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### Introduction

Phosphorescent transition metal complexes have attracted much attention due to their ability to maximize light emitting efficiency by fully utilizing triplet energy for radiation.<sup>1,2</sup> High phosphorescence efficiency comes from the large triplet population through the strong spin–orbital coupling induced by heavy transition metal.<sup>3,4</sup> Ir<sup>3+</sup> complexes have been recognized as promising candidates for phosphorescence organic light emitting diodes due to their outstanding emission properties such as high quantum yields of luminescence, photo stability, and color tuning by electronic control of the main ligand, as well as variation of the ancillary ligand.<sup>5–13</sup>

Dendrimers are highly branched macromolecules. Their monodispersive nature suggests that they can offer many advantageous properties for optoelectronic applications that neither small molecules nor polymers can solely provide in terms of ideal material specification such as thermal or oxidation stability and

# A detailed investigation of light-harvesting efficiency of blue color emitting divergent iridium dendrimers with peripheral phenylcarbazole units<sup>†</sup>

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The increase in phosphorescence efficiency was estimated by the energy transfer mechanism for divergent iridium dendrimers with peripheral phenylcarbazole units. A series of Ir-core/phenylcarbazole-end dendrons of the type, Ir(dfppy)<sub>2</sub>(pic-Cz<sub>n</sub>) (**Gn**, n = 0, 1, 2, and 3), was synthesized, where dfppy, pic, and Cz<sub>n</sub> (n = 2, 4, and 8) are 2-(4,6-difluorophenyl)pyridine, picolinate substituted with Cz<sub>n</sub> at the 3-position, and 4-(9-carbazolyl)phenyldendrons connected with 3,5-di(methyleneoxy)benzyloxy branches, respectively. Selective excitation of the Cz<sub>n</sub> units of **G1–G3** resulted in >90% quenching of the Cz fluorescence accompanied by the growth of phosphorescence from the Ir(dfppy)<sub>2</sub>(pic) core as a consequence of energy transfer from the excited-singlet Cz<sub>n</sub> chromophore to the core. The rate constants of energy transfer were determined by steady-state and transient spectroscopic measurements to be  $4.32 \times 10^9 \text{ s}^{-1}$  (**G1**),  $2.37 \times 10^9 \text{ s}^{-1}$  (**G2**), and  $1.46 \times 10^9 \text{ s}^{-1}$  (**G3**), which were in good agreement with those calculated using the Förster model. The phosphorescence enhancements were 157 (**G1**), 213 (**G2**), and 264% (**G3**) when compared to the phosphorescence of the core Ir(dfppy)<sub>2</sub>(pic-Ph<sub>2</sub>) (**G0**), in which pic-Ph<sub>2</sub> is 3-(3,5-dibenzyloxybenzyl)picolinate.

material purity, respectively.<sup>14–16</sup> Of particular interest are the dendrimers that contain both host and dopant units in a single molecular array facilitating efficient energy transfer. For the divergent iridium-cored dendrimers,<sup>17</sup> systematic generation growth correlates well with the energy transfer efficiency when the number of host end groups varies depending on the choice of end group carrying branches. Since end-on host units surround the iridium core, the photophysical process propagates in a radial manner; in general one can expect that electronically excited end-on host groups can be quenched either by the energy transfer or the electron transfer to the central iridium. The final emission efficiency at the iridium center is determined by the energy transfer from the peripheries and through the branches and finally to the iridium. Consequently, the choice of end group as well as branch can be detrimental to high efficiency. Furthermore, Ir-dendrimers are generally used in order to prevent destructive excited-state interactions between emitting phosphors, like triplet-triplet annihilation, especially under high current density.<sup>18-20</sup> Dendrimers can shield the Ir3+-complex core to weaken the oxygen quenching effect.21

Carbazole (Cz)-based dendrons have been used as effective charge transporting moieties for iridium-based phosphorescent emitters.<sup>22,23</sup> Dendrimers have proved to be successful materials for solution-processible phosphorescent organic light emitting diodes (OLEDs).<sup>24-35</sup> Divergent iridium dendrimers are classified into two types: one with engagement of rigid branching units



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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Absorption and emission spectra of carbazole dendrons, lifetimes of phosphorescence of dendrimers, the energy minimized geometries of **Gn** (n = 1, 2, and 3), energy levels and isodensity plots for selected occupied and unoccupied molecular orbitals of **G1**. See DOI: 10.1039/c3cp53797h



such as alkene and alkyne connectors, and the other with flexible branches, such as connecting with alkyl or alkoxy groups. The flexible branches are generally used in order to secure the synthetic versatility.<sup>36</sup> It has also been reported that energy transfer in Ir<sup>3+</sup>-complex dendrimers with Cz dendrons occurs at efficiencies greater than 90% from the excited-state Cz dendron to the iridium core.<sup>37</sup> However, most dendrimer systems studied only dealt with energy transfer efficiency or in most cases discussed the final emission enhancement. There has been no quantitative analysis between energy transfer and harvesting efficiency to show any correlation amongst iridium dendrimers.<sup>38</sup> In fact, the mechanism for the actual light-harvesting process has not been understood in detail. In this regard, it is important to analyze the relationship between the energy transfer mechanism and light-harvesting efficiency.

In this study, we synthesized new dendritic complexes  $(Ir(dfppy)_2-(pic-Cz_2) (G1), Ir(dfppy)_2(pic-Cz_4) (G2), and Ir(dfppy)_2(pic-Cz_8) (G3)), together with Cz-free reference complex Ir(dfppy)_2(pic-Ph_2) (G0), as shown in Chart 1, where dfppy, pic, and <math>Cz_n$  are 2-(4,6-difluorophenyl)pyridine, picolinate and 4-(9-carbazolyl)phenyl-carbazole dendrons (n = 2, 4 and 8), respectively. The Ir-complex core is connected with  $Cz_n$  units by 3,5-di(methyleneoxy)benzyloxy branches. Herein, Cz works as the energy donor after light absorption, whereas the Ir-complex core acts as the energy acceptor. For quantitative kinetic analysis of the energy transfer, we carried out steady-state and time-resolved spectroscopic measurements.

# Experimental

### **General procedures**

Starting materials were purchased from Aldrich Chemical Co. and TCI Co. and were used without further purification. Reactions were carried out under a dried nitrogen ( $N_2$ ) atmosphere. Solvents were dried according to standard procedures and freshly distilled before use. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), acetonitrile (ACN), and dimethylformamide (DMF) were distilled over calcium hydride under a  $N_2$  atmosphere and stored over molecular sieves. Tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2-MeTHF) were distilled over sodium/benzophenone. Reactions were monitored with thin layer chromatography (TLC) using commercial TLC plates (Merck Co.). Column chromatography was done with silica gel 60G (particle size  $5-40 \ \mu\text{m}$ , Merck Co.). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300.1 and 75.4 MHz, respectively. Elemental analyses were carried out using a Carlo Erba Instruments CHNS-O EA 1108 analyzer. High-resolution tandem mass spectrometry (Jeol LTD JMS-HX 110/110A) and MALDI-TOF mass spectroscopy (ABI Voyager STR) were performed by the Ochang branch of the Korean Basic Science Institute.

#### Spectroscopic measurements

Steady-state absorption and fluorescence spectra were measured using a UV-vis spectrophotometer (Shimadzu, UV-3101PC) and a fluorescence spectrophotometer (Varian, Cary Eclipse), respectively. Time-resolved fluorescence spectra were measured using a single photon counting method with a streak scope (Hamamatsu Photonics, C10627-03) equipped with a polychromator (Acton Research, SP2300).<sup>39</sup> An ultrashort laser pulse was generated with a Ti:sapphire oscillator (Coherent, Vitesse, FWHM 100 fs) pumped with a diode-pumped solid-state laser (Coherent, Verdi). High-power (1.5 mJ) pulses were generated using a Ti:sapphire regenerative amplifier (Coherent, Libra, 1 kHz). For excitation of the sample, the output of the Ti:sapphire regenerative amplifier was converted to 440 nm using an optical parametric amplifier (Coherent, TOPAS). The instrument response function was also determined by measuring the scattered laser light to analyze the temporal profile. This method provides a time resolution of approximately 20 ps after the deconvolution procedure. The temporal emission profiles were well fitted to a single-exponential function. The residuals for each system were less than 1.1. The phosphorescence spectra at 77 K were obtained by photoexcitation with the 355 nm pulses from a nanosecond Q-switched Nd:YAG laser (Continuum, Surelite II-10, pulse width of 10 ns FWHM). The phosphorescence spectra were collected using a monochromator (DongWooOptron, Monora 500i) equipped with an intensified charge-coupled device (ICCD, Ando, iStar). The temporal profiles were measured using a monochromator equipped with a photomultiplier (Zolix Instruments Co., CR 131) and a digital oscilloscope (Tektronix, TDS-784D).

#### **Electrochemistry measurements**

The cyclic voltammetry (CV) experiments were performed using a BAS 100 electrochemical analyzer and a three-electrode cell system comprised of a glassy carbon disk (dia. 3 mm), a platinum disk (dia. 1.6 mm) electrode as the working electrode, and a platinum wire and Ag/AgNO<sub>3</sub> as the counter and reference electrodes, respectively, operated at a scan rate of 0.1 V s<sup>-1</sup>. Freshly distilled, degassed CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The potential values were calibrated with respect to the Fc<sup>+</sup>/Fc (Fc = ferrocene) redox couple.

#### Theoretical calculations

Full geometry optimizations of the dendrimers in their singlet ground state were performed with density functional theory (DFT) using the B3LYP<sup>40</sup> exchange correlation functional (Becke's three parameter (B3) gradient-corrected exchange functional

combined with the correlation Lee–Yang–Parr (LYP) functional), with the relativistic effective core potential and basis set LanL2DZ<sup>41</sup> for the iridium and the 6-31G<sup>\*42</sup> basis set for the remaining atoms. No symmetry constraints were applied during the geometry optimizations, which were carried out with the Gaussian 09 package.<sup>43</sup> The nature of the stationary points location was further checked by computations of harmonic vibrational frequencies at the same level of theory. All isodensity plots (isodensity contour = 0.03 a.u.) of the frontier orbitals were visualized by Chem3D Ultra program. The excitation energies and oscillator strengths for the lowest 30 singlet–singlet and triplet–triplet transitions at the optimized geometry in the ground state were obtained in time-dependent DFT (TD-DFT) calculations using the same basis set and functional as for the ground state.

### Results and discussion

### Electrochemistry

Fig. 1 shows CV traces of **G0**, **G1**, **G2**, and **G3** in  $\text{CH}_2\text{Cl}_2$  solution, from which their oxidation and reduction potentials *versus*  $\text{Fc}^+/\text{Fc}$ were estimated, and are shown in Table 1. All the complexes exhibit one reversible reduction wave at approximately -2.5 V. It has been reported that electrochemical reduction processes of the related Ir(m) complexes proceed on the ligand-centered orbitals, mainly from the fluorinated phenylpyridine ligand.<sup>44-46</sup> DFT calculations on **G1** support that the first reduction potential is due to the reduction of the dfppy ligand, based on the analysis of lowest unoccupied molecular orbital (LUMO).



Fig. 1 Cyclic voltammograms of G0, G1, G2 and G3 taken at a sweep rate of 0.1 V s<sup>-1</sup> for 0.5 mM  $CH_2Cl_2$  solution containing 0.1 M TBAP.

Table 1 Oxidation and reduction potentials of dendritic Ir<sup>3+</sup> complexes

	Oxidation (V)			Reduction (V)		
Compounds	$E_{\mathrm{pa1}}, E_{\mathrm{pa2}}{}^a$	$E_{\rm pc1}, E_{\rm pc2}{}^b$	$E_{1/2}^{\text{ox}}$	Epc1 <sup>b</sup>	$E_{\text{pa1}}^{a}$	$E_{1/2}^{red}$
GO	0.81	0.87	0.84	-2.51	-2.45	-2.48
G1	0.82, 1.06	0.49, 0.74	_	-2.48	-2.40	-2.44
G2	0.78, 1.03	0.47, 0.70	_	-2.50	-2.44	-2.47
G3	0.79, 1.04	0.46, 0.71	—	-2.51	-2.45	-2.48

 $^aE_{\rm pa}$  = anodic peak potential.  $^bE_{\rm pc}$  = cathodic peak potential. In  $\rm CH_2Cl_2.$ 

On the other hand, the oxidation of dendrimers (G1-G3) gives an irreversible wave at around  $\sim 0.8$  V, revealing significantly different behavior from the reversible oxidation of the Ir<sup>3+</sup> complex core (G0) occurring at a similar potential (at 0.87 V). The electrochemical oxidation of the latter compound and the related Ir<sup>3+</sup> heteroleptic complexes has been assigned to the metal-centered Ir<sup>3+/4+</sup> redox process.<sup>47-50</sup> The CVs for G1, G2, and G3 showed additional oxidation peaks at  $\sim 0.80$  and  $\sim 1.05$  V upon scanning toward positive potential and two cathodic peaks at  $\sim 0.72$  and  $\sim$  0.48 V upon reverse scan. This electrochemical behavior was attributed to the oxidation of the Cz and 3,5-bis(benzyloxy)phenyl units, since identical oxidation potentials were reported for 1,3-bis(benzyloxy)benzene<sup>51</sup> and N-alkylated Cz,<sup>52-54</sup> respectively. In accordance with this assignment, all dendrimers revealed two anodic peaks and two cathodic peaks at very similar potentials, and current efficiencies were higher with the greater number of the Cz and 3,5-bis(benzyloxy)phenyl units in the dendrons.

It is well-established that the bridge unit of dibenzoxyphenyl exhibits irreversible one-electron oxidation behavior at around 1.0-1.5 V.<sup>51</sup> Further, the electrochemical properties of *N*-substituted Cz exhibit a unique behavior of quasi-reversible, one anodic and two cathodic peaks upon electrochemical oxidation, which has been interpreted in terms of the initial one-electron oxidation followed by oxidative coupling to generate dimers and polymers susceptible to oxidation at lower potentials.<sup>52-54</sup> Therefore, we assumed that the electrochemical behaviors of dendrimers are basically the sum of their constituent units (Ir<sup>3+</sup> core, bridge unit of 3,5-bis(benzyloxy)phenyl, and carbazoles), indicating negligible interaction of the constituent units.

### Steady-state absorption and emission spectra of Cz-OH and G0

**Cz-OH** exhibits two absorption bands at 292 nm ( ${}^{1}L_{a} \leftarrow {}^{1}A$  transition) and 339 nm ( ${}^{1}L_{b} \leftarrow {}^{1}A$  transition) characteristic of Cz compounds as shown in Fig. 2.<sup>55–57</sup> On the other hand, **G0** shows a strong absorption band at 230–350 nm, assigned as spin-allowed ligand-centered  ${}^{1}\pi$ - $\pi$ \* transitions, and broad absorption bands between 350 and 445 nm, attributed to the



Fig. 2 UV-vis absorption and normalized photoluminescence spectra of G0 and Cz-OH for 4  $\mu$ M solution: fluorescence of Cz-OH in CH<sub>2</sub>Cl<sub>2</sub> at 298 K and phosphorescence of Cz-OH and G0 in 2-MeTHF at 77 K.

metal-to-ligand charge transfer (<sup>1</sup>MLCT) transitions. A noticeable feature of the **G0** spectrum is the long end-tail absorption extending to 470 nm. This wavelength is well overlapped with the onset wavelength (~440 nm) of phosphorescence, suggesting that <sup>3</sup>MLCT transitions might be involved in the end-tail absorption.<sup>58-61</sup>

On the other hand, the phosphorescence of **Cz-OH** was measured at 400–550 nm in 2-MeTHF at 77 K, which is not observed at room temperature. The phosphorescence spectrum of **G0** in 2-MeTHF at 77 K exhibits a vibrational structure. The strong vibrational band at 460 nm is related to the electronic 0–0 transition from the lowest triplet state to the ground state.

#### Steady-state absorption and emission spectra of Gn(n = 1, 2 and 3)

Fig. 3a shows the absorption spectra of **G0** and **Gn** (n = 1, 2, and 3). The absorption spectra of **Gn** in the range 250–350 nm reveal the features very similar to those of **Cz**<sub>n</sub>-**OH** (Fig. S1 in ESI<sup>†</sup>). The absorbance at 293, 327, and 340 nm is proportionally increased with the number of Cz units in the dendron. It should be noted that the spectra of **Gn** (n = 1, 2 and 3) show neither spectral broadening, nor shift of each absorption band independently of the dendrimer generation, and can be reproduced by the sum of **G0** and  $Cz_n$ , indicating that there is no significant electronic interaction between the  $Cz_n$  donor and the Ir-complex acceptor



**Fig. 3** Absorption (a) and photoluminescence spectra (b) of 4.0  $\mu$ M solutions of **G0** and **Gn** (n = 1, 2, and 3) in N<sub>2</sub> saturated CH<sub>2</sub>Cl<sub>2</sub> at 298 K. Inset in figure (a) are magnified spectra using 82  $\mu$ M solution. The emission spectra in (b) were taken by excitation at 290 nm.

in the ground state. Another important point of the **G0** absorption spectrum is the good overlap with the fluorescence emission spectrum of **Cz-OH** in the region of 330–450 nm, which ensures Förster-type energy transfer from the excited-singlet Cz chromophore to the Ir complex core (Table 2).

The emission spectrum of G0 at 298 K shows characteristic MLCT emission bands at around 470 nm (Fig. 3b), which are considerably broader than that observed at 77 K without a significant red shift. For Gn, excitation at 290 nm gave a weak emission at around 350 nm and a much stronger one at  $\sim$ 470 nm, which are attributable to the fluorescence from the Cz unit and the phosphorescence emitted from the Ir-complex core, respectively. Crucially, the excitation of the Cz chromophore in Gn at 290 nm results in the dominant appearance of the Ir-core phosphorescence at  $\sim$  470 nm while the Cz fluorescence at  $\sim$  350 nm is markedly quenched compared with that of Cz<sub>n</sub>-OH when measured under identical experimental conditions (Fig. 3b). Furthermore, the phosphorescence intensities of Gn measured at a fixed concentration are significantly higher than that of G0 and increase with the increase of the dendrimer generation, which demonstrates the occurrence of efficient energy transfer from the excited-singlet state of  $Cz_n$  to the Ir-core associated with the lightharvesting function of the Cz dendron.

#### **Emission lifetimes**

The fluorescence lifetimes of  $Cz_n$ -OH ( $Cz_2$ -OH,  $Cz_4$ -OH, and  $Cz_8$ -OH) are all identical at 6.1 ns, whereas the Cz fluorescence of **Gn** (n = 1, 2, and 3) shows markedly reduced lifetimes of 0.22, 0.40, and 0.62 ns in the order of generation (Fig. 4) accompanied by < 9% contributions of longer lifetime components (~6 ns), which are almost identical to those of **Cz**<sub>n</sub>-OH. The longer component arises from the unquenched residual fraction of excited Cz, in parallel with the weak fluorescence observed in the steady-state emission spectra. On the other hand, the phosphorescence lifetimes of **Gn** are commonly ~1.0 µs, irrespective of the dendrimer generation, as well as of the excitation wavelength, 309 nm for the Cz excitation or 416 nm for the MLCT excitation of the Ir core, as shown in Table 3, and Fig. S2 in ESI.† This means that the final emitting state is the <sup>3</sup>MLCT state of the Ir-complex core.

# Quenching efficiency (energy transfer efficiency)

### Steady-state spectroscopic method (method 1)

The donor  $(Cz_n)$  and acceptor (Ir-complex) pairs in **G***n* are separated with no electronic interaction, as revealed from the absorption spectra of **G***n*. The fixed distance of their separation confirms the dynamic nature of the observed fluorescence quenching. The fluorescence quenching efficiency ( $\varepsilon_q$ ) can be calculated using the following eqn (1);

$$\varepsilon_{\rm q}(\%) = \left(1 - \alpha \times \frac{I_{\rm D}}{I_{\rm D}^0}\right) \times 100 \tag{1}$$

where  $I_D^0$  and  $I_D$  are integrated fluorescence intensities in the absence and presence of the Ir-core acceptor, respectively,

Table 2 Absorption ( $\lambda_{abs}$ ) and emission ( $\lambda_{em}$ ) wavelengths and absorption coefficients of **G0** and **Gn** 

	At $RT^a$		
Compounds	$\lambda_{ m abs}~( m nm)~(arepsilon imes 10^3~( m cm^{-1}~M^{-1}))$	$\lambda_{\rm em}$ (nm)	$\lambda_{\rm em} (\rm nm)$
G0	290 (28.3), 327 (14.9), 340 (9.7), 378 (5.1), 457 (0.6)	473, 494	460, 493
G1	290 (72.9), 293 (75.8), 327 (22.1), 340 (18.9) 378 (5.2), 457 (0.6)	350, 365, 471, 496	458, 491
G2	290 (112.8), 293 (120.4), 327 (30.9), 340 (28.2), 378 (5.4), 457 (0.6)	350, 365, 470, 499	458, 491
G3	290 (198.7), 293 (213.5), 327 (46.9), 340 (46.7), 378 (5.1), 457 (0.6)	352, 365, 471, 498	458, 491
	- h		

<sup>a</sup> In Ar saturated CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> In 2-MeTHF.



Fig. 4 Fluorescence decay profiles of Gn and  $Cz_2$ -OH in  $CH_2Cl_2$  monitored at 360 nm. Excitation wavelength is 309 nm.

Table 3 Fluorescence lifetime  $(\tau_f)$  of Cz and phosphorescence lifetime  $(\tau_p)$  of Ir-core in CH\_2Cl\_2

	$\tau_{\rm f}^{\ a}$ (ns) at 360 nm	$\tau_{\rm p}~(\mu s)$ at 500 nm, rt	$ au_{ m p}{}^d$ (µs) at 470 nm, 77 K
Cz <sub>n</sub> -OH Ir(dfppy) <sub>2</sub> (pic) G0 G1 G2 G3	6.1 — 0.22 (100%) 0.40 (100%) 0.62 (91%), 6.0 (9%)	$\begin{array}{c}\\ 0.97\\ 1.01^b, 0.99^c\\ 0.99^a, 0.98^c\\ 1.07^a, 0.96^c\\ 0.98^a, 0.94^c \end{array}$	2.80 2.85 2.82 2.84 2.92

 $^a$   $\lambda_{\rm ex}$  = 309 nm.  $^b$   $\lambda_{\rm ex}$  = 355 nm.  $^c$   $\lambda_{\rm ex}$  = 416 nm.  $^d$  In 2-MeTHF and at 77 K. Error is less than  $\pm 2\%$ .

and the factor  $\alpha$  (= $A_{DA}/A_D$ ) denotes the light-absorption contribution of the acceptor to the overall absorption at the excitation wavelength. The quenching efficiencies of Cz<sub>n</sub> in **Gn** are 98, 95 and 92% in the order of dendron generation, as listed

**Table 4** Quenching efficiency ( $\varepsilon_q$ ) of Cz in dendrons determined by steady-state emission (method 1) and a time-resolved spectroscopic technique (method 2). The phosphorescence harvesting efficiency ( $\varepsilon_h$ ) of the Ir-complex cores in **Gn** (n = 1, 2, and 3) dendrons

	$\epsilon_{\rm q},$ Cz (%), method 1	$\varepsilon_{\rm q}$ , Cz (%), method 2	$\varepsilon_{\text{LH}}$ , Ir-core <sup><i>a</i></sup> (%)
G1	98	96	157 (158)
G2	95	94	213 (213)
G3	92	90	264 (316)

 $^{a}$  Using reference with **G0**. The parenthesis values are determined by eqn (3) using the data of method 2.

in Table 4. The energy transfer from the excited singlet Cz ( ${}^{1}Cz^{*}$ ) state to the excited singlet of the ligand is difficult, because the excited state of the dfppy-ligand lies above the  ${}^{1}Cz^{*}$  state. On the other hand, the MLCT states of the Ir-complex lie below the  ${}^{1}Cz^{*}$  state and the fluorescence of Cz is well overlapped with the absorption of the Ir-complex core in the range of 340–450 nm. Therefore, we suggest that the energy transfer process takes place through the low-lying MLCT states of the Ir-complex.

### Time-resolved spectroscopic method (method 2)

Based on the fluorescence decay-time constants, the quenching efficiencies of  ${}^{1}Cz^{*}$  were determined using the following eqn (2);<sup>62</sup>

$$\varepsilon_{\rm q}(\%) = \frac{k_{\rm D}}{k_{\rm D} + k_{\rm AD}} \times 100 = 1 - \frac{\tau_{\rm AD}}{\tau_{\rm D}} \times 100$$
 (2)

where  $k_{\rm D}$  and  $k_{\rm AD}$  indicate the Cz fluorescence rate constants in the absence and presence of the acceptor (Ir-complex), respectively. The  $\varepsilon_{\rm q}$  of **Gn** are 96, 94 and 90% in order of generation, as listed in Table 4. These values are quite similar to the results determined by method 1 using the steady-state spectral data. The  $\varepsilon_{\rm q}$  of high generation dendrons slightly decreased because of the longer distance between Cz and the Ir-core.

### Light-harvesting efficiency

The phosphorescence of **Gn** is considerably enhanced compared with that of **G1**, as shown in Fig. 3. The actual enhancement could be calculated by the ratio of  $(I_P/I_P^0) \times 100$ , where  $I_P$  and  $I_P^0$  are integrated phosphorescence intensities of the Ir-complex in the absence and presence of donors, respectively, in N<sub>2</sub> saturated CH<sub>2</sub>Cl<sub>2</sub>. As listed in Table 4, the phosphorescence of the Ir-complex core is enhanced by 157 (**G1**), 213 (**G2**) and 264% (**G3**) through the light-harvesting process.

The light-harvesting process depends on the energy transfer efficiency and the emission quantum yield of the donor. Therefore, the light-harvesting efficiency ( $\varepsilon_{LH}$ ) is given by the following relation:

$$\varepsilon_{\rm LH}(\%) = (1 + n \times \varepsilon_{\rm q} \times \phi_{\rm f}) \times 100 \tag{3}$$

where  $\varepsilon_q$  is the energy transfer efficiency (0.96–0.90),  $\phi_f$  the fluorescence quantum yield (0.3) of the donor (Cz), which is measured in this study using 9,10-diphenylanthracene as a standard, and *n* the number of Cz in dendrons. The expected light-harvesting efficiencies show good agreement with experimental values.

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#### Rate constant of Förster-type energy transfer

The emission-lifetime measurements clearly demonstrated that the excited-singlet Cz chromophore is quenched by the core at rate constants  $(k_{\rm q})$  of  $4.39 \times 10^9$  (G1),  $2.34 \times 10^9$  (G2) and  $1.45 \times 10^{10}$  $10^9$  s<sup>-1</sup> (G3), respectively (Table 5). The non-radiative rate constant for Cz-OH can be easily calculated according to the equation,  $k_{\rm nr} = (1 - \phi_{\rm f}) \times k_{\rm f}$ , using the lifetimes of Cz-OH and their fluorescence quantum yields (0.3) measured in this study, giving a value of  $(k_{nr} = 1.11 \times 10^8 \text{ s}^{-1})$ . The  $k_{nr}$  value for Cz<sub>n</sub>-OH is quite similar to a reported value for the intersystem crossing  $(k_{\rm isc} = 1.24 \times 10^8 \text{ s}^{-1})$  of phenylcarbazole.<sup>63</sup> The excited singlet state of Cz seems to be deactivated non-radiatively through the intersystem crossing process. However, the observed  $k_q$  values for Cz of Gn are over ten-times larger than that of  $k_{isc}$ . Thus, in Gn, the intersystem-crossing process of excited-singlet Cz cannot compete with the quenching of excited-singlet Cz by the Ir-complex core. Consequently, the fluorescence quenching occurs exclusively by energy transfer from the excited-singlet state of Cz to the Ir core with little participation of triplet Cz.

The energy-transfer rate constants can be calculated using the following relationship (eqn (4)):

$$k_{\rm ET} = \frac{1}{\tau_{\rm D}} \left( \frac{1}{(1/\phi_{\rm ET}) - 1} \right)$$
(4)

where  $\tau_D$  is the donor fluorescence lifetime in the absence of the acceptor (Table 3) and  $\phi_{\rm ET}$  is the energy transfer efficiency, which is applied with quenching efficiencies of Cz for each generation (Table 4). The Förster model<sup>64</sup> is appropriate to interpret the rate constant for energy transfer given as

$$k_{\rm ET} = \frac{\phi_{\rm D} \kappa^2}{\tau_{\rm D} R^6} \left( \frac{9000 \ln 10}{128\pi^5 N n^4} \right) J, \quad J = \int_0^\infty F_{\rm D}(\lambda) \varepsilon(\lambda) \lambda^4 \mathrm{d}\lambda \tag{5}$$

where *N* is Avogadro's number,  $\kappa^2$  the orientation factor of the transition dipole moments,  $\phi_D$  the donor quantum yield, *J* the overlap integral of the donor emission spectrum with the acceptor absorption spectrum, *n* the index of refraction of the solvent,  $\tau_D$  the donor lifetime in the absence of the acceptor, and *R* the distance between the donor and acceptor moieties. In the Förster model, all of the variables in the expression except *R* are either constants or can be determined experimentally. We used the following values for the parameters in eqn (5):  $\kappa^2 = 2/3$ ,  $\phi = 0.3$ ,  $J = 2.63 \times 10^{-14}$  M<sup>-1</sup> cm<sup>3</sup>, n = 1.4246, and  $\tau_D = 6.3$  ns. For *R* values, an accurate determination is crucial, because the expression depends on the sixth power of *R*. However, the dendron should take variable distances between donors and acceptor. Therefore, we adopted the

Table 5Experimental and calculated energy transfer rate constants ( $k_{ET}$ )for energy transfer from the excited-singlet Cz unit to the Ir-complex core,and average distances between donor and acceptor estimated by semi-empirical calculations

Compounds	$K_{\rm ET}$ (exp) (s <sup>-1</sup> )	$K_{\rm ET}$ (cal) (s <sup>-1</sup> )	R (Å)
G1 G2 G3	$3.93  imes 10^9 \ 2.57  imes 10^9 \ 1.48  imes 10^9$	$egin{array}{l} 4.95  imes 10^9 \ 2.70  imes 10^9 \ 1.48  imes 10^9 \end{array}$	16 19 21

average distances between Cz and dfppy ( $R_{DA}$  are 16, 19 and 21 Å) for **Gn**, which can be calculated from the energy minimized geometries for many computer-generated conformers using the semi-empirical calculation (PM3 method) (Fig. S3, ESI<sup>†</sup>).<sup>65</sup>

Using these average values, the calculated energy-transfer rate constants ( $k_{\rm ET}$ ) from excited Cz to the core are 4.95 × 10<sup>9</sup>, 2.70 × 10<sup>9</sup>, and 1.48 × 10<sup>9</sup> s<sup>-1</sup> for each generation of dendron, which showed excellent agreement with experimental results, as listed in Table 5. The quenching efficiencies and the rate constants for energy transfer showed the dependency on the center-to-center distances between the donor and acceptor in dendrons.

#### Transient absorption study

In order to confirm the nature of the excited state dynamics of **G***n*, we performed nanosecond laser flash photolysis experiments at room temperature. The transient absorption (TA) difference spectra were collected at 500 ns-delay after excitation at 309 nm. Fig. 5 shows the TA spectra of **G0** and **G***n* in Ar-saturated CH<sub>2</sub>Cl<sub>2</sub> measured under identical conditions. The TA spectra obtained for **G0** exhibit the typical features of a charge transfer state of the Ir-complex core. The strong and sharp TA band at 420 nm can be assigned the characteristic of the formation of a ligand radical anion, which may be formulated as  $Ir^{4+}(dfppy^{\bullet -1/2})_2(pic-Ph)$  *via* the <sup>3</sup>MLCT process.<sup>66</sup> On the other hand, a weaker broad absorption band in the longer wavelength region can be assigned to  $T_1-T_n$  transitions.<sup>66</sup>



**Fig. 5** Transient absorption spectra of **G0**, **G1**, **G2**, and **G3** measured at 500 ns delay after excitation in Ar-saturated CH<sub>2</sub>Cl<sub>2</sub> as obtained by laser flash photolysis techniques. Excitation wavelength is 309 nm.

#### PCCP

time constant of the Ir-complex core, indicating that the transient spectra are associated with the emissive MLCT state. The similarity between the transient spectra of G0 and those of Gn suggests that the lowest excited state (emissive state) is MLCT in character.

#### Density functional calculations

It is now widely accepted that DFT/TD-DFT calculations are useful for obtaining insights into different electronic states related to the relevant absorption and emission processes. Following accurate geometry optimization, we modeled the electronic structure of **G1**. As shown in Fig. 6, the highest occupied molecular orbital (HOMO, H) consists principally of a Cz unit. Similar features can be observed for the other occupied MOs, H – 1 and H – 2, whereas the H – 3, H – 5 and H – 7 orbitals consist principally of the dfppy  $\pi$ -orbitals with a substantial contribution of Ir<sup>III</sup> d-orbitals, as shown in Fig. S4 (ESI†). The H – 4 orbital is populated on 3,5-bis(benzyloxy)phenyl branches. The first oxidation of **G1** can be assigned as the oxidation of Cz units, because the higher occupied orbitals, such as HOMO – H – 2, are related to Cz. By contrast, LUMO (L) is largely localized on the main ligand with little ancillary ligand orbital character,

#### 0 -1.23 eV номо LUMO+3 .59 eV .74 eV -1 -1 -2 179 eV LUMO+2 HOMO-1 -3 Š ş. E<sub>g</sub>= 3.45 eV -4 HOMO-2 LUMO+1 -5 eV 5 60 eV LUMO HOMO-3 -6

Fig. 6 Energy levels and isodensity plots for selected occupied and unoccupied molecular orbitals of **G1** obtained by DFT calculations.

which is also true for L + 2 and L + 3. On the other hand, L + 1 is
mainly populated on the ancillary ligand part. The orbitals
from L + 1 to L + 5 are also associated with the dfppy and
picolinate ligands around the Ir-atom, which are lower excited
states, whereas L + 6 and L + 7 orbitals are located at higher
energy states attributable to the Cz and 3,5-bis(benzyloxy)-
phenyl branch, respectively (see diagrams in Fig. S4, ESI†).67
Table 6 lists the typical electronic transitions with significant
oscillator strengths ( $f$ > 0.001 on singlet, lowest four transitions
on triplet) produced by TD-DFT calculations. The calculated
results in Table 6 imply that the observed absorption bands of
G1 at 350–450 nm involve the transitions from H $-$ 3, H $-$ 5,
and H $-$ 7 to LUMO $-$ L $+$ 2. These transitions apparently
possess mixed characters of $[d\pi(Ir) \rightarrow \pi^*_{dfppy \text{ or } pic}]$ MLCT and
$[\pi_{dfppy \text{ or } pic} \rightarrow \pi^*_{pic \text{ or } dfppy}]$ ligand-to-ligand charge transfer.
Among them, the transitions from H $-$ 3 to LUMO or L $+$ 2
and from H $-$ 5 to LUMO or L + 1 with a dominant triplet
MLCT character are expected to have a major impact on the
400-500 nm band.

### Conclusions

We have synthesized the series of  $Ir(dfppy)_2(pic-Cz_n)$  dendrimers. The light-harvesting process and photophysical properties of



Fig. 7 Schematic energy diagram for  $Ir(dfppy)_2(pic-Cz_n)$  dendrimers.

#### Table 6 Selected oscillator strength (f) and calculated electronic transitions of G1

No.	λ (nm)	f	Transition (contribution)	Assignment <sup>a</sup>
1	398	0.0049	$H - 3 \rightarrow LUMO (56\%), H - 3 \rightarrow L + 1 (27\%)$	MLCT
2	387	0.0054	$H - 5 \rightarrow LUMO(67\%), H - 5 \rightarrow L + 1(14\%)$	MLCT
3	377	0.0228	$H - 5 \rightarrow L + 1 (42\%), H - 7 \rightarrow L + 1 (33\%)$	ML'CT
4	374	0.0549	$H - 7 \rightarrow LUMO(45\%), H - 5 \rightarrow LUMO(14\%), H - 3 \rightarrow L + 2(14\%)$	MLCT
5	372	0.0106	$H - 3 \rightarrow L + 2 (72\%)$	LL'CT
6	367	0.038	$H - 7 \rightarrow L + 1$ (31%), $H - 7 \rightarrow LUMO$ (19%)	MLCT
7	360	0.017	$H - 9 \rightarrow L + 1$ (14%), $H - 8 \rightarrow LUMO$ (14%)	MLCT
8	358	0.0023	$H - 5 \rightarrow L + 2(77\%)$	MLCT
9	348	0.0327	$H - 7 \rightarrow L + 2 (82\%)$	MLCT
10	335	0.0014	$H - 5 \rightarrow L + 12(25\%), H - 3 \rightarrow L + 12(46\%)$	MLCT
11	326	0.0019	$H - 7 \rightarrow L + 12(25\%), H - 5 \rightarrow L + 12(24\%), H - 3 \rightarrow L + 12(27\%)$	MLCT
12	324	0.0077	$H - 5 \rightarrow L + 3 (95\%)$	MLCT
13	323	0.005	$H - 9 \rightarrow LUMO(38\%), H - 8 \rightarrow LUMO(43\%)$	MLCT

<sup>*a*</sup> M = Ir(III), L = dfppy, and L' = pic.

dendrimers have been determined. The Cz-dendrons act as extremely efficient light-harvesting antennas capable of transferring light energy through space to their Ir-core complex. The fluorescence of Cz overlapped well with the MLCT absorption band of the Ir-complex. The energy transfer can be explained by the Förster model as shown in Fig. 7. The energy transfer efficiency (>90%) was found to be quantitative for generation, with a slight decrease observed for the high generations, which was determined by the steady-state and the time-resolved spectroscopic methods. The energy transfer rate constants calculated by the Förster model showed good agreement with the experimental values. The CV result and DFT calculation imply the occurrence of energy transfer from the Cz-unit to the Ir-core complex. Most importantly, actual enhancement of light-harvesting is strongly dependent on key factors such as the number of Cz-units, the fluorescence quantum yield of Cz and the energy transfer efficiency. As a result, the light harvesting efficiencies of 157 (G1), 213 (G2), and 264% (G3), are measured, and showed good agreement with expected values.

#### Synthetic details

All complexes were synthesized following the synthetic route shown in Scheme 1. All procedures were carried out in an inert atmosphere. Cyclometalated Ir<sup>III</sup>-chloro-bridged dimers of general formula [(dfppy)<sub>2</sub>Ir( $\mu$ -Cl)]<sub>2</sub> were synthesized by the method reported by Nonoyama.<sup>68</sup>

**Ph<sub>2</sub>-OMe.** A mixture of benzyl bromide (7.2 g, 42 mmol), methyl-3,5-dihydroxybenzoate (3.5 g, 21 mmol), and potassium carbonate (11.6 g, 84 mmol) was dissolved in dry ACN (50 ml). The reaction mixture was heated at 85 °C for 15 h. After cooling to room temperature, the reaction mixture was poured into water. The organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried using MgSO<sub>4</sub>. After removal of the solvents under reduced pressure, the residue was purified by column chromatography (CC) on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>–*n*-hexane (v/v = 2 : 1)) to provide a white solid product in 76% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ 7.30–7.45 (m, 12H), 6.81 (s, 1H), 5.08 (s, 4H), 3.91 (s, 3H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 166.8, 159.8, 136.5, 132.1, 128.7, 128.2, 127.7, 108.4, 107.3, 70.4, 52.4. HRMS (FAB): *m*/z 348.1366 (calcd for [M + H]<sup>+</sup> 348.1362). Anal. Calcd for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>: C, 75.84; H, 5.79. Found: C, 75.85; H, 5.74.

**Ph**<sub>2</sub>-**OH. Ph**<sub>2</sub>-**OH** was prepared according to the general method for LiAlH<sub>4</sub> reduction of aromatic esters to benzylic alcohols. **Ph**<sub>2</sub>-**OMe** (6.2 g, 18 mmol) was added dropwise to a suspension of LiAlH<sub>4</sub> (0.81 g, 21 mmol) in dry THF (30 ml) at 0 °C. The suspension was warmed to room temperature and stirred until the reaction was completed as indicated by TLC. The reaction was quenched by adding water with an ice bath. It was stirred at room temperature for 15 min, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were combined, washed with water, dried under MgSO<sub>4</sub> and filtered. The filtrate was concentrated using a rotary evaporator under reduced pressure. The residue was purified by CC on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>) to give a white solid in 74% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ 7.44–7.33 (m, 10H), 6.63 (s, 2H), 6.55 (s, 1H), 5.04 (s, 4H), 4.63 (s, 2H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 160.2, 143.5, 136.9, 128.7, 128.1,

127.6, 105.8, 101.4, 70.2, 65.4. HRMS (FAB): m/z 320.1410 (calcd for  $[M + H]^+$  320.1412). Anal. Calcd for  $C_{21}H_{20}O_3$ : C, 78.73; H, 6.29. Found: C, 78.70; H, 6.31.

**Ph<sub>2</sub>-Br.** Triphenylphosphine (6.7 g, 26 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (24 ml) was added to bromine (1.3 mL, 26 mmol) dropwise at 0 °C and stirred for 15 min. The salt was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> and added to a solution of Ph2-OH (4.1 g, 13 mmol) in dry  $CH_2Cl_2$  (20 ml) via a cannula. The solution was then allowed to warm to room temperature and was stirred for 1 h. The reaction was quenched by adding water, and the aqueous layer was extracted using CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phase was dried using MgSO<sub>4</sub>, and the solvent was removed by reduced pressure. The product was purified by column chromatography on silica gel (eluent:  $CH_2Cl_2$ -*n*-hexane (v/v = 1:5) and then  $CH_2Cl_2$ ) to give a white solid in 90% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  7.44–7.35 (m, 10H), 6.65 (s, 2H), 6.56 (s, 1H), 5.03 (s, 4H), 4.42 (s, 2H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 160.1, 139.8, 136.6, 128.7, 128.7, 128.1, 127.6, 127.0, 108.2, 102.2, 70.2, 33.8. HRMS (FAB): m/z 382.0571 (calcd for  $[M + H]^+$  382.0568). Anal. Calcd for C<sub>21</sub>H<sub>19</sub>BrO<sub>2</sub>: C, 65.81; H, 5.00. Found: C, 65.79; H, 4.99.

**Cz<sub>2</sub>-Br.** The synthesis of **Cz<sub>2</sub>-OH** has been described earlier.<sup>69</sup> The reaction of triphenylphosphine (3.7 g, 14 mmol) and bromine (0.7 mL, 14 mmol) in minimal CH<sub>2</sub>Cl<sub>2</sub> with a solution of **Cz<sub>2</sub>-OH** (4.6 g, 7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> afforded a white solid in 80% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ 8.17 (d, 4H), 7.69 (d, 4H), 7.62 (d, 4H), 7.45–7.41 (m, 8H), 7.31 (t, 4H), 6.77 (s, 2H), 6.71 (s, 1H), 5.19 (s, 4H), 4.49 (s, 2H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 161.3, 141.0, 140.3, 137.8, 136.0, 129.3, 127.5, 126.2, 123.6, 120.6, 120.3, 110.0, 108.5, 102.5, 70.0, 33.7. HRMS (FAB): *m*/z 712.1721 (calcd for [M + H]<sup>+</sup> 712.1725). Anal. Calcd for C<sub>45</sub>H<sub>33</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 75.73; H, 4.66; N, 3.93. Found: C, 75.91; H, 4.68; N, 3.92.

**Cz**<sub>4</sub>**-OMe. Cz**<sub>2</sub>-**Br** (4.0 g, 5.6 mmol) and methyl 3,5-dihydroxybenzoate (0.47 g, 2.8 mmol) were reacted with potassium carbonate (22.4 g, 3 mmol) in ACN/THF (30 ml/10 ml). The crude product was separated by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane (v/v = 2 : 1)) to give a white powder in 91% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ 8.17 (d, 8H), 7.71 (d, 8H), 7.67 (d, 8H), 7.49–7.44 (m, 18H), 7.36 (t, 8H) 6.91 (s, 1H), 6.82 (s, 4H), 6.74 (s, 2H), 5.19 (s, 8H), 5.11 (s, 4H), 3.91 (s, 3H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 166.5, 160.4, 160.0, 141.0, 139.4, 137.7, 136.1, 132.4, 129.4, 127.4, 126.2, 123.6, 120.6, 120.3, 110.0, 108.7, 107.5, 106.8, 102.0, 70.4, 69.9, 52.6. HRMS (FAB): *m/z* 1432.5341 (calcd for [M + H]<sup>+</sup> 1432.5350). Anal. Calcd for C<sub>98</sub>H<sub>72</sub>N<sub>4</sub>O<sub>8</sub>: C, 82.10; H, 5.06; N, 3.91. Found: C, 82.41; H, 5.08; N, 3.90.

**Cz<sub>4</sub>-OH.** The reaction of **Cz<sub>4</sub>-OMe** (3.7 g, 2.6 mmol) with LiAlH<sub>4</sub> (0.13 g, 3.3 mmol) in 30 ml of THF afforded a white solid in 88% yield. The crude product was separated by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  8.19 (d, 8H), 7.69 (d, 8H), 7.67 (d, 8H), 7.46–7.42 (m, 16H), 7.33 (t, 8H), 6.85 (s, 4H), 6.76 (s, 2H), 6.73 (s, 2H), 5.18 (s, 8H), 5.09 (s, 4H), 4.67 (s, 2H), 4.29 (s, 1H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  160.4, 141.0, 139.8, 137.8, 136.1, 129.4, 127.4, 126.2, 123.7, 120.6, 120.3, 110.0, 106.8, 101.9, 70.2, 70.0, 65.5. MALDI-TOF: *m*/*z* 1404.53 (calcd for [M + H]<sup>+</sup> 1404.54). Anal. Calcd for C<sub>97</sub>H<sub>72</sub>N<sub>4</sub>O<sub>7</sub>: C, 82.88; H, 5.16; N, 3.99. Found: C, 83.16; H, 5.18; N, 3.98.



Scheme 1 Synthetic route of  $Ir(dfppy)_2(pic-Ph_2)$  and Ir(dfppy)(pic-Czn) (n = 2, 4, and 8). (a)  $K_2CO_3$ , ACN, 85 °C, 15 h; (b) LiAlH\_4, THF, 0 °C; (c) PPh\_3, Br\_2, CH\_2Cl\_2, 0 °C, 1 h; (d) LiAlH\_4, THF, room temperature, 12 h; (e) 1/2  $IrCl_3 \cdot H_2O$ , 2-ethoxyethanol:  $H_2O$  (v/v = 3:1), 120 °C; (f)  $Na_2CO_3$ , 2-ethoxyethanol, 140 °C; (g)  $Cz_n$ -Br or Ph\_2-Br,  $K_2CO_3$ , ACN:THF (v/v = 3:1), 85 °C.

**Cz<sub>4</sub>-Br.** The reaction of triphenylphosphine (1.2 g, 4.5 mmol) and bromine (0.2 ml, 4.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) with a solution of **Cz<sub>4</sub>-OH** (3.1 g, 2.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> afforded a white solid in 94% yield. The reaction mixture was purified by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>–*n*-hexane (v/v = 1 : 1)). <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ 8.20 (d, 8H), 7.71 (d, 8H), 7.67 (d, 8H), 7.49–7.44 (m, 16H), 7.36 (t, 8H), 6.86 (s, 4H), 6.78 (s, 2H), 6.77 (s, 2H), 6.71 (s, 1H), 5.20 (s, 8H), 5.08 (s, 4H), 4.47 (s, 2H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 160.4, 160.3, 141.0, 139.6, 137.8, 136.1, 129.4, 127.4, 126.3, 123.7, 120.6, 120.3, 110.0, 108.5, 106.9, 102.6, 102.0, 70.3, 70.0, 33.9. MALDI-TOF: *m*/*z* 1466.44 (calcd for [M + H]<sup>+</sup> 1466.46). Anal. Calcd for C<sub>97</sub>H<sub>71</sub>BrN<sub>4</sub>O<sub>6</sub>: C, 79.33; H, 4.87; N, 3.82. Found: C, 79.56; H, 4.88; N, 3.81.

 $Cz_8$ -OMe.  $Cz_4$ -Br (1.7 g, 1.1 mmol) and methyl 3,5-dihydroxybenzoate (0.1 g, 0.6 mmol) were reacted with potassium carbonate (0.6 g, 4.6 mmol) in ACN/THF (30 ml/10 ml). The crude product was separated by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>–*n*-hexane (v/v = 2 : 1)) to give a white powder in 62% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  8.21 (d, 16H), 7.67 (d, 16H), 7.61 (d, 16H), 7.50–7.42 (m, 32H), 7.35 (t, 16H), 6.9 (s, 2H), 6.87 (s, 7H), 6.85 (s, 4H), 6.75 (s, 8H), 5.16 (s, 16H), 5.11 (s, 8H), 5.07 (s, 4H), 3.94 (s, 3H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  166.9, 160.5, 160.0, 141.0, 139.8, 137.8, 130.5, 129.4, 127.3, 126.2, 123.7, 120.7, 120.6, 120.4, 120.1, 117.7, 110.1, 106.8, 102.0, 70.3, 69.9, 52.6. MALDI-TOF: *m*/*z* 2941.03 (calcd for [M + H]<sup>+</sup> 2941.10). Anal. Calcd for C<sub>202</sub>H<sub>148</sub>N<sub>8</sub>O<sub>16</sub>: C, 82.43; H, 5.07; N, 3.81. Found: C, 82.80; H, 5.09; N, 3.80.

**Cz<sub>8</sub>-OH.** The reaction of **Cz<sub>8</sub>-OMe** (1.1 g, 0.4 mmol) with LiAlH<sub>4</sub> (0.03 g, 0.7 mmol) in 10 ml of THF afforded a white solid in 88% yield. The crude product was separated by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  8.17 (d, 16H), 7.70 (d, 16H), 7.62 (d, 16H), 7.46–7.41 (m, 32H), 7.31 (t, 16H), 6.76 (s, 14H), 6.70 (s, 7H), 5.28 (s, 1H), 5.19 (s, 28H), 4.73 (d, 2H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  160.4, 144.0, 141.0,

137.7, 136.2, 129.3, 127.5, 126.2, 123.6, 120.6, 120.3, 110.0, 106.1, 101.6, 70.0, 68.2, 65.5. MALDI-TOF: m/z 2913.07 (calcd for 2913.11). Anal. Calcd for  $C_{201}H_{148}N_8O_{15}$ : C, 82.81; H, 5.12; N, 3.84. Found: C, 83.05; H, 5.13; N, 3.83.

**Cz<sub>8</sub>-Br.** The reaction of triphenylphosphine (0.6 g, 2.4 mmol) and bromine (0.12 ml, 2.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) with a solution of **Cz<sub>4</sub>-OH** (3.5 g, 1.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> afforded a white solid in 70% yield. The residue was purified by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>–*n*-hexane (v/v = 1 : 1)) to give a white solid. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ 8.12 (d, 16H), 7.62 (d, 16H), 7.55 (m, 16H), 7.24–7.37 (m, 48H), 6.61–6.77 (m, 19H), 6.43–6.48 (m, 2H), 4.99–5.16 (m, 28H), 4.25 (s, 2H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 160.4, 141.0, 139.8, 136.1, 130.4, 129.4, 127.4, 126.1, 123.5, 120.3, 110.0, 106.8, 101.9, 70.3, 69.9. MALDI-TOF: *m*/z 2974.98 (calcd for [M + H]<sup>+</sup> 2975.02). Anal. Calcd for C<sub>201</sub>H<sub>147</sub>BrN<sub>8</sub>O<sub>14</sub>: C, 81.06; H, 4.97; N, 3.76. Found: C, 81.40; H, 4.99; N, 3.75.

 $Ir(dfppy)_2(pic)$ . A mixture of  $[(dfppy)_2Ir(\mu-Cl)]_2$  (0.48 g, 0.4 mmol), 3-hydroxypicolinic acid (0.16 g, 1.2 mmol), and sodium carbonate (0.33 g, 3.1 mmol) was dissolved in 2-ethoxyethanol (25 ml) and heated to 120 °C for 15 h. After cooling to room temperature, the mixture was quenched with water. The organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> and then dried using MgSO<sub>4</sub>. After the removal of solvents under reduced pressure, the residue was purified by column chromatography on silica gel (eluent:  $CH_2Cl_2$ -methanol (v/v = 100:1)) to give the desired product (yield: 0.9 g, 65%). <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$ 13.56 (s, 1H), 8.65 (d, 1H), 8.29 (d, 1H), 8.23 (d, 1H), 8.79 (t, 3H), 7.46 (d, 1H), 7.42 (dd, 1H), 7.25(d, 2H), 7.21 (t, 1H), 7.02 (t, 1H), 6.46 (t, 1H), 6.40 (t, 1H), 5.77 (d, 1H), 5.56 (d, 1H). <sup>13</sup>C NMR  $(75.4 \text{ MHz}, \text{CDCl}_3)$ :  $\delta$  177.7, 165.8, 164.3, 162.6, 162.3, 160.9, 160.5, 152.3, 149.9, 148.8, 148.2, 139.8, 138.7, 138.6, 134.5, 130.2, 128.4, 127.5, 123.6, 123.5, 123.1, 123.0, 122.9, 122.7, 114.8, 114.7, 98.6, 98.1. HRMS (FAB): m/z 711.0752 (calcd for  $[M + H]^+$  711.0757). Anal. Calcd for C<sub>28</sub>H<sub>16</sub>F<sub>4</sub>IrN<sub>3</sub>O<sub>3</sub>: C, 47.32; H, 2.27; N, 5.91. Found: C, 47.47; H, 2.28; N, 5.89.

### General procedure for $Ir(dfppy)_2(pic-Ph_2)$ or $Ir(dfppy)_2(pic-Cz_n)$ (*n* = 2, 4, and 8) complexes

A mixture of **Ph**<sub>2</sub>-**Br** or **Cz**<sub>*n*</sub>-**Br** (0.27 mmol),  $Ir(dfppy)_2(pic)$  (0.27 mmol) and  $K_2CO_3$  (0.3 g, 2.17 mmol) in ACN/THF (12 ml/4 ml) was refluxed under a N<sub>2</sub> environment for 12 h. After cooling to room temperature, the reaction mixture was poured into water. The organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried under MgSO<sub>4</sub>. After removal of solvents under reduced pressure, the residue was purified by silica gel column chromatography to provide the desired product.

**Ir(dfppy)**<sub>2</sub>(**pic-Ph**<sub>2</sub>). This product was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> to remove the Ph<sub>2</sub>-Br and then CH<sub>2</sub>Cl<sub>2</sub>-ethylacetate (v/v = 1 : 1) to provide the desired product as a solid in 76% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ 8.82 (d, 1H), 8.23 (t, 2H), 7.73–7.65 (m, 2H), 7.42–7.13 (m, 14H), 6.91 (t, 1H), 6.84 (d, 2H), 6.55 (s, 1H), 6.49–6.34 (m, 3H), 5.78 (d, 1H), 5.44 (d, 1H), 5.30 (s, 2H), 5.03 (s, 4H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 171.2, 160.3, 158.6, 152.9, 152.8, 138.2, 136.7, 128.9, 128.6, 128.1, 127.8, 70.3. HRMS (FAB): *m/z* 1013.18

(calcd for  $[M + H]^+$  1013.21). Anal. Calcd for  $C_{49}H_{34}F_4IrN_3O_5$ : C, 58.10; H, 3.38; N, 4.15. Found: C, 47.47; H, 2.28; N, 5.89.

**Ir**(**dfppy**)<sub>2</sub>(**pic**-**Cz**<sub>2</sub>). This compound was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> to remove the **Cz**<sub>2</sub>-**Br** and then CH<sub>2</sub>Cl<sub>2</sub>-ethylacetate (v/v = 1:1) to provide the desired product as a white solid in 80% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  8.83 (d, 1H), 8.20 (t, 2H), 8.13 (d, 3H), 7.66 (d, 6H), 7.55 (d, 4H), 7.43–7.48 (m, 2H), 7.39 (t, 9H), 7.28 (t, 5H), 7.09–7.14 (m, 2H), 7.05 (s, 2H), 6.89 (s, 1H), 6.68 (s, 1H), 6.44 (t, 1H), 6.35 (t, 1H), 5.79 (d, 1H), 5.53 (d, 1H), 5.28 (s, 2H), 5.18 (s, 4H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>):  $\delta$  171.4, 164.6, 162.8, 162.3, 160.5, 158.8, 153.0, 149.0, 148.1, 141.3, 141.2, 138.6, 138.4, 137.6, 136.6, 129.6, 127.2, 126.2, 124.17, 123.6, 122.5, 120.6, 120.2, 114.6, 110.0, 105.7, 102.1, 98.0, 71.0, 70.0. HRMS (FAB): *m/z* 1343.3216 (calcd for [M + H]<sup>+</sup> 1343.3221). Anal. Calcd for C<sub>73</sub>H<sub>48</sub>F<sub>4</sub>IrN<sub>5</sub>O<sub>5</sub>: C, 65.27; H, 3.60; N, 5.21. Found: C, 65.48; H, 3.61; N, 5.19.

**Ir(dfppy)**<sub>2</sub>(**pic-Cz**<sub>4</sub>). This product was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> to remove the **Cz**<sub>4</sub>-**Br** and then CH<sub>2</sub>Cl<sub>2</sub>-ethylacetate (v/v = 1 : 4) to provide the desired product as a white solid in 57% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ 8.80 (d, 1H), 8.20 (t, 2H), 8.13 (s, 9H), 7.64 (d, 10H), 7.56 (d, 10H), 7.38–7.43 (m, 20H), 7.23–7.28 (m, 10H), 6.98 (s, 2H), 6.80 (s, 4H), 6.44 (t, 1H), 6.33 (t, 1H), 5.79 (d, 1H), 5.55 (d, 1H), 5.15–5.18 (m, 12H), 5.04–5.09 (m, 2H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 171.5, 165.9, 164.6, 160.4, 160.3, 158.7, 153.0, 149.0, 148.1, 141.3, 140.9, 140.5, 139.8, 138.4, 137.7, 136.2, 129.3, 127.4, 126.2, 124.2, 123.6, 122.6, 120.6, 120.3, 114.7, 110.0, 106.9, 105.6, 102.1, 98.02, 70.2, 69.9. MALDI-TOF: *m*/*z* 2097.64 (calcd for [M + H]<sup>+</sup> 2097.60). Anal. Calcd for C<sub>125</sub>H<sub>86</sub>F<sub>4</sub>IrN<sub>7</sub>O<sub>9</sub>: C, 71.55; H, 4.13; N, 4.67. Found: C, 71.70; H, 4.14; N, 4.65.

**Ir(dfppy)**<sub>2</sub>(**pic-Cz**<sub>8</sub>). This product was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub> to remove the Cz<sub>8</sub>-Br and then CH<sub>2</sub>Cl<sub>2</sub>-ethylacetate (1:5 v/v) to provide the desired product as a white solid in 24% yield. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ 8.77 (d, 1H), 8.10 (d, 18H), 7.60 (d, 20H), 7.52 (d, 20H), 7.35-7.42 (m, 40H), 7.23-7.25 (m, 20H), 6.62-6.66 (m, 9H), 6.41 (t, 1H), 6.29 (t, 1H), 5.75 (d, 1H), 5.51 (d, 1H), 5.01 (bs, 20H), 4.95-5.00 (m, 10H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ 171.4, 160.3, 148.1, 141.1, 140.9, 139.7, 139.6, 138.3, 137.6, 136.1, 130.4, 129.3, 127.3, 126.2, 123.5, 122.6, 120.5, 120.2, 120.0, 109.9, 106.7, 105.5, 101.8, 70.2, 69.9. MALDI-TOF: *m*/z 3606.12 (calcd for [M + H]<sup>+</sup> 3606.17). Anal. Calcd for C<sub>229</sub>H<sub>162</sub>F<sub>4</sub>IrN<sub>11</sub>O<sub>17</sub>: C, 76.23; H, 4.53; N, 4.27. Found: C, 76.55; H, 4.55; N, 4.25.

# Abbreviations and full names

Ph <sub>2</sub> -OMe	3,5-Bis-benzyloxybenzoic acid methyl ester
Ph <sub>2</sub> -OH	(3,5-Bis-benzyloxyphenyl)methanol
Ph <sub>2</sub> -Br	1,3-Bis-benzyloxy-5-bromomethylbenzene
Cz <sub>2</sub> -Br	9,9'-(4,4'-(5-(Bromomethyl)-1,3-phenylene)-
	bis(oxy)bis(methylene)bis(4,1-phenylene))-
	bis(9 <i>H</i> -carbazole)

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Cz <sub>4</sub> -OMe	Methyl 3,5-bis(3,5-bis(4-(9 <i>H</i> -carbazol-9-yl)-
	benzyloxy)benzyloxy)benzoate
Cz <sub>4</sub> -OH	(3,5-Bis(3,5-bis(4-(9H-carbazol-9-yl)benzyloxy)-
	benzyloxy)phenyl)methanol
Cz <sub>4</sub> -Br	9,9',9",9'''-(4,4',4",4'''-(5,5'-(5-(Bromomethyl)-
	1,3-phenylene)bis(oxy)bis(methylene)-
	bis(benzene-5,3,1-triyl))tetrakis(oxy)tetrakis-
	(methylene)tetrakis(4,1-phenylene))tetrakis-
	(9H-carbazole)
Cz <sub>8</sub> -OMe	Methyl 3,5-bis(3,5-bis(3,5-bis(4-(9H-carbazol-
	9-yl)benzyloxy)benzyloxy)benzyloxy)benzoate
Cz <sub>8</sub> -OH	(3,5-Bis(3,5-bis(3,5-bis(4-(9H-carbazol-9-yl)-
	benzyloxy)benzyloxy)benzyloxy)phenyl)-
	methanol
Cz <sub>8</sub> -Br	9,9',9",9''',9'''',9''''',9''''',9'''''',9''''''
	4'''',4''''',4''''''-(5,5',5'',5'''-(5,5'-(5-
	(Bromo methyl)-1,3-phenylene)bis(oxy)-
	bis(methylene)bis(benzene-5,3,1-triyl))tetra-
	kis(oxy)tetrakis(methyl-ene)tetrakis-
	(benzene-5,3,1-triyl))octakis(oxy)octakis-
	(methylene)octakis(4,1-phenylene))octakis-
	(9 <i>H</i> -carbazole)
Ir(dfppy) <sub>2</sub> (pic)	Iridium(III) bis[(4,6-difluorophenyl)-
	pyridinato-N,C <sup>2</sup> ]3-hydroxypicolinate
Ir(dfppy) <sub>2</sub> (pic-Ph <sub>2</sub> )	Iridium(III) bis[(4,6-difluorophenyl)-
	pyridinato-N,C <sup>2</sup> ]3-(3,5-dibenzyloxybenzyl)-
	picolinate
Ir(dfppy) <sub>2</sub> (pic-Cz <sub>2</sub> )	Iridium(III) bis[(4,6-difluorophenyl)-
	pyridinato-N, $C^2$ ] (3,5-bis(4-(9 <i>H</i> -carbazol-9-yl)-
	benzyloxy)phenyl)picolinate
Ir(dfppy) <sub>2</sub> (pic-Cz <sub>4</sub> )	Iridium(III) bis[(4,6-difluorophenyl)-
	pyridinato-N,C <sup>2</sup> ] (3,5-bis(3,5-bis-
	(4-(9H-carbazol-9-yl)benzyloxy)benzyloxy)-
	phenyl)picolinate
Ir(dfppy) <sub>2</sub> (pic-Cz <sub>8</sub> )	Iridium(III) bis[(4,6-difluorophenyl)-
	pyridinato-N,C <sup>2</sup> ] (3,5-bis(3,5-bis(3,5-bis-
	(4-(9H-carbazol-9-yl)benzyloxy)benzyloxy)-
	benzyloxy)phenyl)picolinate

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# Notes and references

 M. A. Baldo, D. F. O'Brian, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, 395, 151–154.

- 2 M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 1999, 75, 4–6.
- 3 M. A. Baldo, M. E. Thompson and S. R. Forrest, *Nature*, 2000, **403**, 750–753.
- 4 F. C. Chen, Y. Yang, M. E. Thompson and J. Kido, *Appl. Phys. Lett.*, 2002, **80**, 2308–2310.
- 5 S. Lamansky, P. I. Djurovich, F. Abdel-Razzaq, S. Garon, D. L. Murphy and M. E. Thompson, *J. Appl. Phys.*, 2002, **92**, 1570–1575.
- 6 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.
- 7 C. Adachi, S. Lamansky, M. A. Baldo, R. C. Kwong,
   M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 2001,
   78, 1622–1624.
- 8 J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard and G. G. Malliaras, *J. Am. Chem. Soc.*, 2004, **126**, 2763–2767.
- 9 M. S. Lowry and S. Bernhard, *Chem.-Eur. J.*, 2006, **12**, 7970-7977.
- 10 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.
- 11 P. Coppo, E. A. Plummer and L. De Cola, *Chem. Commun.*, 2004, 1774–1775.
- 12 I. M. Dixon, J.-P. Collin, J.-P. Sauvage, L. Flamingni, S. Encinas and F. Barigelletti, *Chem. Soc. Rev.*, 2000, 29, 385–391.
- 13 P.-T. Chou and Y. Chi, Chem.-Eur. J., 2007, 13, 380-395.
- 14 M. Pleovets, F. Vögtle, L. De Cola and V. Balzani, *New J. Chem.*, 1999, **23**, 63–69.
- 15 F. Vögtle, M. Plevoets, M. Nieger, G. C. Azzellini, A. Credi, L. De Cola, V. De Marchis, M. Venturi and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 6290–6298.
- 16 J. Ding, B. Wang, Z. Yue, B. Yao, Z. Xie, Y. Cheng, L. Wang, X. Jing and F. Wang, *Angew. Chem., Int. Ed.*, 2009, 48, 6664–6666.
- 17 L. Chen, Z. Ma, J. Ding, L. Wang, X. Jinga and F. Wanga, *Chem. Commun.*, 2011, 47, 9519–9521.
- 18 M. A. Baldo, C. Adachi and S. R. Forrest, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, 62, 10967–10977.
- 19 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**, 017402.
- 20 T. Qin, J. Ding, L. Wang, M. Baumgarten, G. Zhou and K. Müllen, J. Am. Chem. Soc., 2009, 131, 14329–14336.
- 21 Y. Li, Y. Liu and M. Zhou, Dalton Trans., 2012, 41, 2582-2591.
- 22 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.
- 23 S. Gambino, S. G. Stevenson, K. A. Knights, P. L. Burn and I. D. W. Samuel, *Adv. Funct. Mater.*, 2009, **19**, 317–323.
- 24 J. W. Levell, W.-Y. Lai, R. J. Borthwick, P. L. Burn, S.-C. Lob and I. D. W. Samuel, *New J. Chem.*, 2012, **36**, 407–413.
- 25 J. Ding, J. Gao, Y. Cheng, Z. Xie, L. Wang, D. Ma, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2006, **16**, 575–581.
- 26 S.-C. Lo, R. N. Bera, R. E. Harding, P. L. Burn and I. D. W. Samuel, *Adv. Funct. Mater.*, 2008, **18**, 3080–3090.

- 28 G. Zhou, W.-Y. Wong, B. Yao, Z. Xie and L. Wang, Angew. Chem., Int. Ed., 2007, 46, 1149–1151.
- 29 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.
- 30 S.-C. Lo, T. D. Anthopoulos, E. B. Namdas, P. L. Burn and
   I. D. W. Samuel, *Adv. Mater.*, 2005, 17, 1945–1948.
- 31 M. J. Frampton, E. B. Namdas, S.-C. Lo, P. L. Burn and I. D. W. Samuel, *J. Mater. Chem.*, 2004, **14**, 2881–2888.
- 32 T. D. Anthopoulos, J. P. J. Markham, E. B. Namdas, I. D. W. Samuel, S.-C. Lo and P. L. Burn, *Appl. Phys. Lett.*, 2003, 82, 4824–4826.
- 33 W.-Y. Lai, M. N. Balfour, J. W. Levell, A. K. Bansal, P. L. Burn, S.-C. Lo and I. D. W. Samuel, *Macromolecules*, 2012, 45, 2963–2971.
- 34 S.-C. Lo, R. E. Harding, C. P. Shipley, S. G. Stevenson, P. L. Burn and I. D. W. Samuel, *J. Am. Chem. Soc.*, 2009, 131, 16681–16688.
- 35 J. Ding, J. Lü, Y. Cheng, Z. Xie, L. Wang, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2008, **18**, 2754–2762.
- 36 B.-L. Li, L. Wu, Y.-H. He and Q.-H. Fan, *Dalton Trans.*, 2007, 2048–2057.
- 37 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.
- 38 W.-Y. Wong and C.-L. Ho, J. Mater. Chem., 2009, 19, 4457–4482.
- 39 D. W. Cho, M. Fujitsuka, J. H. Ryu, M. H. Lee, H. K. Kim, T. Majima and C. Im, *Chem. Commun.*, 2012, 48, 3424–3426.
- 40 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627.
- 41 P. J. Hay and W. R. Wadt, J. Chem. Phys., 1985, 82, 299-310.
- 42 E. R. Davidson and D. Feller, Chem. Rev., 1986, 86, 681-696.
- 43 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2010.
- 44 J. V. Caspar and T. J. Meyer, Inorg. Chem., 1983, 22, 2444-2453.

- 45 F. Neve, A. Crispini, S. Campagna and S. Serroni, *Inorg. Chem.*, 1999, **38**, 2250–2258.
- 46 I. Avilov, P. Minoofar, J. Cornil and L. De Cola, J. Am. Chem. Soc., 2007, 129, 8247–8258.
- 47 G. Calogero, G. Giuffrida, S. Serroni, V. Ricevuto and S. Campagna, *Inorg. Chem.*, 1995, 34, 541–545.
- 48 K. K.-W. Lo, C.-K. Chung, T. K.-M. Lee, L.-H. Lui, K. H.-K. Tsang and N. Zhu, *Inorg. Chem.*, 2003, **42**, 6886–6897.
- 49 K. K. W. Lo, K. Y. Zhang, C.-K. Chung and K. Y. Kwok, *Chem.-Eur. J.*, 2007, 13, 7110–7120.
- 50 J. S. Y. Lau, P.-K. Lee, K. H.-K. Tsang, C. H.-C. Ng, Y.-W. Lam, S.-H. Cheng and K. K.-W. Lo, *Inorg. Chem.*, 2009, 48, 708–718.
- 51 Y. Martinez, R. Ortiz, O. P. Marquez, J. Marquez,
   G. Perdomo and T. F. Otero, *J. Electrochem. Soc.*, 1994,
   141, 1109–1113.
- 52 J. F. Ambrose, L. L. Carpenter and R. F. Nelson, J. Electrochem. Soc., 1975, 122, 876–894.
- 53 J. F. Ambrose and R. F. Nelson, J. Electrochem. Soc., 1968, 115, 1159–1164.
- 54 K. Abbey, B. R. Hsieh and M. H. Litt, *Macromolecules*, 1986, **19**, 521–529.
- 55 J. R. Platt, J. Chem. Phys., 1949, 17, 484–495.
- 56 G. E. Johnson, J. Phys. Chem., 1974, 78, 1512-1521.
- 57 H. Ohkita, S. Ito, M. Yamamoto, Y. Tohda and K. Tani, J. Phys. Chem. A, 2002, 106, 2140–2145.
- 58 A. P. Wilde, K. A. King and R. J. Watts, J. Phys. Chem., 1991, 95, 629–634.
- 59 Y. You, K. S. Kim, T. K. Ahn, D. Kim and S. Y. Park, J. Phys. Chem. C, 2007, 111, 4052–4060.
- 60 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.
- 61 S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2001, 40, 1704–1711.
- 62 K. R. J. Thomas, A. L. Thompson, A. V. Sivakumar, C. J. Bardeen and S. Thayumanavan, *J. Am. Chem. Soc.*, 2005, **127**, 373–383.
- 63 S. M. Bonesi and R. Erra-Balsells, J. Lumin., 2001, 93, 51-74.
- 64 J. R. Lakowicz, *Principles of fluorescence spectroscopy*, ch. 13, 3rd edn, Springer Science, Singapore, 2006.
- 65 W. Ortiz, A. E. Roitberg and J. L. Krause, *J. Phys. Chem. B*, 2004, **108**, 8218–8225.
- 66 M. Felici, P. Contreras-Carballada, Y. Vida, J. M. M. Smits, R. J. M. Nolte, L. De Cola, R. M. Williams and M. C. Feiters, *Chem.-Eur. J.*, 2009, 15, 13124–13134.
- 67 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.
- 68 M. Nonoyama, Bull. Chem. Soc. Jpn., 1974, 47, 767-768.
- 69 A.-R. Hwang, W.-S. Han, K.-R. Wee, H. Y. Kim, D. W. Cho,
  B. K. Min, S. W. Nam, C. Pac and S. O. Kang, *J. Phys. Chem. C*, 2012, **116**, 1973–1986.