

Solution-Processible Conjugated Electrophosphorescent Polymers

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Abstract: We report the synthesis and photophysical study of a series of solution-processible phosphorescent iridium complexes. These comprise bis-cyclometalated iridium units [Ir(*ppy*)₂(*acac*)] or [Ir(*btp*)₂(*acac*)] where *ppy* is 2-phenylpyridinato, *btp* is 2-(2'-benzo[*b*]thienyl)pyridinato, and *acac* is acetylacetonate. The iridium units are covalently attached to and in conjugation with oligo(9,9-dioctylfluorenyl-2,7-diyl) [(FO)_{*n*}] to form complexes [Ir(*ppy*-(FO)_{*n*})₂(*acac*)] or [Ir(*btp*-(FO)_{*n*})₂(*acac*)], where the number of fluorene units, *n*, is 1, 2, 3, ~10, ~20, ~30, or ~40. All the complexes exhibit emission from a mixed triplet state in both photoluminescence and electroluminescence, with efficient quenching of the fluorene singlet emission. Short-chain complexes, **11–13**, [Ir(*ppy*-(FO)_{*n*}-FH)₂(*acac*)] where *n* = 0, 1, or 2, show green light emission, red-shifted through the FO attachment by about 70 meV, but for longer chains there is quenching because of the lower energy triplet state associated with polyfluorene. In contrast, polymer complexes **18–21** [Ir(*btp*-(FO)_{*n*})₂(*acac*)] where *n* is 5–40 have better triplet energy level matching and can be used to provide efficient red phosphorescent polymer light-emitting diodes, with a red shift due to the fluorene attachment of about 50 meV. We contrast this small (50–70 meV) and short-range modification of the triplet energies through extended conjugation, with the much more substantial evolution of the π–π* singlet transitions, which saturate at about *n* = 10. These covalently bound materials show improvements in efficiency over simple blends and will form the basis of future investigations into energy-transfer processes occurring in light-emitting diodes.

Introduction

The discovery of electroluminescence from conjugated polymers has led to the development of and intense interest in the field of polymer optoelectronics.^{1–3} The chemical synthesis, photophysics, and material properties are of interest not only as an academic curiosity but also as a commercial reality. Luminescent conjugated polymers show real promise as the active material in light-emitting display devices for the next generation of information technology based consumer products. The principle interest in the use of these polymers lies in the scope for low-cost, large surface area manufacturing, facilitated by solution-processing of film-forming materials.⁴ The widespread commercialization of light-emitting polymers is dependent on improving device efficiencies; this can be achieved both by improvements in device engineering and by insights into their fundamental chemistry and physics enabling design of intrinsically more efficient materials.

In light-emitting diodes (LEDs), electrons and holes are injected from opposite electrodes and combine to form spin-singlet or spin-triplet excitons. Radiative decay from the singlets is fast (fluorescence) whereas that from the triplets (phosphorescence) is formally forbidden by the requirement of spin conservation. The inclusion of heavy metal atoms in the molecular structure can give strong spin–orbit coupling which renders phosphorescence partially allowed. Models of spin statistics predict that the electron–hole recombination event should produce three times as many triplets as singlets,⁵ and this has been confirmed experimentally for electroluminescent devices (OLEDs) fabricated from small molecules.⁶ For polymers, there is growing evidence that the triplet–singlet ratio can be as low as 1:1^{7,8} and recent work on polyacetylenes containing heavy metal atoms incorporated into the backbone has enabled a detailed study of singlet and triplet excited states.^{9–12}

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The energy of the non emissive triplet state in organic compounds can be harvested by energy transfer to a phosphorescent dopant such as a lanthanide or heavy metal organometallic complex. As early as 1990, Kido and colleagues described an OLED employing [Tb(*acac*)₃] as the phosphor and giving green light emission,¹³ and Wittmann, et al.⁹ proposed the use of platinum-containing poly-ynes both as semiconductor and as triplet emitter. In 1998, Thompson and Forrest and their co-workers published a seminal paper describing the use of platinum(II) porphyrins (PtOEP) as the phosphor in an OLED and were able to obtain higher efficiency red-light emission than had proved possible with lanthanide dopants.^{14,15} Energy-transfer processes and the sites of electron–hole recombination in blends of PtOEP in conjugated polymer hosts have been studied in some detail by the Cambridge^{16–18} and Sheffield^{19,20} groups. More recently, Thompson and Forrest and colleagues demonstrated spectacular enhancements in OLED efficiencies, with external quantum efficiencies as high as 19%, using Ir(III) cyclometalated complexes as blends in host luminescent materials.^{21–29} However, the processing of such materials can be complex and costly, often requiring deposition under high vacuum and controlled temperature, and the use of multiple layers.

Spin-coatable solutions of well-defined amorphous iridium complexes blended in polycarbazole and poly(phenylenevinylene) hosts were described by Bazan and Heeger,³⁰ with the ultimate production of efficient, but multilayer devices.^{31,32} Considerable attention has been focused on blending of phos-

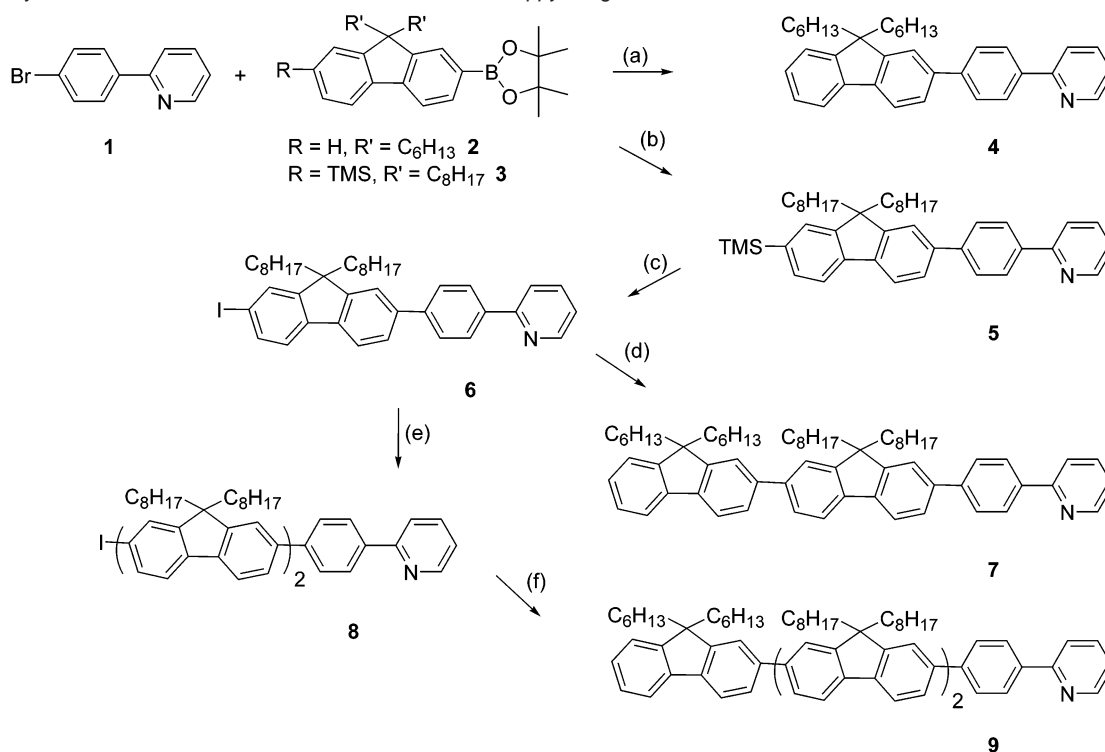
phors into conjugated polymer hosts and the fabrication of LEDs using these composite materials; however, the improvements in device efficiency have been modest.^{16–20,33–40} It has been proposed that energy is lost by transfer to low-lying triplet states in the polymer host⁴¹ or by triplet–triplet annihilation; under such conditions, the efficiency is limited by phase separation and aggregation of dopants even at low-blending concentrations. It is recognized that this could be suppressed when the phosphorescent dopant and polymer host have similar surface functional groups⁴² or when they are implemented in one composite material.^{34,43,44} In a recent paper, statistical copolymers based on dioctylfluorene, with hole-transporting moieties and phosphorescent Ir(III) complexes attached as pendant groups to the main backbone, were synthesized and showed some improvements in device efficiency.⁴⁵

We aim to attach phosphors covalently to a conjugated polymer backbone so as to allow efficient energy transfer between polymer and phosphor and further to minimize aggregation and quenching of phosphorescence. Herein, we describe the controlled synthesis of such oligomers and polymers based on 9,9-dialkylfluorene repeat units in conjugation with bis-cyclometalated iridium(III) *acac* complexes. The photo-physics of optical and electrical excitation are presented and this has enabled insights to be drawn into design criteria for phosphorescent polymer light-emitting devices.

Results and Discussion

Synthesis and Characterization of Ir(III) Complexes. The syntheses of either iridium complexes with 2-phenylpyridinato (*ppy*) coupled to well-defined oligofluorenes of chain length 1–3 units or iridium complexes with 2-(2'-benzo[*b*]thienyl)pyridinato (*btp*) coupled to polyfluorenes of longer chain length (5–40 units) are described. The syntheses presented are controlled, high yielding, and general involve either a stepwise building up of oligofluorenes or the application of the Suzuki polycondensation reaction to yield well-defined polyfluorene complexes.^{46,47}

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Scheme 1. Synthetic Route to Well-Defined Fluorene Substituted *ppyH* Ligands 4–9

Reagents and conditions: (a) **2**, Pd(PPh₃)₄, Et₄NOH, toluene, 90 °C, 47%; (b) **3**, Pd(PPh₃)₄, Et₄NOH, toluene, 90 °C, 88%; (c) ICl, CH₂Cl₂, 25 °C, 85%; (d) **2**, Pd(PPh₃)₄, Et₄NOH, toluene, 110 °C, 86%; (e) **3**, Pd(PPh₃)₄, Et₄NOH, toluene, 90 °C, 88%; ICl, CH₂Cl₂, 25 °C, 85%; (f) **2**, Pd(PPh₃)₄, Et₄NOH, toluene, 90 °C, 52%.

Oligomers. The synthetic strategy for the oligomers, an adaptation of a method used to synthesize oligophenylenes,^{48,49} is shown in Scheme 1. 2-(4'-Bromophenyl)pyridine **1** was used in sequential Suzuki coupling reactions with orthogonally protected fluorene monomers, followed by deprotection and further coupling reactions to give *ppyH* coupled with one **4** (*ppyH*-FH), two **7** (*ppyH*-FO-FH), and three **9** (*ppyH*-FO-FO-FH) fluorenyl substituents, respectively (where FH is 9,9-dihexylfluorene and FO is 9,9-dioctylfluorene).

A Suzuki coupling of 2-(4'-bromophenyl)pyridine **1**⁵⁰ with 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-9,9-dihexylfluorene **2**⁵¹ gave 2-(4'-(9'',9''-dihexylfluoren-2''-yl)phenyl)pyridine **4**, resulting in the coupling of the *ppyH* ligand to one fluorene unit. The key monomeric building block of the stepwise synthesis, 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-trimethylsilyl-9,9-dioctylfluorene **3**, was made in two steps from 2,7-dibromo-9,9-dioctylfluorene via a controlled monolithiation using 1 equivalent of *n*-BuLi and subsequent reaction of the lithio-derivative with trimethylsilyl chloride (TMSCl), followed by bromine–lithium exchange using *t*-BuLi and boronation with 2-isopropoxy-4,4,5,5 tetramethyl-1,3,2-dioxaborolane. A Suzuki coupling reaction between 2-(4'-bromophenyl)pyridine **1** and the trimethylsilyl protected fluorenyl borolane **3** gave the product **5** where *ppyH* has been coupled with a trimethylsilyl substituted fluorenyl unit; this was iodo-desilylated with iodine monochloride (ICl) to give the iodo-substituted derivative **6**. A second Suzuki coupling reaction of the iodo-substituted derivative **6** with the fluorenyl borolane **2** gave 2-(4'-

(7''-(9''',9'''-dihexylfluoren-2'''-yl)-9'',9''-dioctylfluoren-2''-yl)phenyl)pyridine **7**, the second ligand target in which a *ppyH* unit is coupled to two fluorene moieties. The final target, **9**, was synthesized by a Suzuki coupling of the iodo-fluorenyl substituted ligand **6** and the trimethylsilyl protected fluorenyl borolane **3**, followed by iodo-desilylation to afford the iodo-derivative **8**. A Suzuki coupling of the iodo-derivative **8** with the fluorenyl borolane **2** gave 2-(4'-(7'''-(7''''-(9''''',9'''''-dihexylfluoren-2''''-yl)-9''''',9'''''-dioctylfluoren-2''''-yl)-9''-9''-dioctylfluoren-2''-yl)phenyl)pyridine **9**. The new ligands were characterized by ¹H NMR spectroscopy; the signal due to the pyridyl proton at δ 8.74 could be integrated and compared with those in the fluorenyl units at δ 7.85–7.70 thus allowing the number of fluorene units attached to the ligand to be quantified.

The dibrominated bis-cyclometalated iridium complex **10** was synthesized by a modification of the route that was recently reported by Lamansky, et al.²⁷ The chloride bridged dimeric complexes, from the reaction of IrCl₃·*x*H₂O with excess ligand, were cleaved by reaction with acetyl acetone to yield monomeric acetylacetonate (*acac*) complexes **10**–**13** as shown in Scheme 2. The ¹H NMR spectra showed that the peaks due to the *ppy* ligand are more widely spaced compared with the free ligand and in general these shifted to lower field on increasing the number of fluorene units. On the basis of the similarity of their ¹H NMR spectra to crystallographically characterized compounds,^{27,28} the complexes are assigned an octahedral coordination environment with the two nitrogen atoms of the cyclometalating ligands being trans to one another and the two carbon atoms being *cis*.²⁷

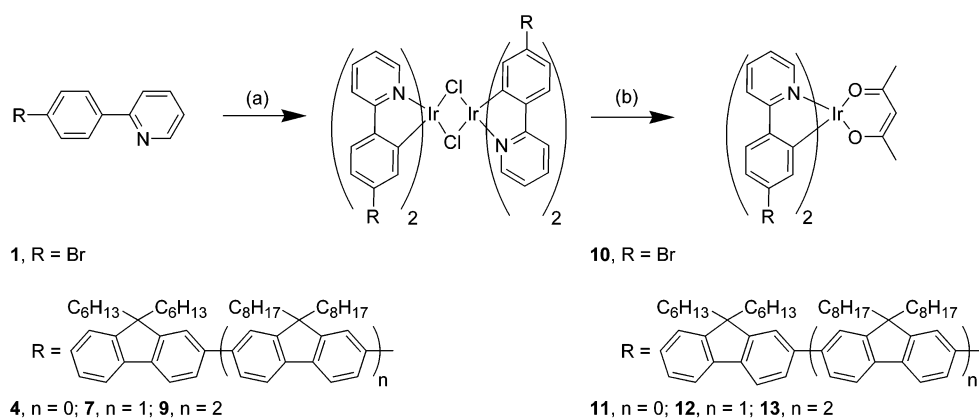
Polymers. Ligands with polyfluorene chains attached to the *ppyH* group were synthesized using the Suzuki polycondensation

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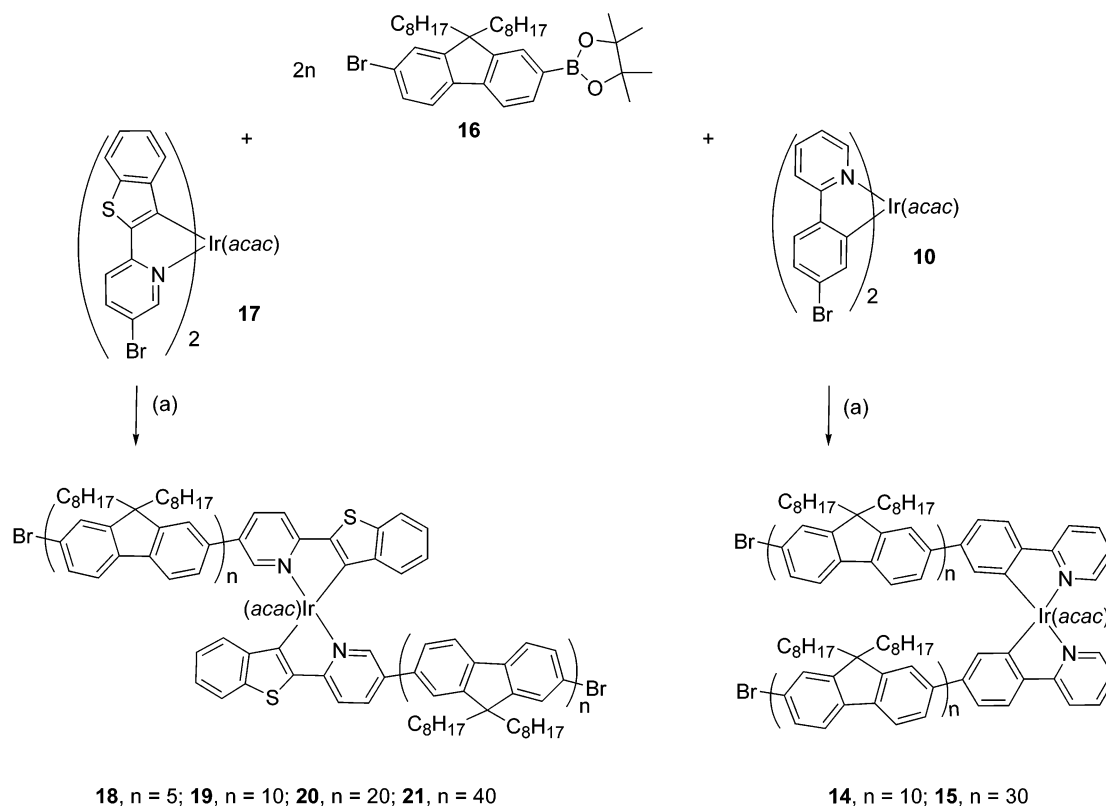
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Scheme 2. Synthesis of 10–13

Reagents and conditions: (a) $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, 2-ethoxyethanol (aq), reflux, 60–66%; (b) acetyl acetone, Na_2CO_3 , 2-ethoxyethanol, reflux, 50–60%.

Scheme 3. Synthetic Route to Polyfluorene Triplet Emitters 14–21

Reagents and conditions: (a) $(\text{Pd}(\text{OAc})_2)$, 2 PCy_3 , Et_4NOH , toluene, reflux, 24 h, 50–60%.

protocol developed in Cambridge for poly(9,9-dioctylfluorene) (PFO)^{46,47} and terminating the reaction with 2-(4'-bromophenyl)pyridine **1**. However, the iridium coordination chemistry of these species was frustrated by gelation of the reaction mixture or formation of highly insoluble products, leading to incomplete metal chelation and therefore to lower phosphor loadings than targeted. A simpler route, shown in Scheme 3, was developed using Suzuki homo-polymerization of 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-bromo-9,9-dioctylfluorene **16**, an AB monomer, and chain extension with the bromo-substituted cyclometalated iridium complex **10** to give, after reaction with excess acetyl acetone, polymer complexes composed of 10 fluorene units, (**14**) $[\text{Ir}(\text{ppy}-(\text{FO})_{10})_2(\text{acac})]$, and 30 fluorene units, (**15**) $[\text{Ir}(\text{ppy}-(\text{FO})_{30})_2(\text{acac})]$. The relative chain lengths were calculated by comparing the integration of the ^1H NMR

signal assigned to the *acac* methyl groups at δ 1.90, with the first CH_2 groups of the alkyl chains on the 9-position in the fluorene at δ 2.30–2.00.

The final series of compounds synthesized were Ir(III)-chelating polyfluorenes for red-light emission. The same synthetic strategy was applied as shown in Scheme 3; using a bromo-substituted 2-(2'-benzo[*b*]thienyl)pyridine (*btpH*) cyclometalating reagent, Ir(III) complexes of closely analogous ligands have previously shown red phosphorescence.²⁷ The modified *btpH* ligand was prepared via a Suzuki coupling of 2,5-dibromopyridine with 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)benzo[*b*]thiophene. The ligand was complexed with $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ yielding first a chloride-bridged dimer, which was then cleaved by reaction with acetyl acetone to give iridium(III)bis(2-(2'-benzo[*b*]thienyl)-5-bromopyridinato-*N*, *C*^{3'})(acetyl-

acetate) **17** [Ir(*btp*-Br)₂(*acac*)]. Crystals suitable for an X-ray structure determination were grown and a representation of the structure is shown in the Supporting Information (Figure S1). The iridium atom has octahedral geometry with the pyridyl nitrogen atoms occupying a trans disposition and the benzo[*b*]-thienyl carbon atoms being cis to one another. There are some distortions from ideal octahedral geometry exemplified by the largest bond angle being between the two carbon atoms [92.1-(8)°] and the smallest being between carbon and nitrogen atoms on the same ligand [78.9(8)°]. The bond lengths and angles are within the range found for other such iridium complexes.^{27,52–57}

The polymers, **18–21**, were synthesized by a Suzuki polymerization reaction of 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-bromo-9,9-dioctylfluorene **16** as the monomer and in the presence of bromo-substituted bis-cyclometalated iridium complex **17**. Chain lengths from 5 to 40 units were obtained by varying the reaction stoichiometry and were calculated by integration of signals due to the *acac* methyl groups at δ 1.92, and the first CH₂ groups of the alkyl chains on the nine-position in the fluorene at δ 2.30–2.00, in the ¹H NMR spectra. Gel permeation chromatography was run in chloroform against polystyrene standards and confirmed the high molar masses expected. Molecular weights higher than predicted were found, probably because of the rigid rod nature of the polymers in solution, and showed polydispersities between 2 and 3, as predicted for condensation polymerizations.

Optical Spectroscopy

Absorption. The thin-film absorption spectra of the series of *ppy* substituted iridium complexes, **10–15**, and *btp* substituted iridium complexes, **17–21**, are shown in Figure 1. Complex **10** [Ir(*ppy*-Br)₂(*acac*)] shows several low-intensity metal to ligand charge transfer (MLCT) transitions from 2.50 to 3.60 eV; the lowest energy transitions being the MLCT d- π^* (*ppy*) excitations, with ³MLCT triplet states at 2.50 eV and ¹MLCT singlet states at 2.65 eV. The high-intensity peak centered at 4.70 eV is assigned to the $\pi \rightarrow \pi^*$ transition of the *ppy* ligands.^{27,28,58} Increasing the conjugation of the cyclometalating ligand passing from **10** [Ir(*ppy*-Br)₂(*acac*)] to **17** [Ir(*btp*-Br)₂(*acac*)] causes a red shift in the $\pi \rightarrow \pi^*$ peak intensity of 0.60 eV and a diminution in peak intensity. The lower energy of the *btp* transition may lead to stronger mixing with the iridium d-orbitals, and this in turn may account for the increased intensity of the MLCT transitions from 2.40 to 3.60 eV in **17** compared to **10**. In contrast to the $\pi \rightarrow \pi^*$ transition, the low-energy MLCT transitions shift only by 0.2 eV between the two compounds and this reflects their more localized character.

When complex **10** is coupled to a single fluorene unit to give **11** [Ir(*ppy*-(FH))₂(*acac*)], the $\pi \rightarrow \pi^*$ peak at 4.70 eV shifts to 3.65 eV, consistent with the extended conjugation length of the ligand. As the number of fluorene units is increased from 1 in complex **11** to 30 in complex **15**, the main $\pi \rightarrow \pi^*$ peak shifts

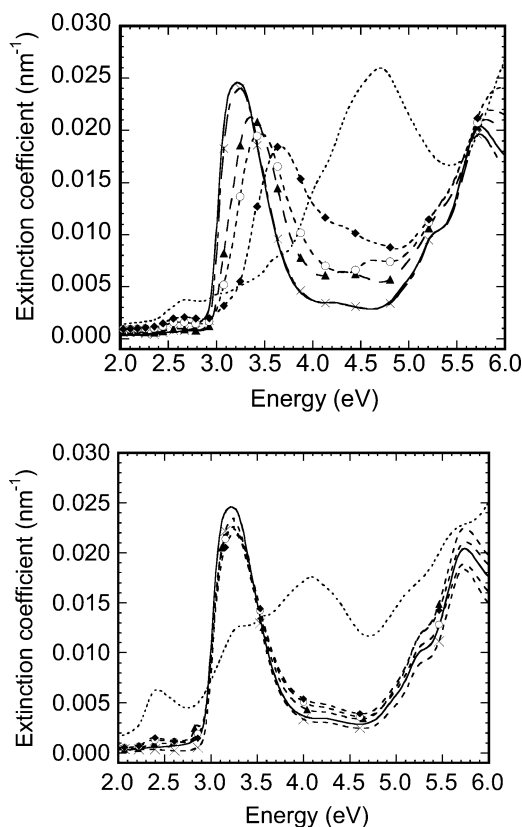


Figure 1. (a) The thin-film room temperature absorption spectra of compounds **10–15**. **10** [Ir(*ppy*-Br)₂(*acac*)] dashed line with no markers, **11** [Ir(*ppy*-FH)₂(*acac*)] has filled squares, **12** [Ir(*ppy*-FO-FH)₂(*acac*)] has open circles, **13** [Ir(*ppy*-(FO)₂-FH)₂(*acac*)] has filled triangles, **14** [Ir(*ppy*-(FO)₁₀)₂(*acac*)] (same spectrum as **15** [Ir(*ppy*-(FO)₃₀)₂(*acac*)] has crosses, and PFO has a solid line with no markers. (b) The thin-film room temperature absorption spectra of compounds **17–21**. **17** [Ir(*btp*-Br)₂(*acac*)] dashed line with no markers, **18** [Ir(*btp*-(FO)₅)₂(*acac*)] has filled squares, **19** [Ir(*btp*-(FO)₁₀)₂(*acac*)] has open circles, **20** [Ir(*btp*-(FO)₂₀)₂(*acac*)] has filled triangles, **21** [Ir(*btp*-(FO)₄₀)₂(*acac*)] has crosses, and PFO has a solid line with no markers.

further to the red and increases in oscillator strength, tending toward the absorption spectrum of PFO. In a similar way, the $\pi \rightarrow \pi^*$ peak at 4.10 eV in **17** [Ir(*btp*-Br)₂(*acac*)] shifts to 3.20 eV in **18** [Ir(*btp*-(FO)₅)₂(*acac*)]. No further red shift occurs on increasing the number of fluorene units from five in complex **18** to forty in complex **21**, indicating that five fluorene units are already sufficient to shift the $\pi \rightarrow \pi^*$ peak into that of PFO. For both series, the intensity of the MLCT transitions decreases in the larger oligomers and polymers because of the decreased loading of the complex in the materials. The absorption spectra of *ppy* substituted iridium complexes **11–15** and *btp* substituted iridium complexes **18–21** do not correspond to the sum of the individual absorption spectra of **10** or **17** and PFO, but instead show a shift of the iridium complex $\pi \rightarrow \pi^*$ transition upon coupling with fluorene units. This suggests that the energy levels of the iridium complex and the short fluorene chains cannot be separated but that the whole oligomer forms a single conjugated entity with a common $\pi \rightarrow \pi^*$ singlet state.

Photoluminescence. The photoluminescence (PL) spectra of the series taken from thin films at 5 K are shown in Figure 2a and b, respectively, along with the PL spectra of blends of [Ir(*ppy*)₂(*acac*)] or [Ir(*btp*)₂(*acac*)] and PFO.

The PL spectrum for complex **10** [Ir(*ppy*-Br)₂(*acac*)] is characterized by a 0–0 peak at 2.28 eV and broad vibronic

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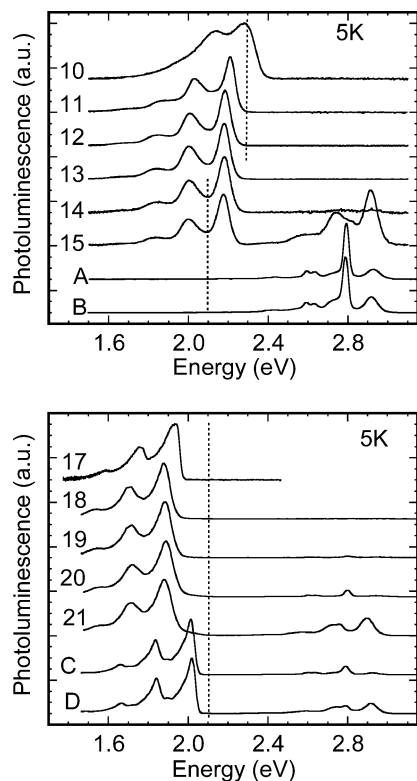


Figure 2. (a) The thin-film photoluminescence spectra at 5 K of compounds **10** [Ir(*ppy*-Br)₂(*acac*)], **11** [Ir(*ppy*-(FH))₂(*acac*)], **12** [Ir(*ppy*-FO-FH)₂(*acac*)], **13** [Ir(*ppy*-(FO)₂-FH)₂(*acac*)], **14** [Ir(*ppy*-(FO)₁₀)₂(*acac*)], **15** [Ir(*ppy*-(FO)₃₀)₂(*acac*)], blend **A** (same molecular percentage of [Ir(*ppy*)₂(*acac*)] in PFO as for **14**), and blend **B** (same molecular percentage of [Ir(*ppy*)₂(*acac*)] in PFO as for **15**). Spectra are normalized and offset along the vertical axis for ease of comparison. The dotted line indicates the position of the triplet state in PFO polymer at 2.1 eV and trimer at 2.3 eV. (b) The thin-film photoluminescence spectra at 5 K of compounds **17** [Ir(*btp*-Br)₂(*acac*)], **18** [Ir(*btp*-(FO)₅(*acac*)], **19** [Ir(*btp*-(FO)₁₀)₂(*acac*)], **20** [Ir(*btp*-(FO)₂₀)₂(*acac*)], **21** [Ir(*btp*-(FO)₄₀)₂(*acac*)], blend **C** (same molecular percentage of [Ir(*btp*)₂(*acac*)] in PFO as for **20**), and blend **D** (same molecular percentage of [Ir(*btp*)₂(*acac*)] in PFO as for **21**). Spectra are normalized and offset along the vertical axis for ease of comparison. The dotted line indicates the position of the triplet state in PFO polymer at 2.1 eV.

structure, while in the PL spectrum of **17** [Ir(*btp*-Br)₂(*acac*)], the 0–0 peak is at 1.95 eV with a narrower and better resolved vibronic structure. The small Stokes shift between absorption and emission maxima for **10** indicates emission from a mixed MLCT/ $\pi \rightarrow \pi^*$ state whose character is predominately that of the MLCT transition, as observed for the related complex [Ir(*ppy*)₂(*acac*)].²⁸ The PL emission maximum for **17**, on the other hand, has a larger Stokes shift, inconsistent with a localized charge-transfer transition. This transition therefore has a strong $\pi \rightarrow \pi^*$ character, as has been observed for the related complex [Ir(*btp*)₂(*acac*)] by Lamansky et al.²⁷

The triplet states of a fluorene trimer and polymer are reported at about 2.30 and 2.10 eV, respectively.⁵⁹ Therefore, while the triplet state of **10** is equal to or slightly higher than that of the polyfluorene oligomers, the triplet state in **17** is at lower energy. Consequently, Figure 2 and Tables 1 and 2 show how thin-film phosphorescence is efficiently quenched for [Ir(*ppy*)₂(*acac*)] blended in PFO (Table 1, entries A and B), while this is not the case for [Ir(*btp*)₂(*acac*)] blended in PFO (Table 2, entries C

Table 1. EL and PL Efficiencies in Thin Films at Room Temperature for Compounds **10–15**, Blend **A**, Blend **B**, and PFO

#	molar % of Ir complex	total ELQY (%)	triplet ELQY (%)	singlet ELQY (%)	total PLOQ (%)		
					1% in PS	triplet PLOQ (%)	singlet PLOQ (%)
10	100.0	0.012	0.012		0.2	40.0	0.2
11	33.3	0.030	0.030		0.8		0.8
12	20.0	0.110	0.110		0.8	26.0	0.8
13	14.3	0.115	0.115		0.5		0.5
14	4.8	0.045	0.034	0.011	3.0		2.3
15	1.6	0.070	0.048	0.022	2.0	4.0	0.2
A	4.8	0.025	0.023	0.002	2.2		2.2
B	1.6	0.055	0.006	0.049	7.2		7.2
PFO	0	0.250		0.250	50.0		50.0

Table 2. EL and PL Efficiencies in Thin Films at Room Temperature for Compounds **17–21**, Blend **C**, Blend **D**, and PFO

material	molar % of Ir complex	total ELQY (%)	triplet ELQY (%)	singlet ELQY (%)	total PLOQ (%)	triplet PLOQ (%)	singlet PLOQ (%)
18	9.1	0.150	0.150		9.9		9.9
19	4.8	0.200	0.200		12.1		11.7
20	2.4	0.450	0.450		21.8		20.7
21	1.2	1.500	1.500		26.6		23.1
C	2.4	0.70	0.686	0.014	25.5		24.0
D	1.2	0.50	0.480	0.020	23.0		20.7
PFO	0	0.250		0.250	50.0		50.0

and D). Polyfluorene fluorescence is also strongly quenched in the blends (Tables 1 and 2) as there is good spectral overlap between the emission of PFO and the MLCT absorptions of [Ir(*ppy*)₂(*acac*)] and this allows for efficient Förster transfer from PFO to the complexes.

In contrast, in a conjugatively linked system, a mixed triplet state may be formed between the iridium complex and the polyfluorene, as both triplet states are energetically similar. We would therefore expect phosphorescence to occur in both series, and this is indeed observed. On the coupling of a fluorene unit to **10** to give complex **11** [Ir(*ppy*-(FH))₂(*acac*)], the emission band shifts from 2.28 to 2.21 eV, and shows a well-resolved, narrower vibronic structure. The increase in structure indicates that the emission is dominated by a $\pi \rightarrow \pi^*$ transition and that the fluorene units are indeed electronically coupled to the complex. This emission displays strong temperature dependence in thin films, is quenched by the presence of oxygen, and is energetically placed near the triplet states of both **10** and polyfluorene; therefore, it is attributable to a triplet excited state. The energy shifts from **10** to **11** and **12** are to lower energies, even though the triplet state of polyfluorene trimer is at higher energy. This confirms the mixed nature of the state and also suggests the triplet wave function is sensitive to oligomer length despite being a localized state. No further shift is observed on increasing the number of fluorene units from 2 in the oligomer **12** to 30 in the polymer **15**, even though the triplet level in polyfluorene is at lower energy. This suggests that phosphorescence occurs from the first few fluorene units nearest the iridium and that more distant units have little effect on the emission maximum. In a similar way, the triplet emission shifts by 0.05 eV to lower energies when a fluorene-pentamer is coupled to **17**, even though the triplet state in polyfluorene itself is at higher energy than in **17**.

We have been able to follow the evolution of the energy of the triplet state centered on the Ir complex as a function of the

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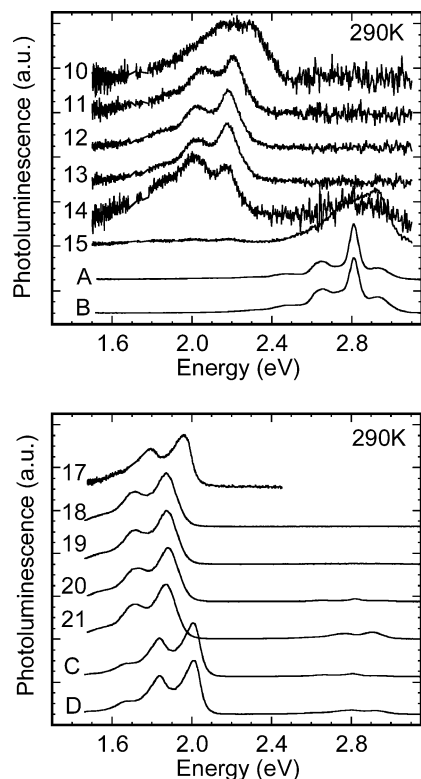


Figure 3. (a) The thin-film photoluminescence spectra at 290 K of compounds **10** [Ir(*ppy*-Br)₂(*acac*)], **11** [Ir(*ppy*-(FH))₂(*acac*)], **12** [Ir(*ppy*-FO-FH)₂(*acac*)], **13** [Ir(*ppy*-(FO)₂-FH)₂(*acac*)], **14** [Ir(*ppy*-(FO)₁₀)₂(*acac*)], **15** [Ir(*ppy*-(FO)₃₀)₂(*acac*)], blend **A**, and blend **B**. Spectra are normalized and offset along the vertical axis for ease of comparison. (b) The thin-film photoluminescence spectra at 290 K of compounds **17** [Ir(*btp*-Br)₂(*acac*)], **18** [Ir(*btp*-(FO)₅)₂(*acac*)], **19** [Ir(*btp*-(FO)₁₀)₂(*acac*)], **20** [Ir(*btp*-(FO)₂₀)₂(*acac*)], **21** [Ir(*btp*-(FO)₄₀)₂(*acac*)], blend **C**, and blend **D**. Spectra are normalized and offset along the vertical axis for ease of comparison.

extension of conjugation of the polyfluorene chain and find that this is sensitive to only the first attached fluorene group. This indicates that this triplet state is much more strongly localized than is the case for singlet states on conjugated chains, as can be seen here by the considerable downward evolution of the π - π^* singlet transition energies with chain length (Figure 1) saturating at about 3.2 eV for $n = 10$.

Singlet emission is also observed at 2.90 eV for the materials with the longest fluorene chains, with the energy and the very sharply resolved vibronic structure typical for polyfluorene. The presence of singlet emission is most likely due to insufficient singlet energy transfer from polyfluorene segments to the iridium.

Figure 3 shows the photoluminescence spectra of thin films of the new materials at room temperature. In both series, inhomogeneous broadening occurs, yet the energy of the 0–0 peak in the triplet emission remains unaltered, which further underscores the notion that phosphorescence occurs localized on the conjugated segment involving the iridium site and immediately adjacent ligands. The singlet emission observed for the longer chain complexes and blends shifts to slightly higher energies when the temperature is raised from 5 to 290 K possibly because of thermally activated exciton diffusion between segments with different singlet energies.⁶⁰

In the series of compounds where fluorene units are coupled to complex **10**, there is a higher fraction of singlet emission at 290 K than at 5 K in the longer polymer complexes **14** and **15**.

In addition, the PL quantum yield of **15** is quenched by a factor of 10 upon raising the temperature. For the longer oligomers, polyfluorene segments far away from the iridium site may have an electronic structure close to that of polyfluorene polymer itself, with a non-emissive triplet energy level below that of the mixed state. It is therefore possible that thermally activated exciton diffusion may occur to such electronically decoupled polyfluorene units where phosphorescence is quenched in the same way as has been observed in the blends of the [Ir(*ppy*)₂(*acac*)] with PFO. A comparison of the PL spectrum of **14** with the corresponding blend **A** shows that the blend spectrum is dominated by fluorescence, while **14** is dominated by phosphorescence. When the polyfluorene chain is extended in **15**, both the conjugated compound and the corresponding blend **B** are dominated by fluorescence. This indicates that 10 fluorene units correspond to the extent of conjugation before electronic decoupling occurs, in agreement with measurements.⁶¹

For the series of compounds coupled to complex **17**, the triplet energy level is below that of the polyfluorene oligomers and so the ratio of triplet to singlet state emission is hardly affected by temperature. In addition, we observe similar fluorescence and phosphorescence quantum yields for the blends **C** and **D** as for the corresponding compounds **20** and **21** (in contrast to the EL quantum yields, as detailed further below).

Electroluminescence. The electroluminescence (EL) spectra of the compounds (Figure 4) were measured at room temperature in a device structure of ITO/PEDOT:PSS/compound/Ca/Al as described in the Supporting Information. For the short-chain complexes of *ppy* ligands **10**–**13**, all of the emission occurs from the triplet state. Longer chain complexes **14** and **15**, and the blend with high iridium complex loading, **A**, show mostly triplet emission, but a small peak due to polyfluorene singlet emission is also observed. The blend with low iridium complex loading, **B**, on the other hand gives almost exclusively singlet emission. This demonstrates the potential for these polymer complexes to phosphoresce even at iridium loadings which lead to quenching of such emission in blended materials. The series of complexes with fluorene units bound to *btp* ligands, **17**–**21**, all show exclusive triplet emission in their EL spectra pointing to charge trapping at iridium being the dominant process under EL excitation.

Efficiencies. The photoluminescence and electroluminescence efficiencies (PLQY and ELQY respectively) of the series linked to **10** are low (Table 1) for several reasons. For the short oligomers, concentration quenching occurs in the neat films. The PL efficiencies of **10** and **12**, for example, increased from 0.2% to 40% and from 0.8% to 26% when blended in a polystyrene (PS) matrix at 1% concentration. For longer oligomers, concentration quenching should be less significant but triplet efficiencies are now low because there is triplet energy transfer onto FO segments. This study of the energy transfer in the solid state shows that the triplet energy reduces with increasing length of the FO segment, and transfer from the iridium site to the FO chromophore then becomes an exothermic and thus more efficient process. This was previously noted by Thompson and co-workers, when studying the triplet transfer in solution between iridium-containing phosphors with a range of triplet energies and a fluorene trimer.⁴¹ Thus, for the long

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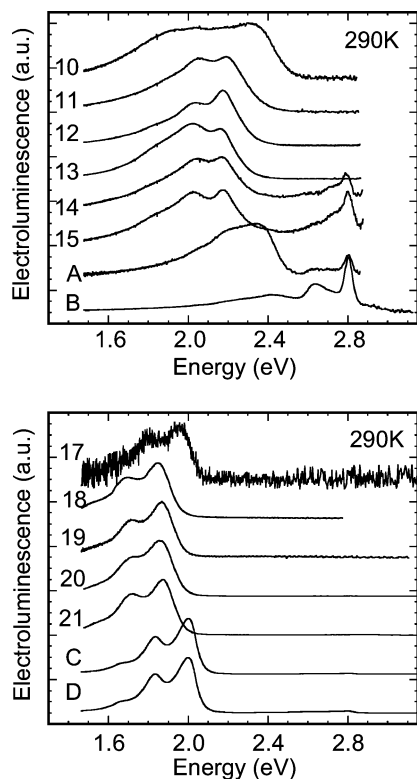


Figure 4. (a) Room temperature electroluminescence spectra of **10** [Ir(*ppy-Br*)₂(*acac*)], **11** [Ir(*ppy*-(FH))₂(*acac*)], **12** [Ir(*ppy*-FO-FH)₂(*acac*)], **13** [Ir(*ppy*-(FO)₂-FH)₂(*acac*)], **14** [Ir(*ppy*-(FO)₁₀)₂(*acac*)], **15** [Ir(*ppy*-(FO)₃₀)₂(*acac*)], blend **A**, and blend **B**. Spectra are normalized and offset along the vertical axis for ease of comparison. The LEDs were made in a layer structure of ITO/PEDOT:PSS/compound/Ca/Al. (b) Room temperature electroluminescence spectra of **17** [Ir(*btp-Br*)₂(*acac*)], **18** [Ir(*btp*-(FO)₅)₂(*acac*)], **19** [Ir(*btp*-(FO)₁₀)₂(*acac*)], **20** [Ir(*btp*-(FO)₂₀)₂(*acac*)], **21** [Ir(*btp*-(FO)₄₀)₂(*acac*)], blend **C**, and blend **D**. Spectra are normalized and offset along the vertical axis for ease of comparison. The LEDs were made in a layer structure of ITO/PEDOT:PSS/compound/Ca/Al.

oligomer **15**, energy transfer occurs onto electronically decoupled polyfluorene segments and singlet emission is now seen with modest efficiency. Nevertheless, electroluminescence from the triplet state is more efficient than in the corresponding blends, where it occurs predominately from the singlet state.

The compounds linked to **17** show high PL and EL yields (Table 2). The PL yields increase along the series, which we attribute to reduced self-quenching. The same trend is observed for the EL yields, with values up to 1.5% for **21**, which exceeds the 0.5% reported for nonconjugated analogs.⁴⁵ The conjugated polymer complex **20** has a slightly lower electroluminescence quantum yield (ELQY) than the blended device of equivalent iridium loading, blend **C**, although the film quality of the blends is poor with crystalline phase separated regions visible by eye and inhomogeneous light emission. On the other hand, the longer chain complex **21** shows 3 times the efficiency of the corresponding blend, **D**. These results demonstrate the subtle influences of phosphor concentration on device efficiency, a phenomenon which has previously been observed but as yet remains poorly understood.⁶² It is clear that further fine-tuning of the polymer structure, by, for example, substitution of the

fluorene chains with carbazole units, and variation of chain length may enable optimization of these promising initial results.

Conclusions

Controlled, high-yielding, and general synthetic routes have been developed to a series of well-defined oligo and polyfluorenyl bis-cyclometalated iridium complexes. The addition of fluorene substituents to *ppyH* and *btpH* ligands under optimized Suzuki coupling conditions and their coordination complexes with Ir(III) yielded materials that are readily spin-coated from solution as neat materials. Photophysical studies revealed that there is mixing of the triplet levels of the fluorene and cyclometalating ligand to give a hybrid mixed triplet state as the lowest energy level. Photoluminescence emission occurs from this mixed triplet state and its wavelength may be tuned from green to red by judicious choice of cyclometalating ligand and fluorene chain length. The EL spectra are dominated by triplet emission, even at low iridium loadings, indicating that charge trapping at the metal center may be the dominant mechanism. The efficiencies of the green devices are moderate, yet the devices still represent improvements over blended composite materials of organometallic phosphors in polyfluorene host. The red devices, on the other hand, were designed to have improved energy matching between iridium and fluorene energy levels and show significant improvements in device efficiency.

The new solution-processible triplet emitters have the potential for further optimizations by structural modifications to the iridium polyfluorene complexes which can be accomplished by adapting the synthetic strategies described herein. In addition, the new polymers represent a fascinating class of materials in their own right for further study of the fundamental photophysics of light-emitting polymers.

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Supporting Information Available: General experimental techniques and optical measurements. Experimental procedure for the synthesis of **1**, **3–21**, diiridium(III) di- μ -chlorotetrakis-(2-(4'-bromophenyl)pyridinato-*N,C*^{2'}), 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolane)benzo[*b*]thiophene, 2-(2'-benzo[*b*]thienyl)-5-bromopyridine, diiridium(III) di- μ -chlorotetrakis(2-(2'-benzo[*b*]thienyl)-5-bromopyridinato-*N,C*^{3'}). The X-ray CIF file and representation of the crystal structure of **17** (the data has been deposited with the Cambridge Crystallographic Database: CCDC 223879). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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