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Cationic Iridium Dendrimers: Synthesis and Photophysical Properties

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Two dendrimers, **D1** and **D2**, containing the cationic iridium complexes (**C1** and **C2**) as cores and truxene-functionalized chromophores as the branches, have been developed by a convergent synthetic strategy. The cationic complexes employ 3-(pyridin-2-yl)-1*H*-1,2,4-triazole and 2-(pyridin-2-yl)-benzimidazole derivatives as the ancillary ligands. To avoid the change in emission colour arising from the iridium complex, the conjugation between the dendron and the ligand is decoupled by separating them using the alkyl chain. An investigation of their photoluminescent features reveals that efficient energy transfer happens from the dendrons to the core in the solid state. Likewise, the charged dendritic structure is demonstrated to be an efficient method to improve the compatibility between the polar charged iridium complexes and typical hydrophobic hosts with the additional benefit of excellent solution processability. Both dendrimers exhibit strong solvatochromic behaviours in solvents and exclusive green and yellow-orange light in the solid state.

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Introduction

The development of transition metal complexes has attracted considerable attention because of their potential for applications in organic optoelectronic devices.[1–7] A substantial amount of the earlier work focussed on the development of neutral iridium complexes in the field of optoelectronics, owing to easy purification, and their lack of counterions leading to time delay between bias and light emission in display-related devices. However, cationic iridium complexes also showed unique virtues as the active materials for optoelectronics, such as excellent electrochemical and photochemical properties, good charge-transporting properties, long-lived excited states, and high photoluminescence (PL) efficiency.[8–15] Efforts have recently been devoted to the design and synthesis of cationic iridium(III) complexes with various types of ligands and to gain more understanding of their associated photophysical properties for applications in material science. Indeed, some cationic iridium complexes with a higher volatility and a lack of internal defects exhibited good performance in the fabrication of optoelectronic devices.[16–21] Despite considerable attention towards charged iridium complexes, there are few reports on dendrimers[22] containing cationic iridium complexes, the bulky substituents of which can enhance the steric hindrance of the molecules and suppress the quenching of luminescence effectively.

As most cationic Ir^{III} diimine-containing complexes employ bipyridyl or phenanthroline units as ancillary ligands, the emissive metal–ligand charge transfer (MLCT) excited state limits the utilization of these complexes in light-emitting devices.[23] Some metal complexes[24–26] using 3-(pyridin-2-yl)-1*H*-1,2,4-triazole and 2-(pyridin-2-yl)-benzimidazole derivatives have shown intriguing properties as the active materials for optoelectronics. Moreover, the strong σ-donor property of the triazole, together with the π-accepting ability of the second pyridyl fragment, provides a synergism of the electron delocalization so that the electron density is transferred from triazole to the metal ion and back to the pyridyl side of the ligand, thus enhancing the chelating interaction.[27] So far, very few cationic iridium complexes utilizing these ligands have been developed. Meanwhile, the truxene unit, a heptacyclic polyarene, can act as a desirable building block for larger polyarenes and bowl-shaped fragments of fullerenes, liquid crystals, and C_3 tripod materials, owing to its unique three-dimensional topology and readily available functionality.[28] Notably, Ru-based π-conjugated dendrimers based on truxene units exhibit potential applications as light harvesting materials.[29]

In this contribution, we have developed a new phosphorescent dendrimer system in which cationic phosphorescent acceptors at the core sites are covalently attached to a donor at the peripheral site by a non-conjugated bridge, as shown in Fig. 1. The dendrimers utilize 5-methyl-3-(pyridin-2-yl)-1,2,4-triazole and 2-(pyridin-2-yl)-benzimidazole as the diimine ligands, as well as truxene-based units as the branches. The alkyl linker was introduced to isolate the photophysical properties of both the donor and the acceptor. In this system, the truxene-functionalized donors not only prevent intermolecular self-aggregation but also donate energy to the cationic iridium complexes, which provide us a good model for the upcoming research of intramolecular

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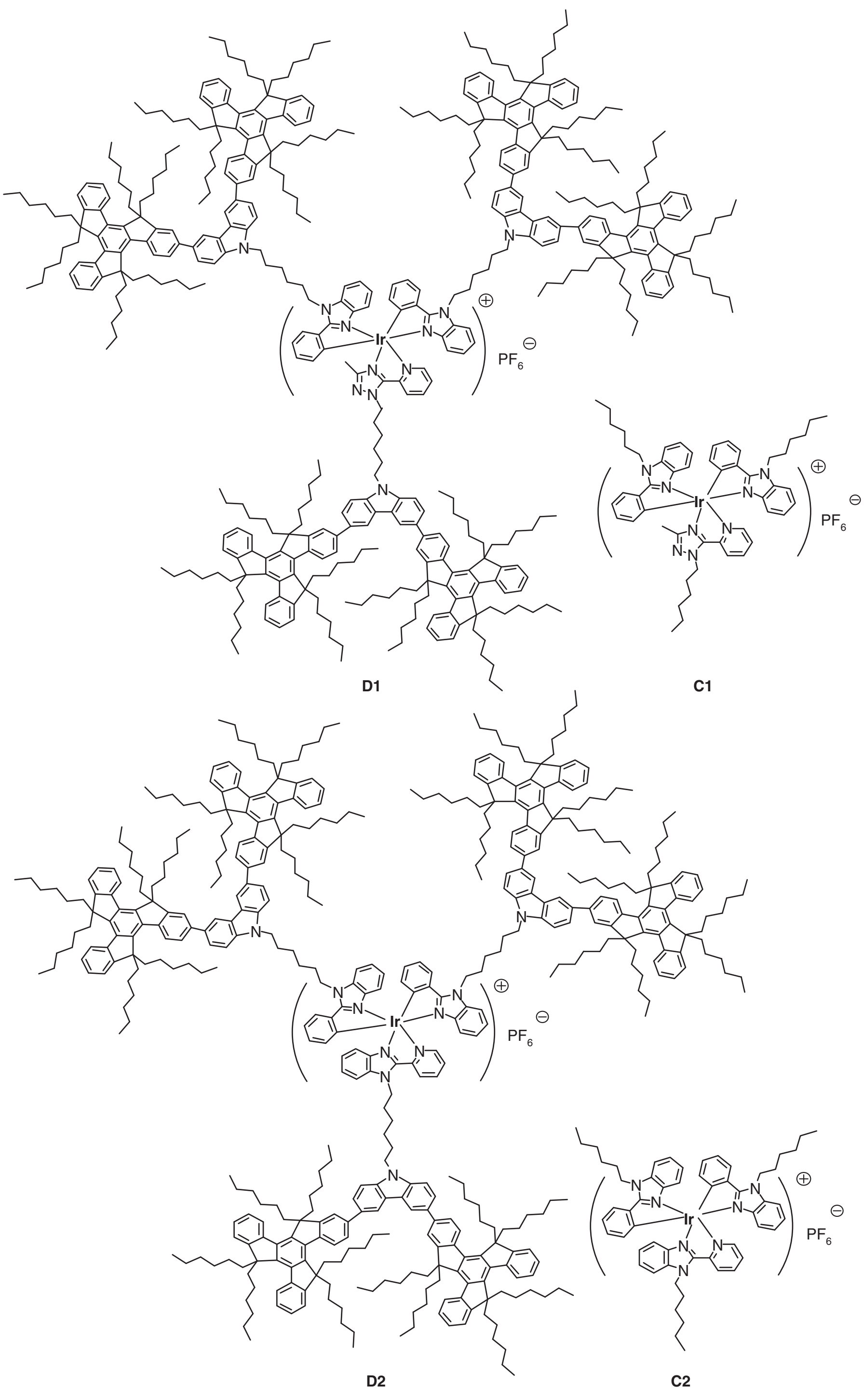


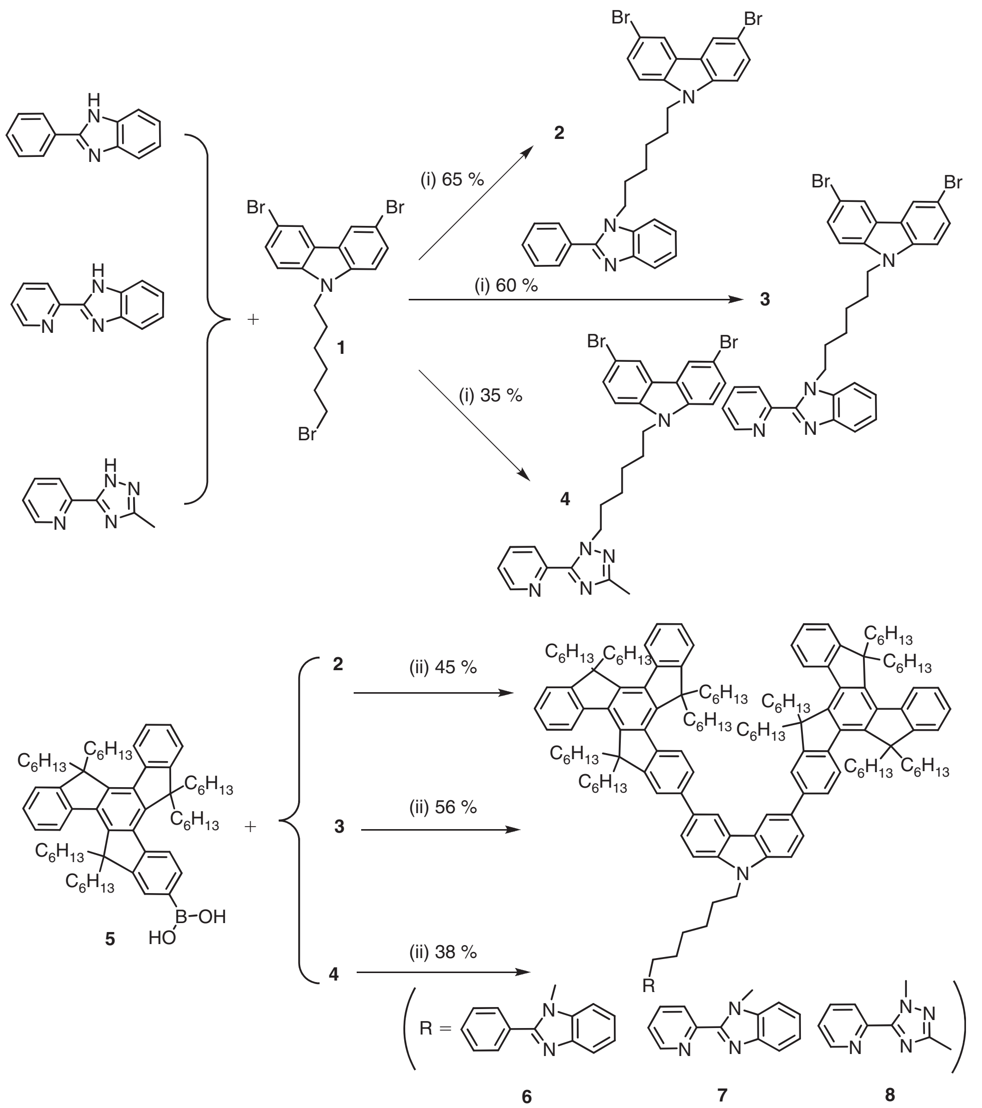
Fig. 1. Chemical structures of cationic Ir dendrimers **D1** and **D2** and complexes **C1** and **C2**.

singlet–singlet (S-S) and triplet–triplet (T-T) energy transfer (ET) mechanisms in addition to the advantages of a typical conjugated dendrimer. Furthermore, Holmes et al.[30] has reported that the triplet energy back transfer, which will reduce the triplet population at the iridium complexes, can be avoided by the incorporation of a spacer between the host and polymer phosphorescent guest to achieve higher efficiencies in electrophosphorescent devices for which the triplet energy levels of the host and guest are similar. It is envisioned that this new family of dendritic architectures will be helpful to further understand the structure–property relationship of charged iridium complexes by investigating their physical and chemical properties.

Results and Discussion

Synthesis and Characterization

The synthetic routes to prepare the target dendrimers **D1** and **D2** and model complexes **C1** and **C2** are presented in Scheme 1. 5-Methyl-3-(pyridin-2-yl)-1*H*-1,2,4-triazole was prepared according to the literature procedure[31] by the reaction between

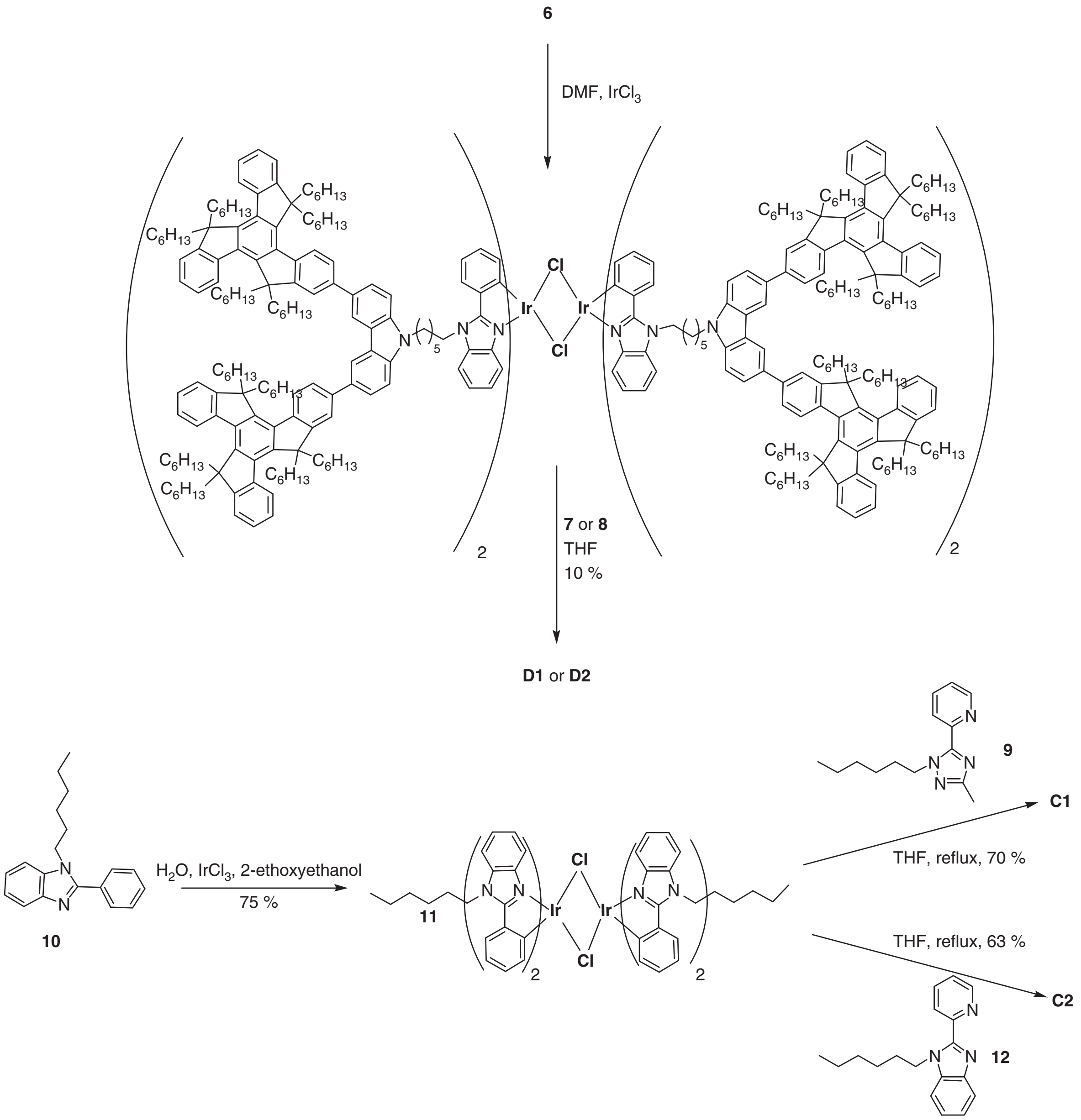


(i) NaOH, DMF, reflux; (ii) $Pd(OAc)_2$, Cy_3P, THF, Na_2CO_3, 80°C

Scheme 1. Synthetic routes to cationic iridium dendrimers **D1** and **D2**, and model complexes **C1** and **C2**.

2-pyridinecarboxamidrazone and acetic anhydride in acetic acid at 0°C with 30 % yield. 3,6-Dibromo-9-(6′-bromohexyl)carbazole[32] (**1**) was obtained through the classical nuleophilic reaction between the 3,6-dibromocarbazole and 1,6-dibromohexane in the presence of sodium hydride in 75 % yield. 2-(2′-Phenyl)-1*H*-benzimidazole, 2-(2′-pyridyl)-1*H*-benzimidazole, or 5-methyl-3-(pyridin-2-yl)-1*H*-1,2,4-triazole can undergo a nuleophilic reation with **1** in the presence of sodium hydroxide as a base to produce **2**, **3**, and **4** in 60, 65, and 35 % yield, respectively. Likewise, oily compounds **9**, **10**, and **12** can be prepared according to the same procedure as used to produce **2**. Monobromo-5,5,10,10,15,15-hexahexyltruxene was lithiated using *n*-BuLi followed by reacting with trimethyl borate and then acidic hydrolysis to afford boronic acid **5** in 56 % yield.[28] Suzuki coupling reaction between **2** and **5** catalyzed by $Pd(OAc)_2$ and Cy_3P afforded **6** as a white solid in 45 % yield. Following the same procedures, we also obtained **7** and **8** in 56 and 38 % yields, respectively.

Cationic iridium dimers **D1** and **D2** were formed from iridium chloride trihydrate using a two-step procedure. Originally, the first step towards the dendritic iridium dimers **D1** and **D2** involved directly heating iridium chloride trihydrate with an excess of the requisite dendritic ligand in a 3 : 1 mixture of 2-methoxyethanol and water. However, we did not obtain the corresponding intermediate iridium dimers using this typical method,[16] owing to the poor solubility of **6** in a highly polar solvent. With a modified approach using DMF as the solvent, the intermediate, denoted $C^\wedge N_2Ir(\mu\text{-}Cl)_2IrC^\wedge N_2$, could be successfully obtained, which was directly used for the next step without further purification. A general preparation of the mixed ligand cationic orthometallated iridium(III) dendrimers **D1** and **D2** was afforded by the bridge-splitting reaction between $C^\wedge N_2Ir(\mu\text{-}Cl)_2IrC^\wedge N_2$ and an excess of ligand **7** or **8** in THF under reflux in argon atmosphere, followed by a counterion exchange process in the presence of a saturated methanolic solution of $NaPF_6$. The charged iridium dendrimers **D1** and **D2** were purified in ~10 % yield by silica column chromatography in two steps to give rise to the air-stable green and yellow-orange solids. The complexes were characterized by ^1H and ^{13}C NMR spectroscopy, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS, and elemental analysis.



Scheme 1. (*Continued*)

Likewise, for comparison, we prepared the corresponding model complexes **C1** and **C2**. The bridged iridium dimer **11** can be produced by the reaction between iridium chloride trihydrate with an excess of ligand **10** in a 3:1 mixture of 2-methoxyethanol and water in high yield. The cationic model **C1** was obtained through the bridge-splitting reaction between **11** and **9** in 70 % yield. C2 was generated using the same procedure to that of C1 with a yield of 63 %.

Successful synthesis of dendrimers **D1** and **D2** could be directly probed by the appearance of the characteristic resonances for the protons assigned to **C1** and **C2**, and through the increased complexity of the aromatic region in the ^{1}H NMR spectra of **D1** and **D2**, as shown in Fig. 2. In comparison with the ^{1}H NMR spectra of **C1** and **C2** some ^{1}H resonances of the Ir complex in the **D1** and **D2** dendrimers, such as the peaks with a red mark in Fig. 2 in the range of 5.5 to 7.2 ppm are undoubtedly assigned to the protons of **C1** and **C2**.

The signals assigned to the molecular ions of **D1** and **D2** in the MALDI-TOF mass spectra also directly verified the presence of the desired dendrimers, as shown in Fig. 3. For **D1**, the clear molecular ion signal peaked at 6554.6 Da (calc.: 6554.7), which corresponds to the signal after loss of one PF_6^- unit. For **D2**, the MALDI-TOF MS signal for the molecular ion exhibited at 6589.6 Da (calc.: 6589.7). Interestingly, both dendrimers **D1** and **D2** showed different behaviours in solubility relative to a dispersion of **C1** and **C2** in the dendrons (**6**, **7**, or **8**). All dendrimers exhibited good solubility in common organic solvents, such as hexane, THF, and dichloromethane, as well as facile film forming properties. However, **C1** and **C2** are insoluble in non-polar solvents. Therefore, the strategy used here for the construction of cationic dendrimers could also be regarded as an efficient solution to improve the compatibility between the polar charged iridium complexes and typical hydrophobic hosts with the additional benefits of excellent

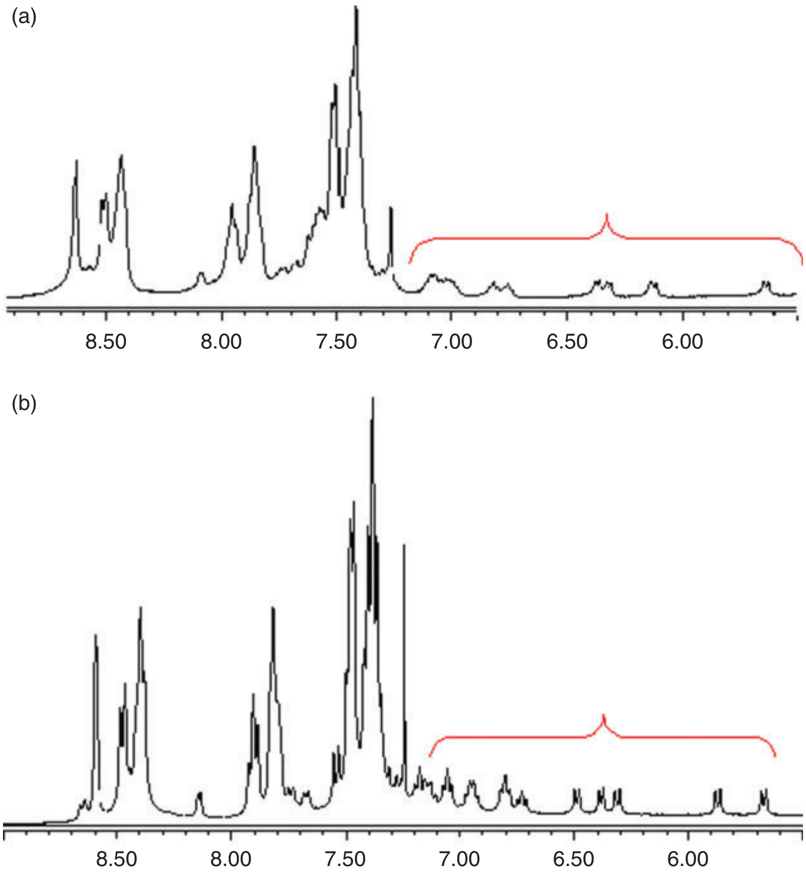


Fig. 2. ^{1}H NMR spectrum of **D1** (a) and **D2** (b).

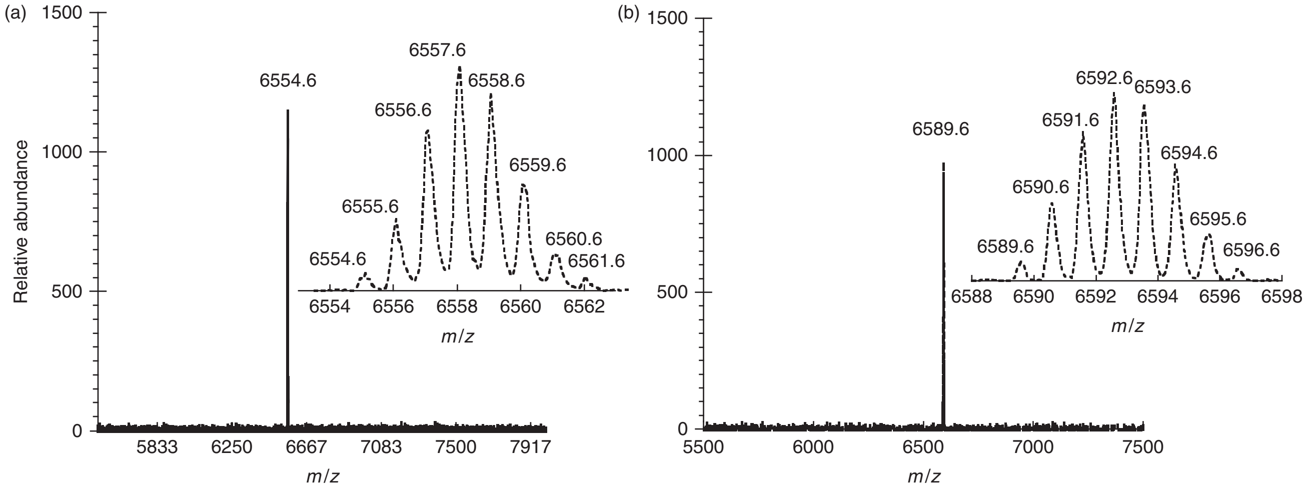


Fig. 3. MALDI-TOF MS spectra of **D1** (a) and **D2** (b).

solution processability in the upcoming application of optoelectronic devices. Thermogravimetric analyses (TGA) indicated that dendrimers **D1** and **D2** had a thermal stability with a decomposition temperature, corresponding to a 5 % weight loss, at 380 and 387°C, respectively.

Optical Properties

The absorption and emission spectra of **D1** and **D2** in solution are shown in Fig. 4. Their absorption features showed broad bands in the range of 300 to 400 nm, which are assigned to both the absorption bands from dendron units and the iridium complexes in the cores. The emission features of **D1** exhibited a emission peak at 399 nm assigned to truxene-functionalized branches, and at 548 nm assigned to the iridium core (**C1**) at room temperature. A strong phosphorescence band ($\lambda_{\max}$: 569 nm) assigned to the acceptor (**C2**) was observed for **D2**, with the donor emission peak at 397 nm. In comparison with the phosphorescence of **D1**, **D2** exhibited a relatively red-shifted luminescence, which should be ascribed to the different auxiliary ligand. As expected, this donor–acceptor system did not

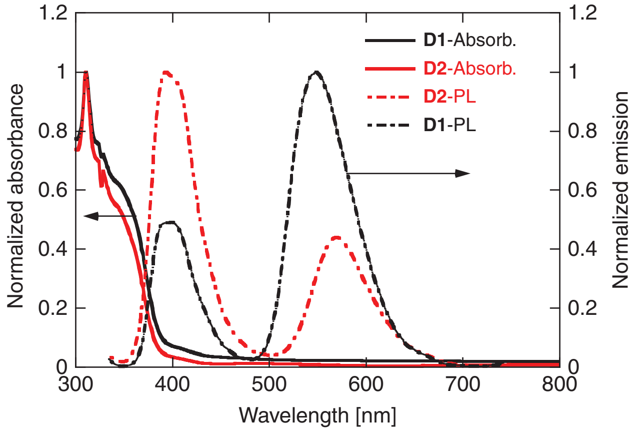


Fig. 4. The absorption and emission spectra of **D1** and **D2** in dichloromethane at 298 K, with the excitation wavelength of 310 nm.

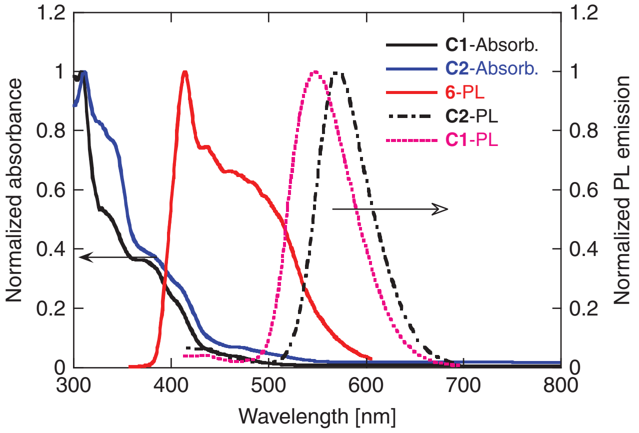


Fig. 5. The absorption and emission of complexes **C1**, **C2**, and **6** in the solid state.

exhibit a good ET from the donor to the acceptor by both the S-S and the T-T ET mechanisms and the strong remaining emission arising from donors can be observed in solution, because of the absence of conjugation and long distance between donors and acceptors.

The steady state photophysical properties of **6**, **C1**, and **C2** in a thin film were investigated at room temperature. As shown in Fig. 5, compound **6** showed the PL features of the functionalized truxene unit with a maximum emission peak at 410 nm. The absorption spectra of **C1** and **C2** showed two distinct absorption bands ranging from 320 to 425 nm. With reference to the previous work[14] on $\mathrm{Ir^{III}}$ complexes, the intense absorptions at 260–350 nm most likely originate from phenyl- and pyridyl-based ligand-centred π–π^* transitions. The absorption band at 350–450 nm was identified as the MLCT transitions from the d_π orbital of the Ir-metal centre to the unoccupied π^* orbital of ligands, mixed with some intra-ligand charge transfer transition from ligands. None of the complexes absorbed significantly at wavelengths longer than 500 nm. Importantly, the absorption features of **C1** and **C2** over 375 nm (^{1}MLCT and ^{3}LC region) had a large overlap with the emission band of compound **6**, which ensured the energy transfer from the branches to the cores (**C1** and **C2**) in the solid state. The emission energy of **C2** is lower than that of **C1** in the solid state, with a red-shift of around 26 nm, which was attributed to the lower energy of the benzimidazole acceptor orbital compared with that of 1,2,4-triazole. Thus, it is possible to control the energy of the lowest excited state by deliberately adjusting the energy of the metal and ligand orbital, which can be achieved by changing the ligand parent structure entirely (e.g., 1,2,4-triazole versus benzimidazole).[14]

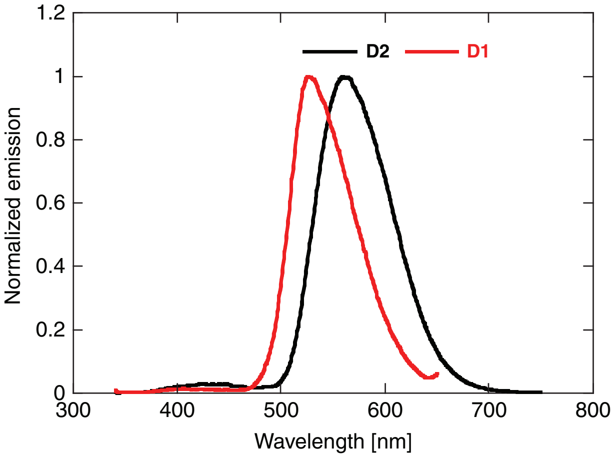


Fig. 6. The emission spectra of both dendrimers **D1** and **D2** in the solid state.

As observed from the emission features of **D1** and **D2**, the blue-light emission from the truxene-functionalized dendrons was almost completely quenched after excitation at the absorption maximum of the branches, with emission peaks at only 526 and 560 nm, indicating the very effective energy transfer from the truxene-based branches to the emissive cationic iridium complexes in the solid state, as shown in Fig. 6. The phosphorescent emission spectrum of **D1** and **D2** blue-shifted (~19 and 11 nm) relative to the emission of the parent complexes **C1** and **C2** (545 nm for **C1** and 571 nm for **C2**) in the solid state, respectively, because of the decreased intermolecular interactions of the iridium cores, attributable to such large sizes of the dendrons with multiple hexyl substituents and truxene moieties. Therefore, it would be expected that the presence of giant truxene-functionalized branches probably can hinder a close overlapping among emissive metal cores, thus decreasing the possibility of non-radiative intermolecular carrier recombination as a result of steric hindrance and rendering the iridium complexes more hydrophobic to reduce the degradation of devices as a consequence of a reaction with water which usually leads to EL quenching of light-emitting electrochemical cells[30] based on cationic transition metal complexes in our upcoming investigation of optoelectronic devices.

The reason for the complete ET in the film as opposed to in solution may be attributable to the shorter distance for the intermolecular ET between the donor and the acceptor, as well as a less flexible film phase structure, which leads to reduced non-radiative decay.[33]

The phosphorescence spectra of both **D1** and **D2** were observed to be dependent on solvent polarity. In the case of **D1**, the wavelength of the emission peak was red-shifted by 48 nm by changing the solvent from hexane (520 nm) to toluene (568 nm), as shown in Table 1 and Fig. 7a. Likewise, a remarkably large red-shifted emission was observed for the phosphorescence of **D2**. Since the absorption band of the cationic iridium cores (**C1** and **C2**) has an significant overlap with that of the truxene-functionalized branches in the range of 280 to 400 nm, it

Table 1. Solvatochromic behaviour of dendrimers

Solvent	λ_{max} emission [nm]	
	Core of **D1**	Core of **D2**
Hexane	520	545
Toluene	568	575
DCM	548	569
THF	552	573
Methanol/DCM (4/1)	539	571

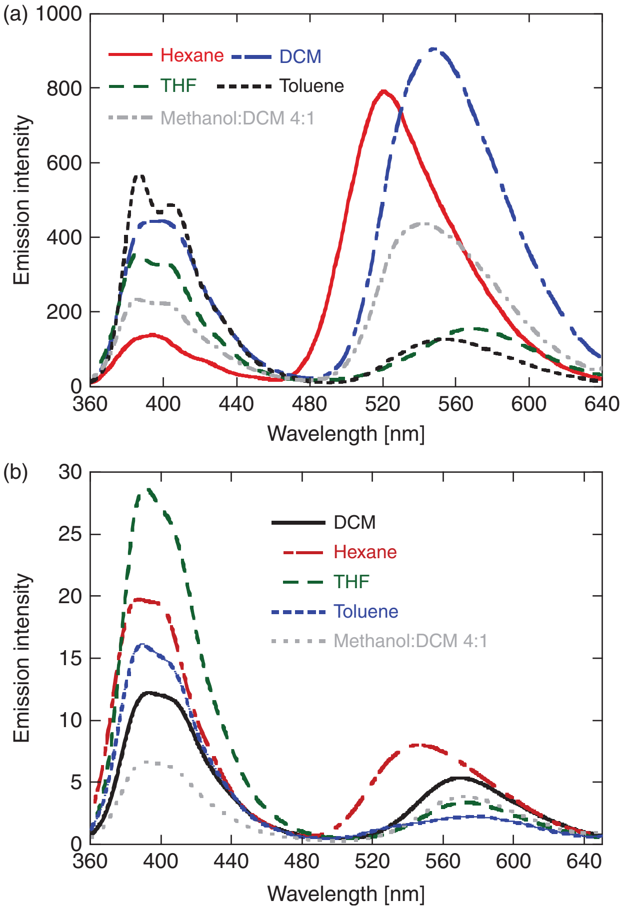


Fig. 7. The photoluminescence spectra of **D1** (M) (a) and **D2** (1×10^{-6} M) (b) in different solutions. The emission spectra were obtained with an excitation wavelength of 310 nm.

is difficult to determine the red-shifted change of the absorption spectra of **D1** and **D2**. In addition, because **C1** and **C2** are totally insoluble in hexane and toluene, the absorption spectra for **C1** and **C2** alone in these solvent are unavailable. Based on the above, we cannot investigate the phosphorescence change of **C1** and **C2** in different solvents.

According to the literature,[34] the large red-shifted phosphorescence observed for **D1** and **D2** should probably be assigned to a large change in the dipolar vector of the T_1 state. The solvent dipolar relaxation takes place during the T_1–S_0 transition, leading to an obvious phosphorescence solvatochromism. This viewpoint can be supported by the previous solvatochromism studies of osmium(II) complexes, $[Ru(CN)_4(bpy)]$ and $[W(CO)_4(bpy)]$ (bpy = 2,2′-bipyridine),[35–37] which are the most significant solvatochromic MLCT emissive systems. In these systems, the phosphorescence is not only sensitive to solvent polarity, but also to other factors such as temperature and concentration.

Conclusion

In conclusion, two cationic iridium dendrimers (**D1** and **D2**) built from functionalized-truxene have been synthesized in a convergent strategy. PL results revealed that energy could be transferred efficiently from the dendrons to the core in the solid state. The dendrimers exhibited strong phosphorescence solvatochromism in different solvents. Evidence showed that the dendritic structure could be regarded as an efficient solution to improve the compatibility between the polar charged iridium complexes and typical hydrophobic hosts with the additional benefits of excellent solution processability. Further investigation of the optical properties of the dendrimers, such as electrophosphorescence, are still in progress.

Experimental

General Methods

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury plus 300 MHz and Bruker ARX-400 (400 MHz) spectrometers using $CDCl_3$ as solvent. All chemical shifts were reported in parts per million (ppm), ^{1}H NMR chemical shifts were referenced to TMS (0 ppm) or $CHCl_3$ (7.26 ppm), and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.00 ppm). Cz: carbazole, Tr: truxene, Ir: iridium complex, Ar: phenyl. Absorption spectra were recorded on a Perkin–Elmer Lambda 705UV-vis Spectrometer. PL spectra were carried out on Perkin–Elmer LS55 Luminescence Spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III TOF mass spectrometer (Bruker Daltonics, Billerica, MA, USA) using a 337 nm nitrogen laser with dithranol as matrix. Elemental analyses were carried out on an Elementar Vario EL (Germany).

Synthesis

Chemicals were purchased and used as received. All air and water sensitive reactions were performed under a nitrogen atmosphere. Tetrahydrofuran was distilled over sodium. Compounds **3**, **4**, and **5** were prepared according to the previous literature procedures.[31]

Compound **2**

A mixture of 3,6-dibromo-9-(6′bromohexyl)-carbazole (4.88 g, 10 mmol), 2-(2′-phenyl)-benzimidazole (1.95 g, 10 mmol), sodium hydroxide (0.44 g, 11 mmol), and DMSO (30 mL) were heated at 130°C for 24 h under an argon atmosphere. After the reaction was cooled to room temperature, the mixture was poured into ice water (100 mL). The mixture was extrated with chloroform and the organic layer was washed with water and brine, and dried over anhydrous $MgSO_4$. After removal of the solvents under reduced pressure, the residue was purified by silica gel column chromatography using pentane/ethyl acetate, 2/1, as eluent to give **2** as a white solid (3.90 g, 65 %). δ_H 8.13–8.12 (2H, d, J 2.1, Cz-H), 7.85–7.82 (1H, m, Ar-H), 7.69–7.66 (2H, m, Ar-H), 7.55–7.48 (5H, m, Cz-H and Ar-H), 7.42–7.30 (3H, m, Ar-H), 7.27–7.15 (2H, m, Cz-H), 4.21–4.10 (4H, m, N-CH_2), 1.78–1.71 (4H, m, CH_2), 1.18–1.16 (4H, m, CH_2). δ_C 153.5, 142.9, 138.9, 135.3, 130.5, 129.6, 129.1, 128.8, 128.6, 123.2, 123.0, 122.6, 122.3, 119.8, 111.8, 110.1, 109.9, 44.1, 43.6, 29.1, 28.3, 26.3, 26.0. m/z (ESI) Calc. for $C_{31}H_{27}Br_2N_3$: 599.06. Found: 600.08 [M^+].

*Compound **6***

To a solution of **2** (1.25 g, 2.0 mmol) and boronic acid **5** (5.34 g, 6.0 mmol) in toluene (20 mL), was added $Pd(OAc)_2$ (1.0 mol-%), Cy_3P (2.0 mol-%), and 2 M aqueous KOH solution (12 mL). The mixture was degassed and stirred at 90°C for 24 h, and the mixture was poured into a saturated solution of NH_4Cl and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. After removal of the solvents under reduced pressure, the residue was purified by column chromatography using pentane/ethyl acetate (4/1) as eluent to give **6** as a white solid (1.90 g, 45 %). δ_H 8.60–8.58 (2H, m, Cz-H), 8.50–8.40 (6H, m, Tr-H), 7.90–7.72 (11H, m, Ar-H, Cz-H and Tr-H), 7.55–7.25 (18H, m, Ar-H and Tr-H), 4.37–4.24 (4H, m, N-CH_2), 3.04–3.01 (12H, m, CH_2), 2.26–2.09 (12H, m, CH_2), 1.91–1.82 (4H, m, CH_2), 1.39–1.28 (4H, m, CH_2), 0.63–0.53 (132H, m, CH_2 and CH_3). δ_C 154.4, 153.5, 153.1, 144.9, 144.6, 140.4, 140.3, 139.7, 138.9, 138.3, 138.0, 134.9, 132.7, 130.1, 129.3, 128.8, 126.2, 125.9, 125.4, 125.1, 124.9. 124.6, 123.6, 123.1, 122.9, 122.1, 120.6, 119.6, 118.9, 110.1, 108.9, 55.7, 55.5, 44.5, 36.9, 36.9, 31.5, 31.4, 29.5, 29.4, 28.9, 26.7, 26.4, 23.9, 23.8, 22.2, 13.8, 13.8. *m/z* (ESI) Calc. for $C_{157}H_{205}N_3$: 2132.61. Found: 2133.60 [M^+]. Anal. Calc. for $C_{157}H_{205}N_3$: C 88.35, H 9.68, N 1.97. Found: C 88.59, H 9.37, N 1.89 %.

*Compound **7***

This compound was prepared by the same procedure as used to produce **6** albeit using compound **3** in place of **2**. Yield: 56 %. δ_H 8.64–8.59 (3H, m, Cz-H and Py-H), 8.53–8.45 (7H, m, Py-H and Tr-H), 7.96–7.57 (8H, m, Cz-H, Py-H and Tr-H), 7.42–7.25 (18H, m, Ar-H and Tr-H), 4.91–4.88 (2H, m, N–CH_2), 4.50–4.44 (2H, m, N–CH_2), 3.04–3.01 (12H, m, –CH_2), 2.24–198 (12H, m, CH_2), 1.91–1.82 (4H, m, CH_2), 1.39–1.28 (4H, m, CH_2), 0.63–0.53 (132H, m). δ_C 154.4, 153.6, 150.7, 149.8, 148.6, 145.0, 144.7, 142.7, 140.4, 139.9, 138.9, 138.4, 136.7, 136.6, 132.8, 126.3, 125.9, 125.4, 125.2, 124.9, 124.6, 123.7, 123.3, 122.5, 122.2, 120.7, 120.1, 118.9, 115.8, 110.1, 109.1, 55.8, 55.6, 45.3, 43.2, 36.9, 31.5, 29.9, 29.5, 29.0, 26.9, 26.7, 24.0, 22.8, 13.9. *m/z* (ESI) Calc. for $C_{157}H_{205}N_4$: 2133.61. Found: 2134.63 [M^+]. Anal. Calc. for $C_{156}H_{204}N_4$: C 87.75, H 9.63, N 2.62. Found: C 87.92, H 9.49, N 2.66 %.

*Compound **8***

This compound was prepared by the same procedure as used to produce **6** albeit using compound **4** in place of **2**. Yield: 38 %. δ_H 8.60–8.58(2H, m, Cz-H), 8.49–8.41 (7H, m, Py-H and Tr-H), 8.20–8.18 (1H, m, Py-H), 7.93–7.78 (9H, m, Py-H, Cz-H and Tr-H), 7.55–7.40 (13H, m, Tr-H and Py-H), 4.76–4.21 (4H, m, N–CH_2), 3.04–3.01 (12H, m, CH_2), 2.40 (3H, s, CH_3), 2.12–1.93 (12H, m, CH_2), 1.66–0.61 (140H, m). δ_C 159.3, 154.4, 153.6, 151.6, 148.9, 148.0, 145.0, 144.7, 140.4, 139.9, 138.9, 138.4, 138.2, 136.9, 132.7, 126.3, 125.4, 125.2, 124.9, 124.6, 123.9, 123.7, 122.2, 120.6, 118.9, 109.1, 55.8, 55.6, 50.4, 43.2, 36.9, 31.5, 30.0, 29.5, 29.5, 29.0, 26.9, 26.3, 23.9, 22.3, 13.9, 13.9. *m/z* (ESI) Calc. for $C_{152}H_{203}N_5$: 2098.60. Found: 2099.60 [M^+]. Anal. Calc. for $C_{152}H_{203}N_5$: C 86.92, H 9.74, N 3.33. Found: C 87.25, H 9.82, N 3.29 %.

*Compound **9***

A mixture of 1-bromohexane (2.46 g, 15 mmol) and 2-(5-methyl-1*H*-[1,2,4-triazol]-3-yl)-pyridine (1.60 g, 10 mmol), sodium hydroxide (0.44 g, 11 mmol), and anhydrous DMSO (30 mL) were heated at 130°C for 24 h under an argon atomsphere. The reaction was then cooled to room temperature and the mixture was subsequently poured into ice water (100 mL). The mixture was extracted with chloroform, and the organic layer was washed with water and brine, and dried with anhydrous Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by silica gel column chromatography using pentane/ethyl aceate (10/1) to afford 2-(1-hexyl-5-methyl-[1,2,4-triazol]-3-yl)-pyridine (**9**) as an oily product (0.98 g, 40 %). δ_H 8.66–8.64 (1H, m, Py-H), 8.17–8.13 (1H, m, Py-H), 7.84–7.78 (1H, m, Py-H), 7.34–7.30 (1H, m, Py-H), 4.75–4.70 (2H, t, J_1 7.5, N–CH_2), 2.40 (3H, s, CH_3), 1.85–0.85 (11H, m, CH_2 and CH_3).

*Compound **10***

1-Bromohexane (2.46 g, 15 mmol) and 2-(2′-phenyl)-benzimidazole (1.95 g, 10 mmol), and sodium hydroxide (0.44 g, 11 mmol), were dissolved in anhydrous DMSO (30 mL) and were heated at 130°C overnight under an argon atomsphere. After cooling to room temperature the mixture was poured into ice water (100 mL). The mixture was extracted with chloroform, the organic layer was washed with water and brine, and dried with anhydrous Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by silica gel column chromatography using pentane/ethyl aceate (20/1) to afford **10** as an oily product (2.1 g, 75 %). δ_H 7.84–7.81 (1H, m, Ar-H), 7.71–7.69 (2H, m Ar-H), 7.52–7.51 (2H, m, Ar-H), 7.42–7.40 (1H, m, Ar-H), 7.32–7.10 (3H, m, Ar-H), 4.25–4.20 (2H, t, J_1 8.4, J_2 6.9, N–CH_2), 1.89–0.83 (11H, m, CH_2 and CH_3).

*Tetrakis(1-hexyl-2-phenylbenzimidazole N,C2′) (μ-chlorobridged) Diiridium (**11**)*

Iridium trichloride hydrate (1.318 g, 3.8 mmol) and **10** (2.6 g, 9.4 mmol) were dissolved in a mixture of 2-ethoxyethanol and water (3:1, 20 mL), and the mixture was refluxed for 24 h under argon atomsphere. The mixture was allowed to cool to room temperature, and the yellow precipitate was collected on a glass filter. The precipitate was washed with ethanol and ethyl ether to obtain a yellow power (2.7 g, 75 %), which was used directly for the next step without purification.

*Complex **C1***

In a round-bottomed flask, complex **11** (1.0 g, 0.64 mmol) and compound **9** (0.32 g, 1.3 mmol) were mixed together in THF (25 mL) and the mixture was refluxed overnight under an argon atmosphere. After cooling to room temperature, excessive $NaPF_6$ in methanol was added dropwise and the mixture was stirred for an additional 4 h. After the counterion exchange from Cl^- to PF_6^- was accomplished, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL), filtered, and precipitated in hexane. The product was purified by recrystallization using ethanol as solvent (0.88 g, 70 %). δ_H 8.46–8.38 (2H, m), 8.07–8.06 (1H, d, *J* 4.8), 7.70–7.76 (2H, m), 7.51–7.25 (5H, m), 7.10–6.83 (4H, m), 6.80–6.72 (2H, m), 6.32–6.28 (2H, m), 6.11–6.08 (1H, m), 5.59–5.56 (1H, m), 4.75–4.64 (6H, m), 2.02–1.89 (5H, m), 1.70 (3H, s), 1.48–1.19 (16H, m), 0.90–0.77 (8H, m). δ_C 162.5, 159.9, 155.5, 152.3, 151.7, 149.1, 145.3, 140.5, 139.1, 138.8, 135.2, 135.1, 133.8, 133.3, 130.6, 130.0, 128.1, 124.9, 124.6, 124.5, 124.3, 123.6, 123.5, 122.5, 122.16, 113.7, 113.6, 110.9, 110.7, 52.2, 45.0, 31.3, 31.1, 29.6, 29.5, 29.3, 26.3, 25.7, 22.3, 22.3, 13.9, 12.5. *m/z* (ESI) Calc. for $[M - PF_6^-]^+$: 991.4. Found: 991.5.

*Complex **C2***

The procedure followed was the same as for the synthesis of **C1** albeit using compound **12** in place of **9** (yield: 63 %). δ_H 8.54–8.51 (d, 1H, *J* 8.4), 8.38–8.33 (m, 1H), 8.17–8.15 (d, 1H, *J* 5.4), 7.80–7.55 (m, 2H), 7.51–7.43 (m, 5H), 7.26–6.95 (m, 6H), 6.90–6.72 (m, 2H), 6.48–6.28 (m, 3H), 5.91–5.88 (d, 1H, *J* 8.1), 5.68–5.65 (d, 1H, *J* 8.4), 4.82–4.57 (m, 6H), 2.07–1.86 (m, 6H), 1.49–0.72 (m, 27H); δ_C 162.6, 162.5, 153.4, 152.4, 151.9, 149.5, 148.1, 140.1, 139.9, 139.0, 138.7, 136.1, 135.1, 135.0, 134.5, 134.3, 133.9, 133.6, 130.4, 129.7, 127.5, 125.9, 125.1, 124.9, 124.6, 124.6, 124.1, 123.9, 123.4, 123.2, 122.3, 122.1, 118.5, 114.3, 113.6, 111.4, 110.6, 45.8, 44.9, 44.7, 31.3, 31.2, 31.2, 29.8, 29.5, 29.4, 26.3, 26.2, 26.0, 22.4, 22.3, 22.2, 13.9, 13.8, 13.8. *m*/*z* (ESI) Calc. for $[M - PF_6^-]^+$: 1026.5. Found: 1026.5.

*Dendrimer **D1***

A mixture of **6** (5.7 g, 2.47 mmol), iridium chloride trihydrate (174 mg, 0.50 mmol), and DMF (13 mL) was heated (bath temperature: 130°C) under argon for 48 h. After the reaction was cooled to room temperature, the mixture was extracted with dichloromethane and washed with water and brine. The organic layer was dried over $MgSO_4$. After removal of the solvents under reduced pressure, the residue was filtered through a short silica column using pentane as eluent to give $C^\wedge N_2Ir(\mu\text{-}Cl)_2IrC^\wedge N_2$ as a yellow solid powder . The chloro-bridged iridium dimer $C^\wedge N_2Ir(\mu\text{-}Cl)_2IrC^\wedge N_2$ was used for the next step without further purification. A mixture of $C^\wedge N_2Ir(\mu\text{-}Cl)_2IrC^\wedge N_2$ (1.3 g, 0.15 mmol) and compound **7** (1.0 g, 0.47 mmol) was heated in THF at 75°C under an argon atmosphere for 3 days. After cooling to room temperature, excess $NaPF_6$ in methanol was added dropwise and the mixture was stirred for an additional 4 h. After the counterion exchange from Cl^- to PF_6^- was accomplished, the solvent was removed under reduced pressure and the mixture was extracted with chloroform. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The product was purified by silica gel column chromatography using petroleum ether and ethyl acetate (20:1) as eluents (yield: 10 %) in two steps.

δ_H 8.60–8.58 (6H, m, Cz-H), 8.63–8.43 (20H, m, Ir-H and Tr-H), 8.10–8.07 (1H, m, Ir-H), 7.95–7.72 (24H, m, Cz-H and Tr-H), 7.72–7.70 (2H, m, Ir-H) 7.50–7.26 (41H, m, Tr-H and Ir-H), 7.07–7.02 (4H, m, Ir-H), 6.81–6.75 (2H, m, Ir-H), 6.38–6.32 (2H, m, Ir-H), 6.13–6.11 (1H, d, *J* 8.0 , Ir-H), 5.64–5.62 (1H, d, *J* 8.1, Ir-H), 4.77–4.38 (12H, m, N-CH_2), 3.01–2.99 (36H, m, CH_2), 2.22–2.04 (36H, m, CH_2), 1.70 (3H, s, CH_3), 1.56–0.53 (420H, m, CH_2 and CH_3). δ_C 162.7, 162.5, 154.4, 153.8, 153.7, 153.6, 152.3, 149.7, 148.1, 145.0, 144.9, 144.8, 144.7, 144.6, 140.5, 140.4, 140.3, 139.9, 139.8, 139.7, 139.1, 139.0, 138.9, 138.8, 138.4, 138.3, 138.2, 138.1, 138.0, 136.0, 134.9, 134.8, 134.5, 133.9, 133.7, 132.6, 130.9, 130.6, 129.8, 128.8, 127.5, 126.3, 125.9, 125.5, 125.2, 124.9, 124.6, 123.7, 123.6, 122.2, 120.6, 119.0, 118.8, 114.5, 113.9, 111.5, 110.4, 109.3, 109.0, 55.8, 55.6, 37.1, 37.0, 36.9, 31.6, 31.5, 29.7, 29.6, 29.5, 24.0, 23.9, 22.3, 14.0, 13.9, 13.8. *m*/*z* (MALDI-TOF) Calc. for $C_{466}H_{611}IrN_{11}$ $[M - PF_6^-]^+$: 6554.7. Found $[M - PF_6^-]^+$: 6554.6. Anal. Calc. for $C_{466}H_{611}F_6IrN_{11}P$: C 83.49, H 9.19, N 2.30. Found: C 83.72, H 9.53, N 2.48 %.

*Dendrimer **D2***

This dendirmer was prepared by the same procedure as used to produce **D1** albeit using compound **8** in place of **7** in the second step δ_H 8.68–8.68 (1H, m, Ir-H), 8.61–8.58 (6H, m, Cz-H), 8.50–8.39 (19H, m, Tr-H and Ir-H), 8.18–8.16 (1H, d, *J* 5.1, Ir-H), 7.95–7.83 (18H, m, Cz-H and Tr-H), 7.77–7.75 (1H, d, *J* 8.3, Ir-H), 7.70–7.68 (1H, d, *J* 7.7, Ir-H), 7.57–7.29 (39H, m, Tr-H and Ir-H), 7.19–7.14 (4H, m, Ir-H), 7.09–7.07 (2H, m, Ir-H), 6.97–6.95 (2H, m, Ir-H), 6.82–6.75 (3H, m, Ir-H), 6.51–6.50 (1H, d, *J* 7.6, Ir-H), 6.41–6.39 (1H, d, *J* 7.5, Ir-H), 6.34–6.32 (1H, d, *J* 8.4, Ir-H), 5.90–5.87 (1H, d, *J* 8.2, Ir-H), 5.70–5.67 (1H, d, *J* 8.3, Ir-H), 4.86–4.32 (12H, m, N-CH_2), 3.04–3.02 (36H, m, CH_2), 2.22–2.20 (36H, m, CH_2), 2.07–0.57 (420H, m, CH_2 and CH_3). δ_C 162.5, 160.0, 155.7, 154.5, 153.7, 153.6, 152.2, 151.9, 149.3, 145.3, 145.1, 145.0, 144.8, 144.7, 140.5, 140.4, 140.0, 139.8, 139.2, 139.1, 138.8, 138.4, 138.2, 138.1, 135.1, 134.9, 134.1, 133.8, 133.4, 133.0, 132.6, 130.7, 130.1, 128.2, 126.4, 126.0, 125.5, 125.2, 124.9, 124.6, 123.7, 123.6, 122.6, 122.2, 120.7, 119.0, 118.8, 113.9, 113.8, 110.7, 110.5, 109. 3, 109.0, 55.8, 55.6, 52.2, 44.8, 43.2, 37.1, 31.9, 31.6, 31.5, 29.7, 29.6, 29.5, 29.2, 28.9, 27.2, 26.8, 25.9, 25.5, 23.9, 23.8, 22.7, 22.3, 22.1, 14.1, 13.9, 13.8, 13.8, 13.7, 12.6. *m*/*z* (MALDI-TOF) Calc. for $C_{470}H_{612}IrN_{10}$: $[M - PF_6^-]^+$: 6589.7. Found $[M - PF_6^-]^+$:6589.6. Anal. Calc. for $C_{470}H_{612}F_6IrN_{10}P \cdot 2H_2O$: C 83.32, H 9.16, N 2.07. Found: C 83.49, H 9.51, N 2.32 %.

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