488.
79 C.-H. Yang, C.-C. Tai and I.-W. Sun, *J. Mater. Chem.*, 2004, **14**, 947–950.
80 J. Ding, J. Gao, Q. Fu, Y. Cheng, D. Ma and L. Wang, *Synth. Met.*, 2005, **155**, 539–548.
81 R. J. Holmes, S. R. Forrest, T. Sajoto, A. Tamayo, P. I. Djurovich, M. E. Thompson, J. Brooks, Y.-J. Tung, B. W. D'Andrade, M. S. Weaver, R. C. Kwong and J. J. Brown, *Appl. Phys. Lett.*, 2005, **87**, 243507–243509.
82 F.-M. Hwang, H.-Y. Chen, P.-S. Chen, C.-S. Liu, Y. Chi, C.-F. Shu, F.-I. Wu, P.-T. Chou, S.-M. Peng and G.-H. Lee, *Inorg. Chem.*, 2005, **44**, 1344–1353.
83 C.-L. Li, Y.-J. Su, Y.-T. Tao, P.-T. Chou, C.-H. Chien, C.-C. Cheng and R.-S. Liu, *Adv. Funct. Mater.*, 2005, **15**, 387–395.
84 C. S. K. Mak, A. Hayer, S. I. Pascu, S. E. Watkins, A. B. Holmes, A. Köhler and R. H. Friend, *Chem. Commun.*, 2005, 4708–4710.
85 M. Xu, W. Li, Z. An, Q. Zhou and G. Wang, *Appl. Organomet. Chem.*, 2005, **19**, 1225–1231.
86 R. Zhu, J. Lin, G.-A. Wen, S.-J. Liu, J.-H. Wan, J.-C. Feng, Q.-L. Fan, G.-Y. Zhong, W. Wei and W. Huang, *Chem. Lett.*, 2005, **34**, 1668–1669.
87 S.-C. Lo, C. P. Shipley, R. N. Bera, R. E. Harding, A. R. Cowley, P. L. Burn and I. D. W. Samuel, *Chem. Mater.*, 2006, **18**, 5119–5129.
88 K. Ono, M. Joho, K. Saito, M. Tomura, Y. Matsushita, S. Naka, H. Okada and H. Onnagawa, *Eur. J. Inorg. Chem.*, 2006, 3676.
89 R. Ragni, E. A. Plummer, K. Brunner, J. W. Hofstraat, F. Babudri, G. M. Farinola, F. Naso and L. De Cola, *J. Mater. Chem.*, 2006, **16**, 1161–1170.
90 S. Takizawa, H. Echizen, J. Nishida, T. Tsuzuki, S. Tokito and Y. Yamashita, *Chem. Lett.*, 2006, **35**, 748–749.
91 Z. Wu, K. Xing, C. Luo, Y. Liu, Y. Yang, Q. Gan, M. Zhu, C. Jiang, Y. Cao and W. Zhu, *Chem. Lett.*, 2006, **35**, 538–539.
92 X. Zhang, J. Gao, C. Yang, L. Zhu, Z. Li, K. Zhang, J. Qin, H. You and D. Ma, *J. Organomet. Chem.*, 2006, **691**, 4312–4319.
93 L.-L. Wu, C.-H. Yang, I.-W. Sun, S.-Y. Chu, P.-C. Kao and H.-H. Huang, *Organometallics*, 2007, **26**, 2017–2023.
94 Y.-S. Yeh, Y.-M. Cheng, P.-T. Chou, G.-H. Lee, C.-H. Yang, Y. Chi, C.-F. Shu and C.-H. Wang, *ChemPhysChem*, 2006, **7**, 2294–2297.
95 C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang and Z. Lin, *Adv. Funct. Mater.*, 2008, **18**, 928–937.
96 D. M. Kang, J.-W. Kang, J. W. Park, S. O. Jung, S.-H. Lee, H.-D. Park, Y.-H. Kim, S. C. Shin, J.-J. Kim and S.-K. Kwon, *Adv. Mater. (Weinheim, Ger.)*, 2008, **20**, 2003–2007.
97 G. Zhou, C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T. B. Marder and A. Beeby, *Adv. Funct. Mater.*, 2008, **18**, 499–511.
98 Y.-S. Park, J.-W. Kang, D. M. Kang, J.-W. Park, Y.-H. Kim, S.-K. Kwon and J.-J. Kim, *Adv. Mater. (Weinheim, Ger.)*, 2008, **20**, 1957–1961.
99 M. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli and M. Graetzel, *J. Am. Chem. Soc.*, 2003, **125**, 8790–8797.
100 H. Yersin, *Top. Curr. Chem.*, 2004, **241**, 1–26.
101 R. C. Evans, P. Douglas and C. J. Winscom, *Coord. Chem. Rev.*, 2006, **250**, 2093–2126.
102 Y. Chi and P.-T. Chou, *Chem. Soc. Rev.*, 2007, **36**, 1421–1431.
103 L. Chen, C. Yang, J. Qin, J. Gao, H. You and D. Ma, *J. Organomet. Chem.*, 2006, **691**, 3519–3530.
104 P. J. Hay, *J. Phys. Chem. A*, 2002, **106**, 1634–1641.
105 T.-H. Kwon, H. S. Cho, M. K. Kim, J.-W. Kim, J.-J. Kim, K. H. Lee, S. J. Park, I.-S. Shin, H. Kim, D. M. Shin, Y. K. Chung and J.-I. Hong, *Organometallics*, 2005, **24**, 1578–1585.
106 Y. You and S. Y. Park, *J. Am. Chem. Soc.*, 2005, **127**, 12438–12439.
107 Y. You, K. S. Kim, T. K. Ahn, D. Kim and S. Y. Park, *J. Phys. Chem. C*, 2007, **111**, 4052–4060.
108 Y. You, J. Seo, S. H. Kim, K. S. Kim, T. K. Ahn, D. Kim and S. Y. Park, *Inorg. Chem.*, 2008, **47**, 1476–1487.
109 A. B. Tamayo, S. Garon, T. Sajoto, P. I. Djurovich, I. M. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2005, **44**, 8723–8732.
110 C.-H. Yang, S.-W. Li, Y. Chi, Y.-M. Cheng, Y.-S. Yeh, P.-T. Chou, G.-H. Lee, C.-H. Wang and C.-F. Shu, *Inorg. Chem.*, 2005, **44**, 7770–7780.
111 R. E. Harding, S.-C. Lo, P. L. Burn and I. D. W. Samuel, *Org. Electron.*, 2008, **9**, 377–384.
112 T. Sajoto, P. I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2005, **44**, 7992–8003.
113 P. K. Mallick, G. D. Danzer, D. P. Strommen and J. R. Kincaid, *J. Phys. Chem.*, 1988, **92**, 5628–5634.
114 Q. Zhao, L. Li, F. Li, M. Yu, Z. Liu, T. Yi and C. Huang, *Chem. Commun.*, 2008, 685–687.
115 Y. You, H. S. Huh, K. S. Kim, S. W. Lee, D. Kim and S. Y. Park, *Chem. Commun.*, 2008, 3998–4000.
116 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991–1024.
117 Y. You, C.-G. An, D.-S. Lee, J.-J. Kim and S. Y. Park, *J. Mater. Chem.*, 2006, **16**, 4706–4713.
118 K. A. King, P. J. Spellane and Richard J. Watts, *J. Am. Chem. Soc.*, 1985, **107**, 1431–1432.
119 Y.-M. Cheng, E. Y. Li, G.-H. Lee, P.-T. Chou, S.-Y. Lin, C.-F. Shu, K.-C. Hwang, Y.-L. Chen, Y.-H. Song and Y. Chi, *Inorg. Chem.*, 2007, **46**, 10276–10286.
120 C.-L. Lee, R. R. Das and J.-J. Kim, *Chem. Mater.*, 2004, **16**, 4642–4646.
121 P. L. Burn, S.-C. Lo and I. D. W. Samuel, *Adv. Mater. (Weinheim, Ger.)*, 2007, **19**, 1675–1688.
122 T. G. Goodson, III, *Acc. Chem. Res.*, 2005, **38**, 99–107.
123 A. Adronov and J. M. J. Frechet, *Chem. Commun.*, 2000, **18**, 1701–1710.
124 H. Z. Xie, M. W. Liu, O. Y. Wang, X. H. Zhang, C. S. Lee, L. S. Hung, S. T. Lee, P. F. Teng, H. L. Kwong, H. Zheng and C. M. Che, *Adv. Mater. (Weinheim, Ger.)*, 2001, **13**, 1245–1248.
125 B. Tong, Q. Mei, S. Wang, Y. Fang, Y. Meng and B. Wang, *J. Mater. Chem.*, 2008, **18**, 1636–1639.
126 Y.-H. Song, S.-J. Yeh, C.-T. Chen, Y. Chi, C.-S. Liu, J.-K. Yu, Y.-H. Hu, P.-T. Chou, S.-M. Peng and G.-H. Lee, *Adv. Funct. Mater.*, 2004, **14**, 1221–1226.
127 S.-C. Lo, N. A. H. Male, J. P. J. Markham, S. W. Magennis, P. L. Burn, O. V. Salata and I. D. W. Samuel, *Adv. Mater. (Weinheim, Ger.)*, 2002, **14**, 975–979.
128 J. P. J. Markham, S.-C. Lo, S. W. Magennis, P. L. Burn and I. D. W. Samuel, *Appl. Phys. Lett.*, 2002, **80**, 2645–2647.
129 T. D. Anthopoulos, J. P. J. N. Markham, B. Ebinazar, I. D. W. Samuel, S.-C. Lo and P. L. Burn, *Appl. Phys. Lett.*, 2003, **86**, 4824–4826.
130 S.-C. Lo, E. B. Namdas, P. L. Burn and I. D. W. Samuel, *Macromolecules*, 2003, **36**, 9721–9730.
131 T. D. Anthopoulos, M. J. Frampton, E. B. Namdas, P. L. Burn and I. D. W. Samuel, *Adv. Mater. (Weinheim, Ger.)*, 2004, **16**, 557–560.
132 M. J. Frampton, E. B. Namdas, S.-C. Lo, P. L. Burn and I. D. W. Samuel, *J. Mater. Chem.*, 2004, **14**, 2881–2888.
133 J. P. J. Markham, I. D. W. Samuel, S.-C. Lo, P. L. Burn, M. Weiter and H. Bassler, *J. Appl. Phys.*, 2004, **95**, 438–445.
134 E. B. Namdas, A. Ruseckas, I. D. W. Samuel, S.-C. Lo and P. L. Burn, *J. Phys. Chem. B*, 2004, **108**, 1570–1577.
135 N. Cumpstey, R. N. Bera, P. L. Burn and I. D. W. Samuel, *Macromolecules*, 2005, **38**, 9564–9570.
136 S.-C. Lo, T. D. Anthopoulos, E. B. Namdas, P. L. Burn and I. D. W. Samuel, *Adv. Mater. (Weinheim, Ger.)*, 2005, **17**, 1945–1948.
137 S.-C. Lo, G. J. Richards, J. P. J. Markham, E. B. Namdas, S. Sharma, P. L. Burn and I. D. W. Samuel, *Adv. Funct. Mater.*, 2005, **15**, 1451–1458.
138 E. B. Namdas, T. D. Anthopoulos, I. D. W. Samuel, M. J. Frampton, S.-C. Lo and P. L. Burn, *Appl. Phys. Lett.*, 2005, **86**, 161104–161106.

139 E. B. Namdas, A. Ruseckas, I. D. W. Samuel, S.-C. Lo and P. L. Burn, *Appl. Phys. Lett.*, 2005, **86**, 91104–91106.
140 S.-C. Lo, E. B. Namdas, C. P. Shipley, J. P. J. Markham, T. D. Anthopolous, P. L. Burn and I. D. W. Samuel, *Org. Electron.*, 2006, **7**, 85–98.
141 C. J. Yates, I. D. W. Samuel, P. L. Burn, S. Wedge and W. L. Barnes, *Appl. Phys. Lett.*, 2006, **88**, 161105–161107.
142 R. N. Bera, N. Cumpstey, P. L. Burn and I. D. W. Samuel, *Adv. Funct. Mater.*, 2007, **17**, 1149–1152.
143 K. A. Knights, S. G. Stevenson, C. P. Shipley, S.-C. Lo, S. Olsen, R. E. Harding, S. Gambino, P. L. Burn and I. D. W. Samuel, *J. Mater. Chem.*, 2008, **18**, 2121–2130.
144 J. C. Ribierre, A. Ruseckas, K. Knights, S. V. Staton, N. Cumpstey, P. L. Burn and I. D. W. Samuel, *Phys. Rev. Lett.*, 2008, **100**, 17402–17405.
145 J. C. Ribierre, A. Ruseckas, I. D. W. Samuel, S. V. Staton and P. L. Burn, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 85211–085215.
146 N. Cumpstey, R. N. Bera, P. L. Burn and I. D. W. Samuel, *Macromolecules*, 2005, **38**, 9564–9570.
147 Y. You, C. -G. An, J. -J. Kim and S. Y. Park, *J. Org. Chem.*, 2007, **72**, 6241–6246.
148 T. Tsuzuki, N. Shirakawa, T. Suzuki and S. Tokito, *Jpn. J. Appl. Phys., Part 1*, 2005, **44**, 4151–4154.
149 J. Ding, J. Gao, Y. Cheng, Z. Xie, L. Wang, D. Ma, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2006, **16**, 575–581.
150 B.-L. Li, L. Wu, Y.-M. He and Q.-H. Fan, *Dalton Trans.*, 2007, 2048–2057.
151 G. Zhou, W.-Y. Wong, B. Yao, Z. Xie and L. Wang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1149–1151.
152 D. Di Censo, S. Fantacci, F. D. Angelis, C. Klein, N. Evans, K. Kalyanasundaram, H. J. Bolink, M. Grätzel and M. K. Nazeeruddin, *Inorg. Chem.*, 2008, **47**, 980–989.
153 F. De Angelis, S. Fantacci, N. Evans, C. Klein, S. M. Zakeeruddin, J.-E. Moser, K. Kalyanasundaram, H. J. Bolink, M. Grätzel and M. K. Nazeeruddin, *Inorg. Chem.*, 2007, **46**, 5989–6001.
154 A. Kapturkiewicz, J. Nowacki and P. Borowicz, *Electrochim. Acta*, 2005, **50**, 3395–3400.
155 S. M. Borisov and I. Klimant, *Anal. Chem.*, 2007, **79**, 7501–7509.
156 K. Dedeian, J. Shi, N. Shepherd, E. Forsythe and D. C. Morton, *Inorg. Chem.*, 2005, **44**, 4445–4447.
157 C.-J. Chang, C.-H. Yang, K. Chen, Y. Chi, C.-F. Shu, M.-L. Ho, Y.-S. Yeh and P.-T. Chou, *Dalton Trans.*, 2007, 1881–1890.
158 V. Pawlowski, H. Kunkely and A. Vogler, *J. Photochem. Photobiol., A*, 2004, **161**, 95–97.
159 S. Kappaun, S. Sax, S. Eder, K. C. Möller, K. Waich, F. Niedermair, R. Saf, K. Mereiter, J. Jacob, K. Müllen, E. J. W. List and C. Slugovc, *Chem. Mater.*, 2007, **19**, 1209–1211.
160 T.-H. Kwon, M. K. Kim, J. Kwon, D.-Y. Shin, S. J. Park, C.-L. Lee, J.-J. Kim and J.-I. Hong, *Chem. Mater.*, 2007, **19**, 3673–3680.
161 T.-H. Kwon, J. Kwon and J.-I. Hong, *J. Am. Chem. Soc.*, 2008, **130**, 3726–3727.
162 X. Gong, J. C. Ostrowski, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Funct. Mater.*, 2003, **13**, 439–444.
163 V. Cleave, G. Yahioglu, P. L. Barny, R. H. Friend and N. Tessler, *Adv. Mater. (Weinheim, Ger.)*, 1999, **11**, 285–288.
164 R. J. Holmes, S. R. Forrest, Y.-J. Tung, R. C. Kwong, J. J. Brown, S. Garon and M. E. Thompson, *Appl. Phys. Lett.*, 2003, **82**, 2422–2424.
165 D. R. Whang, Y. You, S. H. Kim, W.-I. Jeong, Y.-S. Park, J.-J. Kim and S. Y. Park, *Appl. Phys. Lett.*, 2007, **91**, 233501–233503.
166 X. Gong, S.-H. Lim, J. C. Ostrowski, D. Moses, C. J. Bardeen and G. C. Bazan, *J. Appl. Phys.*, 2004, **95**, 948–953.
167 Y. Kawamura, S. Yanagida and S. R. Forrest, *J. Appl. Phys.*, 2002, **92**, 87–93.
168 Y.-Y. Noh, C.-L. Lee, J.-J. Kim and K. Yase, *J. Chem. Phys.*, 2003, **118**, 2853–2864.
169 G. Ramos-Ortiz, Y. Oki, B. Domercq and B. Kippelen, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4109–4114.
170 R. A. Negres, X. Gong, J. C. Ostrowski, G. C. Bazan, D. Moses and A. J. Heeger, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **68**, 115209–115216.
171 Y. You, S. H. Kim, H. K. Jung and S. Y. Park, *Macromolecules*, 2006, **39**, 349–356.
172 X. Chen, J.-L. Liao, Y. Liang, M. O. Ahmed, H. E. Tseng and S. A. Chen, *J. Am. Chem. Soc.*, 2003, **125**, 636–637.
173 V. Marin, E. Holder, R. Hoogenboom and U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4153–4160.
174 J. Jiang, C. Jiang, W. Yang, H. Zhen, F. Huang and Y. Cao, *Macromolecules*, 2005, **38**, 4072–4080.
175 H. Zhen, C. Jiang, W. Yang, J. Jiang, F. Huang and Y. Cao, *Chem.–Eur. J.*, 2005, **11**, 5007–5016.
176 N. R. Evans, L. S. Devi, C. S. K. Mak, S. E. Watkins, S. I. Pascu, A. Koehler, R. H. Friend, C. K. Williams and A. B. Holmes, *J. Am. Chem. Soc.*, 2006, **128**, 6647–6656.
177 S.-J. Liu, Q. Zhao, R.-F. Chen, Y. Deng, Q.-L. Fan, F.-Y. Li, L.-H. Wang, C.-H. Huang and W. Huang, *Chem.–Eur. J.*, 2006, **12**, 4351–4361.
178 G. L. Schulz, X. Chen, S.-A. Chen and S. Holdcroft, *Macromolecules*, 2006, **39**, 9157–9165.
179 K. Zhang, Z. Chen, Y. Zou, C. Yang, J. Qin and Y. Cao, *Organometallics*, 2006, **26**, 3699–3707.
180 H. Zhen, C. Luo, W. Yang, W. Song, B. Du, J. Jiang, C. Jiang, Y. Zhang and Y. Cao, *Macromolecules*, 2006, **39**, 1693–1700.
181 K. A. Aamer and G. N. Tew, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 1109–1121.
182 C. Mei, J. Ding, B. Yao, Y. Cheng, Z. Xie, Y. Geng and L. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 1746–1757.
183 Y. Zhang, Y. Xu, Q. Niu, J. Peng, W. Yang, X. Zhu and Y. Cao, *J. Mater. Chem.*, 2007, **17**, 992–1001.
184 H. Zhen, J. Luo, W. Yang, Q. Chen, L. Ying, J. Zou, H. Wu and Y. Cao, *J. Mater. Chem.*, 2007, **17**, 2824–2831.
185 X.-H. Yang, F.-I. Wu, D. Neher, C.-H. Chien and C.-F. Shu, *Chem. Mater.*, 2008, **20**, 1629–1635.
186 K. Zhang, Z. Chen, C. Yang, Y. Tao, Y. Zou, J. Qin and Y. Cao, *J. Mater. Chem.*, 2008, **18**, 291–298.
187 G. E. Vekikouas and R. C. Powell, *Chem. Phys. Lett.*, 1974, **34**, 601–604.
188 G. E. Johnson, *J. Chem. Phys.*, 1975, **62**, 4697–4709.
189 C.-H. Yang, Y.-M. Cheng, Y. Chi, C.-J. Hsu, F.-C. Fang, K.-T. Wong, P.-T. Chou, C.-H. Chang, M.-H. Tsai and C.-C. Wu, *Angew. Chem., Int. Ed.*, 2007, **46**, 2418–2421.
190 C.-F. Chang, Y.-M. Cheng, Y. Chi, Y.-C. Chiu, C.-C. Lin, G.-H. Lee, P.-T. Chou, C.-C. Chen, C.-H. Chang and C.-C. Wu, *Angew. Chem., Int. Ed.*, 2008, **47**, 4542–4545.