Articles

Phosphorescent Side-Chain Functionalized Poly(norbornene)s Containing Iridium Complexes

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ABSTRACT: Norbornenes containing phosphorescent iridium complexes based on $Ir(ppy)_3$ and $Ir(ppy)_2(bpy)(PF_6)$ were synthesized and copolymerized with alkylnorbornenes via ring-opening metathesis polymerization in nonpolar solvents using ruthenium initiators. The luminescent properties of the resulting polymers both in solution and in the solid state were tested. The polymers were found to retain the optical properties of the phosphorescent small molecule analogues with emission maxima in the yellow/green, quantum yields from 0.23 to 0.24 for $Ir(ppy)_2(bpy)(PF_6)$ analogues, 0.02 to 0.03 for *mer*-$Ir(ppy)_3$ analogues, and 0.20 to 0.24 for *fac*-$Ir(ppy)_3$ analogues, and lifetimes of 0.41 to 0.55 μs for $Ir(ppy)_2(bpy)(PF_6)$ analogues, 0.22 to 0.62 μs for *mer*-$Ir(ppy)_3$ analogues, and 1.28 to 1.48 μs for *fac*-$Ir(ppy)_3$ analogues. By combining the phosphorescent properties of these emissive molecules with the solution processability and ease of synthesis of polynorbornene backbones, these materials might be highly useful in the field of light-emitting devices and emissive display technology.

Introduction

Organic light-emitting diodes (OLEDs) are in high demand today in nearly every facet of the technological world. It is proposed that the next generation of OLED material will be based on phosphorescent materials instead of the current fluorescence-based systems due to the significantly higher quantum yields that are possible.[1] One shortcoming of current OLEDs as well as future systems is their lengthy device fabrication. In this paper, we describe the synthesis and photophysical characterization of a new class of polymer-supported phosphorescent materials, poly(norbornene)-supported iridium complexes. This material can be synthesized in a highly controlled fashion as a result of the polymerization method employed and combines the possibility of solution film processing with phosphorescence.

Phosphorescent coordination complexes, including the class of iridium compounds studied in this paper, already feature prominently in various materials and devices as the emissive species, as a result of their high quantum efficiencies and strong photo- and electroluminescence.[1] In current device technologies, the luminescent molecules are either vacuum-deposited as low molecular weight compounds or doped into a polymeric matrix,[2] requiring lengthy and expensive fabrication of devices.[3] To simplify this fabrication process, recent efforts have been aimed at direct incorporation of the emissive species, via covalent attachment, to a solution-processable polymer backbone.[4] Examples to date include the attachment to poly(dimethylsiloxane)s, poly(fluorene)s, and poly(styrene)s, showing promising results in areas such as solution processing and sensor technology.[5] To meet the needs of the rapidly expanding scope of applications that have been suggested for polymer-supported, highly emissive phosphorescent complexes, further optimization is necessary. This includes synthesizing increasingly robust and durable, yet easily modifiable, polymeric scaffolds in order to facilitate the tuning of materials. Ring-opening metathesis polymerization (ROMP) has been shown to fulfill these criteria.[6] It typically employs straightforward, facile monomer syntheses resulting in a versatile library of monomers.[6] Furthermore, the ruthenium−carbene complexes that catalyze ROMP are extremely efficient as well as highly functional group tolerant.[6] Finally, ROMP is often living and highly controlled allowing for the highest degree of control over the resulting polymer properties such as molecular weight and polydispersity and for the synthesis of block copolymers.

ROMP has also been shown to be an effective method for polymerization and solution processing of such important fluorescent complexes as Alq_3 and $Ru(bpy)_3(PF_6)_2$.[7] Thus, ROMP is an excellent route toward the study, realization, and optimization of the ever-expanding field of polymer-supported phosphorescent materials. In this work, we demonstrate the synthesis of phosphorescent iridium complexes covalently bound to norbornene, the homo- and copolymerization of these monomers, and finally the persistent adherence of the luminescence activity to the known values of the small molecule analogues throughout the entire process for the polymers in solution as well as in the solid state.

Results and Discussion

Monomer Design. Monomers were designed based on choice of phosphorescent complex as well as durability and ease of synthesis. All monomers were synthe-

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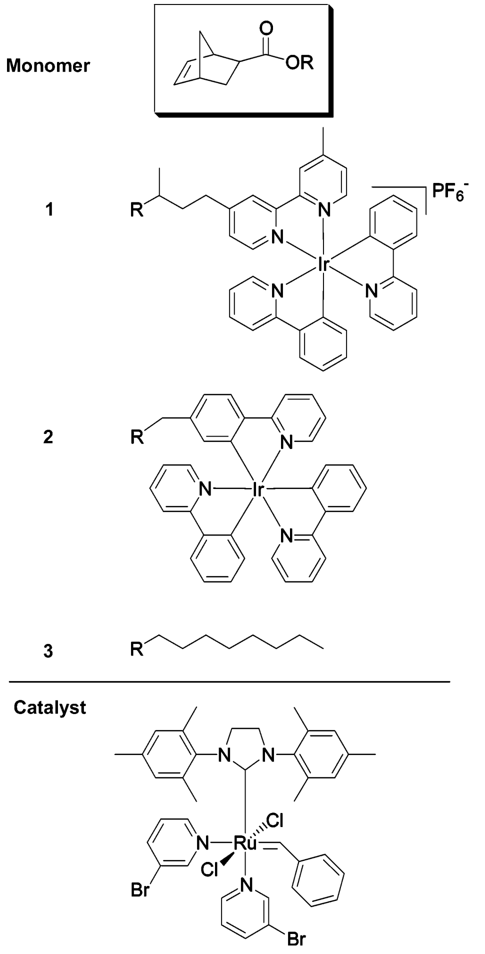
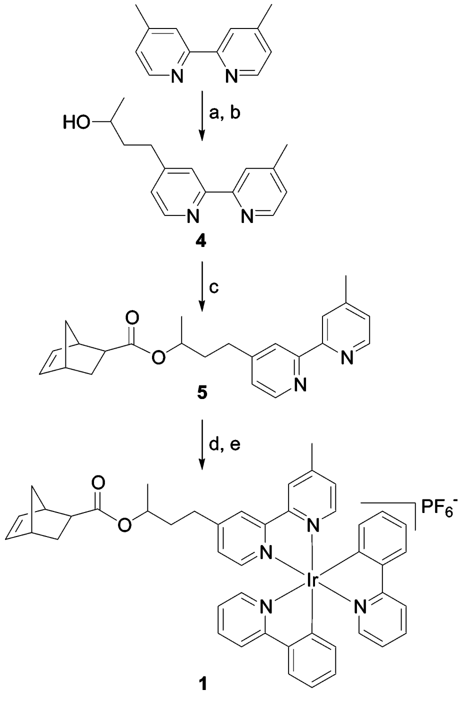


Figure 1. (top) Monomers employed in this study: **1**, bpy-based, charged iridium complex; **2**, ppy-based, neutral iridium complex; **3**, alkyl spacer-based monomer. (bottom) Grubbs' third-generation catalyst.

sized in three steps or less from commercially available starting materials. The emissive complex is attached to the polymerizable unit by a short alkyl linker to a norbornenyl ester which has been shown to be highly stable under a variety of conditions.[8] To investigate the optical effects on the properties of the resulting polymers, both a charged monomer and a neutral monomer are included in this study as well as an alkyl-chain based monomer that can serve to space out the luminescent inorganic complexes and aid polymer solubility (Figure 1).

Monomer Synthesis. Monomers **1**−**3** were readily synthesized in three steps or less in overall good yields. The synthesis of monomer **1** started with the treatment of commercially available 4,4′-dimethyl-2,2′-dipyridyl (dMbpy) with 1 equiv of lithium diisopropylamide (LDA), followed by the addition of 1 equiv of propylene oxide, to give compound **4** in 73% yield. Ring-opening addition of the propylene oxide to form **4** occurred exclusively by the attack of the dMbpy anion on the less substituted carbon of the epoxide. No attack onto the more substituted carbon was detected. Compound **4** was esterified with *exo*-5-norbornene-2-carboxylic acid, using dicyclohexylcarbodiimide (DCC) and a catalytic amount of (dimethylamino)pyridine (DMAP) to afford compound **5** in 42% yield. In a modification to a previously published procedure,[2g] **5** was then combined with [Ir(ppy)$_2$Cl]$_2$ at 150 °C in ethylene glycol, followed by the addition of NH$_4$PF$_6$(aq) to provide iridium-containing monomer **1** in 72% yield (Scheme 1).

Scheme 1. Synthesis of 1[a]



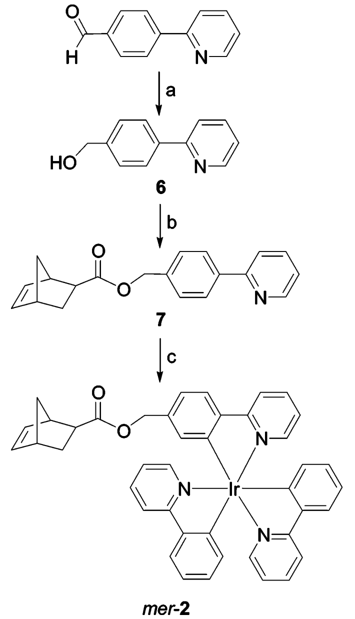
[a] (a) Lithium diisopropylamide, THF, −78 °C; (b) propylene oxide, THF, 0 °C, 73%; (c) *exo*-5-norbornene-2-carboxylic acid, DCC, DMAP, CH$_2$Cl$_2$, 42%; (d) [Ir(ppy)$_2$Cl]$_2$, ethylene glycol, 150 °C, 72%; (e) NH$_4$PF$_6$(aq).

Commercially available 4-(2-pyridine)benzaldehyde was reduced with LiAlH$_4$ to give the corresponding alcohol **6** in 94% yield, which was then esterified with *exo*-5-norbornene-2-carboxylic acid using DCC/DMAP, as described for **1**, to give compound **7** in 80% yield. Simultaneously, [Ir(ppy)$_2$Cl]$_2$ was treated with silver trifluoromethanesulfonate (AgOTf) to transform the chloro complex into the more labile iridium triflate species which is the precursor for the meridional coordination with a third ppy-type ligand. The resulting triflate complex was treated with **7** in acetone at room temperature overnight to give the meridionally oriented iridium-containing monomer *mer*-**2** in 43% yield (Scheme 2).[9]

Monomer *fac*-**2** was obtained by the reduction of the previously reported formylphenyl-substituted iridium complex Ir(ppy)$_2$fppy[2c] with LiAlH$_4$ to give compound **8**, *fac*-Ir(ppy)$_2$(hmppy) (hmppy = hydroxymethyl-ppy) which contains a single hydroxymethyl group as a chemical handle. Esterification with *exo*-5-norbornene-2-carboxylic acid using DMAP and DCC yielded the facially oriented monomer **2** in 40% yield (Scheme 3). The yield-limiting step is the facial coordination of the ligands onto the iridium metal center. This step occurs typically in less than 30% whereas meridional orientation can be achieved in yields as high as70%.[9] Monomer **3** was obtained as described in the literature.[10]

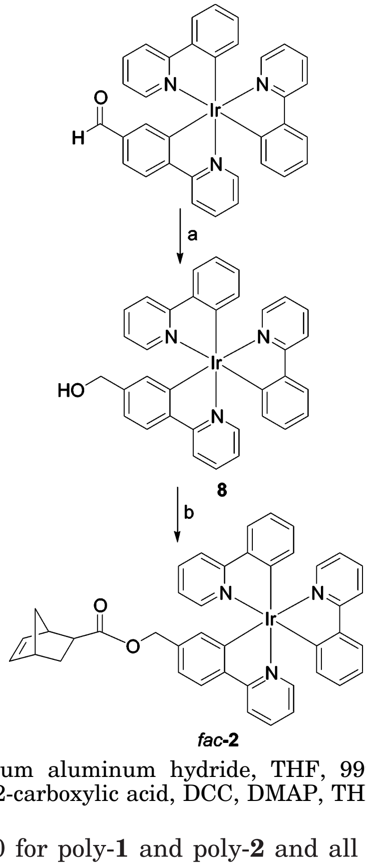
Polymerization. Homo- and copolymerizations were carried out using a standard protocol for all monomers. Monomers **1** and **2** were homo- and copolymerized with **3** in various ratios in dichloromethane and precipitated into either diethyl ether or methanol. All polymerizations were complete within 2−3 min, using Grubbs' third-generation benzyldine initiator as the ROMP catalyst (Figure 1).[11] The target degree of polymeriza-

Scheme 2. Synthesis of *mer*-2[a]



[a] (a) Lithium aluminum hydride, THF, 94%; (b) *exo*-5-norbornene-2-carboxylic acid, DCC, DMAP (cat.), CH_2Cl_2, 80%; (c) $[Ir(ppy)_2OTf]_2$, acetone, ambient temperature, 43%.

Scheme 3. Synthesis of *fac*-2[a]



[a] (a) Lithium aluminum hydride, THF, 99%; (b) *exo*-5-norbornene-2-carboxylic acid, DCC, DMAP, THF, 40%.

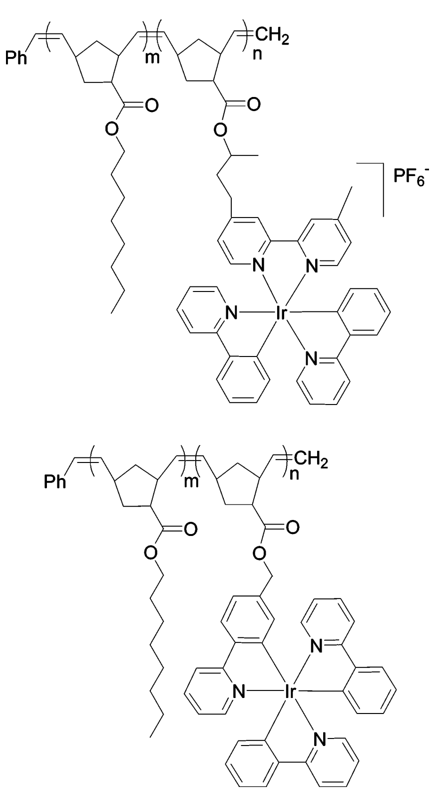


Figure 2. Copolymers poly-**1**-*co*-**3** (top) and poly-**2**-*co*-**3** (bottom).

tion was 50 for poly-**1** and poly-**2** and all copolymers, and copolymer ratios consisted of both 20:1 and 2:1 for the mixtures of both monomers **3**:**1** and **3**:**2** (Figure 2).

Poly-**1** and poly-*mer*-**2**, in contrast to previously published homopolymers that contain charged transition metal complexes on every repeating unit,[7] were fully soluble in dichloromethane without the aid of alkyl spacers or alkylated ligands. In contrast, poly-*fac*-**2** precipitated out during the polymerization and could not be redissolved in any organic solvent. Monomer **3** was thus employed in this study as a means of controlling the chromophore density in the solid state as well as an aid to polymer solubility.

Although all homopolymers of **1**, *mer*-**2**, and **3**[10] were fully soluble in dichloromethane, dichloromethane solutions of poly-**1** or poly-**2** when mixed with a solution of poly-**3** would either become turbid or cause full precipitation of the iridium-containing polymers from solution. This is consistent with observations in the literature that polymers containing metal complexes are often insoluble in strongly nonpolar environments,[12] although it is also possible that the precipitation may have been caused by the formation of polymer aggregates. However, attempts at block copolymerizations of **3** with either **1** or **2** caused the same phenomena, i.e., a 50-fold excess of monomer **3** was added to a homogeneous solution of a short chain polymer (~20 mer, catalyst was still fully initiated and living as observed by ^1H NMR of the carbene signal) of **1** or **2**. Upon addition of this second monomer, turbidity or precipitation occurred instantly. Both poly-**1** and poly-**2** also precipitated quickly in hexanes or diethyl ether, giving the same result as the addition of an excess of alkyl monomer **3**. Copolymers of **1** or **2** with **3** only remained fully soluble when they were copolymerized in a random fashion. Therefore, although the rates of polymerization with the catalyst we employed are very fast, the observed solubility of the copolymers suggests a random nature for the copolymers used in this system.

Gel-permeation chromatography (GPC) was employed for all polymers (Table 1). All GPC traces of poly-*mer*-**2** and its copolymer analogues were multimodal, showing approximately the same elution times as their *fac*-counterparts, but in all cases for poly-*mer*-**2** and its corresponding copolymers there were two highly overlapping, non-baseline-resolved signals. Therefore, while clearly polymers were formed, we are not able to

Table 1. Polymer Characterization Data

polymer	M_n	M_w	PDI	T_g, °C	T_d, °C
poly-**1**	31 000	43 100	1.39		330
poly-**1**-*co*-**3** (1:2)	11 200	19 300	1.71	10	339
poly-**1**-*co*-**3** (1:20)	18 500	47 000	2.55		347
poly-*mer*-**2**					248
poly-*mer*-**2**-*co*-**3** (1:2)				−43	298
poly-*mer*-**2**-*co*-**3** (1:20)					336
poly-*fac*-**2**					
poly-*fac*-**2**-*co*-**3** (1:2)	26 300	30 500	1.16	−53	358
poly-*fac*-**2**-*co*-**3** (1:20)	44 100	54 300	1.23	−44	374

determine molecular weights and polydispersities. The fact that all polymers eluted fully to give baseline-resolved mono- or multimodal signals was unexpected, as it is commonly known for most charged metal-containing polymers that if any sample comes through the columns at all the data will likely be entirely undecipherable due to the formation of either aggregates or at least strong interactions of the metal complex with the stationary phase.[13] This problem can be circumvented for polymers containing a single metal complex by doping the mobile phase with ammonium hexafluorophosphate.[13] However, poly-**1** could be fully characterized using GPC in methylene chloride, with no dopant added to the mobile phase, even though every repeat unit contains a charged moiety. The homopolymer poly-**1** showed the lowest polydispersity index (PDI) with 1.39. A PDI of 1.71 was observed for the 1:2 copolymer of **1** with **3**, while a PDI of 2.55 was observed for the 1:20 copolymer. Copolymers of *fac*-**2** with **3** showed more narrow distributions and lower PDI's. The 1:2 copolymer had a PDI of 1.16, and the 1:20 copolymer had a PDI of 1.23.

The insolubility of the homopolymer of *fac*-**2** was unexpected on the basis of the good solubility of poly-*mer*-**2**. This polymer's insolubility may be due to several factors. First, because of the anionic nature of the phenylpyridine ligand, a relatively strong dipole is created in the facial configuration since the anionic carbon bound to the metal exists on the same face of the molecule for all three ligands. In fact, for the small molecule *fac*-$\mathrm{Ir(ppy)_3}$, a quite large dipole moment of 6.5 D has been calculated.[14] In the homopolymer, when these complexes are forced to be in close proximity along the backbone, aggregation may occur as a result. Conversely, the meridional configuration has anionic carbons that are trans to each other, canceling out any dipolar effects created by two out of the three ligands. This trans effect also causes lengthening of these carbon−iridium organometallic bonds (2.07−2.08 Å),[15] thus distributing the anionic character of the ligands more evenly around the periphery of the complex while maintaining the positive metal center on the interior. These solubility problems were not observed in the case of the monomer *fac*-**2**, or any of its copolymers with **3**, indicating that the insolubility is directly an effect of restraining these complexes into very close proximity with each other in nonpolar solvents, as is the case with the homopolymer only.

There were no distinct glass transition temperatures observable for any of the homopolymers as well as the 1:20 copolymers of **3** with **1** or **2**. However, for the 1:20 copolymer of *fac*-**2** with **3**, a glass transition of −44 °C was observed. The 1:2 copolymers of **3** with **1**, *mer*-**2**, and *fac*-**2** all exhibited distinct T_g values of 10, −43, and −53 °C, respectively. These values may reflect the differences caused by incorporation of a charged polymer (poly-**1** series) compared with a neutral polymer (*mer*- and *fac*-poly-**2** series). In all cases, the polymers exhibited progressively higher decomposition temperatures as the amount of comonomer **3** increased.

Photophysical Properties. The agreement of the luminescent data between the well-studied small phosphorescent iridium complexes and our polymeric material in solution and in the solid state is crucial to the potential development and realization of polymeric OLEDs. In acetonitrile, $\mathrm{Ir(ppy)_2(bpy)(PF_6)}$ has been reported to emit strongly at 606 nm,[16] while *tert*-butyl substitution at the bipyridinyl 4- and 4′-positions gives rise to an emission maximum at 581 nm,[2g] suggesting that alkylation at the *para*-positions of the bipyridine has a blue-shifting effect on the emissive properties of the complex. We measured an emission maximum of 555 nm for compound **1** (Table 2, Figure 3), suggesting that the employment of the norbornenyl ester in close proximity to the emissive complex is responsible for the observed change in wavelength. Poly-**1** has an emission maximum of 556 nm, as do all copolymers of **1** with alkyl spacer monomer **3** (Table 2, Figure 3). The emission quantum yield for **1** of 0.236 is nearly identical to previously reported values in the literature of 0.235 for the *tert*-butyl analogue,[2g] while the luminescence lifetime for **1** (534 ns) was also similar to the small molecule analogue (557 ns). In the solid state, poly-**1** exhibited an emission at 545 nm for the homopolymer and 540 and 531 nm for the copolymers as incorporation of **3** increased (Table 3, Figure 4). This observation is consistent with previously reported trends that show that the emission wavelength is strongly dependent upon the local environment and that a blue shift is observed upon dilution of the luminescent monomer concentration in a copolymer.[2g,7b,17] Similar shifts in

Table 2. Solution Photophysical Data for Compounds 1−3 and Their Corresponding Polymers

complex	λ_{abs},[g] nm	λ_{em}, nm	Φ[h]	τ (μs)[e]	τ (μs)[f]
1		556,[a] 551[b]	0.236[a]	0.145	0.534
poly-**1**[i]		555,[a] 551[b]	0.278[a]	0.207	0.549
poly-**1**-*co*-**3** (1:2)		556,[a] 552[b]	0.225[a]	0.138	0.413
poly-**1**-*co*-**3** (1:20)		557,[a] 554[b]	0.238[a]	0.148	0.486
mer-**2**		546,[a] 543,[b] 537,[c] 540[d]	0.034[a]	0.049	0.498
mer-poly-**2**	388[a]	519,[a] 538,[b] 511,[c] 545[d]	0.022[a]	0.031	0.619
mer-poly-**2**-*co*-**3** (1:2)	385[a]	517,[a] 541[b]	0.025[a]	0.041	0.222
mer-poly-**2**-*co*-**3** (1:20)	385[b]	540[b]	0.022[b]	0.048	0.350
fac-**2**	373[a]	543,[a] 515[b]	0.219[a]	0.033	1.48
fac-poly-**2**					
fac-poly-**2**-*co*-**3** (1:2)	293,[a] 377[a]	517,[a] 515[b]	0.243[b]	0.045	1.28
fac-poly-**2**-*co*-**3** (1:20)	377[b]	514[b]	0.201[b]	0.045	1.43

[a] Acetonitrile. [b] Dichloromethane. [c] Toluene. [d] Dimethyl sulfoxide. [e] THF, ambient conditions. [f] THF, degassed. [g] Most samples showed broad absorbance range with no clear local maximum. [h] Relative to $\mathrm{Ru(bpy)_3(PF_6)_2}$. [i] Lifetimes measured in dichloromethane.

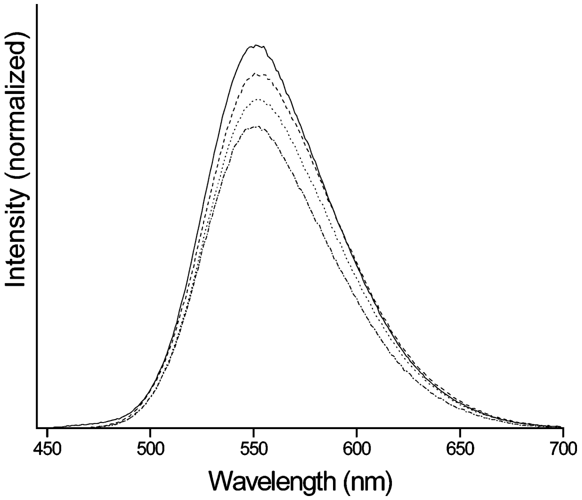


Figure 3. Solution PL emission spectra of (from top to bottom): **1**, poly-**1**, poly-**1**-*co*-**3** (1:2), and poly-**1**-*co*-**3** (1:20) in dichloromethane (ex 400 nm).

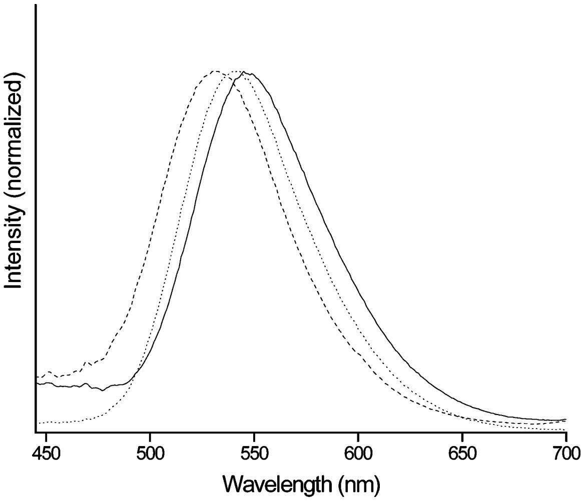


Figure 4. Solid-state PL emission spectra of (right to left): poly-**1**, poly-**1**-*co*-**3** (1:2), and poly-**1**-*co*-**3** (1:20) (ex 400 nm).

Table 3. Solid-State Photophysical Data for All Polymers

polymer	λ_{em} (nm)	polymer	λ_{em} (nm)
1	545	*mer*-**2**-*co*-**3** (1:20)	534
1-*co*-**3** (1:2)	540	*fac*-**2**	
1-*co*-**3** (1:20)	531	*fac*-**2**-*co*-**3** (1:2)	521
mer-**2**	550	*fac*-**2**-*co*-**3** (1:20)	513
mer-**2**-*co*-**3** (1:2)	543		

solid-state emission were observed for polymers of both *mer*-**2** (Figure 5) and *fac*-**2** (Figure 6) as well.

It has been well documented that in dichloromethane, at room temperature, *fac*-Ir(ppy)$_3$ emits strongly at 510 nm,[18] with emission quantum yields as high as 0.40, while *mer*-Ir(ppy)$_3$ emits at 512 nm with lower quantum yields of 0.036.[15] This difference in emission quantum yields, brought about by the large discrepancy in nonradiative decay rates (more than an order of magnitude between facial and meridional Ir(ppy)$_3$), lessens significantly as the temperature decreases from 298 to 77 K, where both complexes are strongly luminescent.[15] We observed similar differences in our observations of the luminescent intensities of polymers containing *mer*-**2** (Figure 7) vs polymers containing *fac*-**2** (Figure 8) in solution as well as in the solid state at room temperature. In accordance with the aforementioned literature trends, *fac*-**2** was significantly more emissive, with an emission quantum yield of 0.219 in acetonitrile. Copolymers of *fac*-**2** with **3** in a 1:2 ratio and 1:20 ratio gave quantum yields of 0.243 and 0.201, respectively. *mer*-

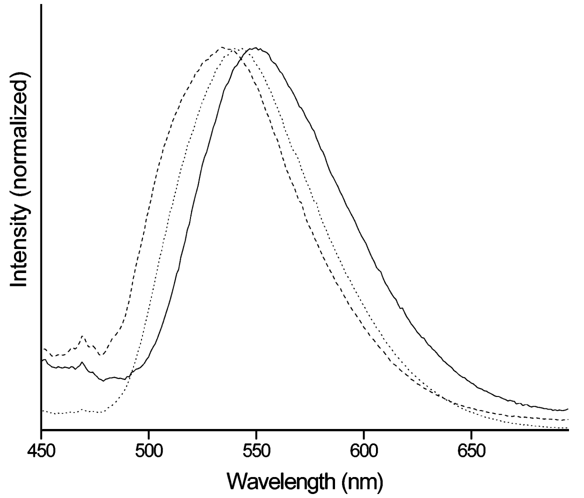


Figure 5. Solid-state PL emission spectra of (from right to left): *mer*-poly-**2**, *mer*-poly-**2**-*co*-**3** (1:2), and *mer*-poly-**2**-*co*-**3** (1:20) (ex 380 nm).

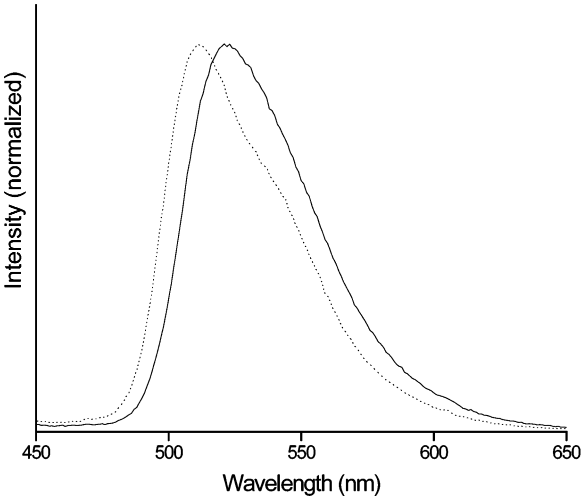


Figure 6. Solid-state PL emission spectra of (from right to left): *fac* -poly-**2**-*co*-**3** (1:2) and *fac*-poly-**2**-*co*-**3** (1:20) (ex 380 nm).

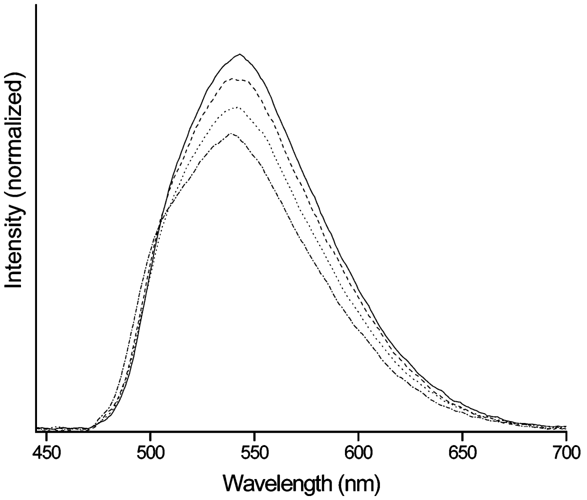


Figure 7. Solution PL emission spectrum of (from top to bottom): *mer*-**2**, *mer*-poly-**2**, *mer*-poly-**2**-*co*-**3** (1:2), and *mer*-poly-**2**-*co*-**3** (1:20) in dichloromethane (ex 380 nm).

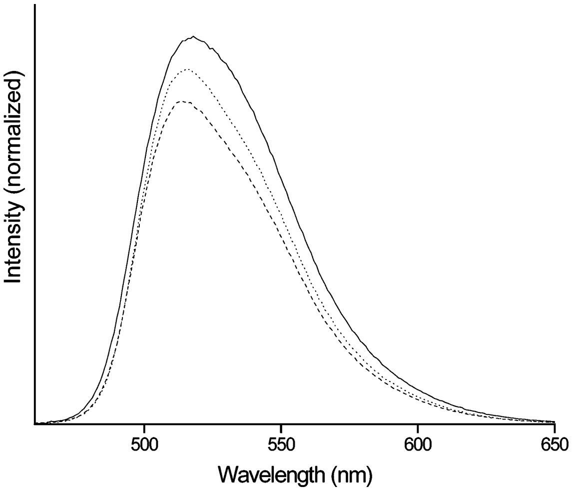


Figure 8. Solution PL emission spectrum of (from top to bottom): *fac*-**2**, *fac*-poly-**2**-*co*-**3** (1:2), and *fac*-poly-**2**-*co*-**3** (1:20) in dichloromethane (ex 380 nm).

2, however, showed a much lower emission quantum yield of 0.034 in acetonitrile. Both homo- and copolymers containing this complex showed slightly lower quantum yields of 0.022−0.025.

The emission maximum for *mer*-**2** and its polymers in acetonitrile was shifted substantially from that expected from the small molecule analogue *mer*-Ir(ppy)$_3$. The only structural difference between *mer*-**2** and the previously reported *mer*-Ir(ppy)$_3$ complex is the addition of the norbornenyl ester *para* to the pyridine on the phenyl group of one of the ppy ligands, although it is electronically separated from the metal complex by a methylene linkage. Despite the expected insulating effect of the methylene unit, a red shift of the emission wavelength from that reported in the literature for the unsubstituted *mer*-Ir(ppy)$_3$ complex (512 nm) to 543 nm is observed. However, when comparing emission spectra for *mer*-**2** and its polymers in various solvents, it becomes evident that the emission from the *mer*-complex is comprised of two different emission maxima: one occurring in the expected range of 510−515 nm and another occurring in the range of 538−546 nm. Depending on the choice of solvent, the intensities of each vary with respect to one another (Figure 9). In dichloromethane (538 nm) or dimethyl sulfoxide (545 nm), the emission for poly-*mer*-**2** is broad and significantly red-shifted from that expected on the basis of the literature reported small molecule by as much as 30 nm in some instances. There is a small shoulder to the left, appearing in the range normally expected for the major signal in the previously reported small molecule. Conversely, in toluene, the emission (510 nm) closely resembles that of the facial complex. It is narrower, with a shoulder to the right, in the range of the other signal observed for the more polar solvents described above. Finally, in acetonitrile, there is a broad emission maximum observed, which appears to span nearly equally the two different emissions observed for the other solvents (516−540 nm). It is interesting to note that in the case of *mer*-**2** this solvent dependence was not observed, and the emission maximum in all four solvents mentioned above remained in the range of 537 nm (toluene) to 546 nm (acetonitrile). Table 4 lists the corresponding lifetimes for each of the aforementioned solvents. In the case of the two solvents that exhibit the most strongly red-shifting effects on the emission, namely dichloromethane and dimethyl sulfoxide, the lifetimes are also markedly different from the other entries, both showing a significant decrease. Neither toluene nor acetonitrile showed the same lowering effect on the excited-state lifetimes for poly-*mer*-**2**.

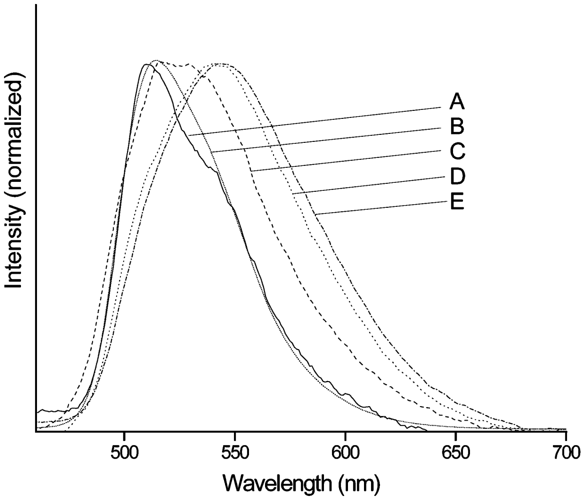


Figure 9. Solvent dependence for *mer*-poly-**2**: A (toluene), C (acetonitrile), D (dichloromethane), E (dimethyl sulfoxide), B (*fac*-**2** in dichloromethane, for comparison).

Table 4. Lifetimes (in μs) Measured for *mer*-2 and Poly-*mer*-2 in Various Solvents, Both in Ambient Conditions and Degassed

	mer-**2**		*mer*-poly-**2**	
solvent	air	degassed	air	degassed
CH_2Cl_2	0.069	0.516	0.042	0.133
DMSO	0.211	0.62	0.145	0.286
CH_3CN	0.022	0.481	0.002	0.717
toluene	0.036	0.348	0.028	0.791

In the *mer*-configuration of Ir(ppy)$_3$, when one ligand is modified as in the case with *mer*-**2**, there are two diastereomers possible. However, since the monomer *mer*-**2** does not show the same solvent-dependent behavior as in the polymer, the observed differences in emission for *mer*-poly-**2** are more likely due to conformational differences in the polymer architecture brought about by the changes in the environment as a result of varying the solvent. Specifically, acetonitrile is a good solvent for the emissive complex but a poor solvent for the poly(norbornene) backbone. Both dichloromethane and dimethyl sulfoxide are good solvents for both the metal complex and the polymer backbone, and toluene is a poor to average solvent for both the complex and the backbone. The various combinations above can create a wide variety of polymer conformations in solution, causing differences in interchromophore distances, potentially giving rise to the observed variations in emission wavelength.

Conclusions

We have demonstrated the ROMP polymerization of several iridium complex containing monomers, their solubility in nonpolar solvents, and the retention of luminescent properties by the emissive complexes both as polymers in both solution and the solid state. The results described herein lay the foundation for further steps into device fabrication using these materials, providing simplification and improvements to the process of polymerizing highly emissive phosphorescent iridium complexes.

Experimental Section

General Methods. All reagents were purchased either from Acros Organics or Aldrich and used without further purification. DMF and $CDCl_3$ were distilled from calcium hydride and degassed prior to use. THF was dried via passage through copper oxide and alumina columns. NMR spectra were taken using a 300 MHz Varian Mercury spectrometer. All spectra are referenced to residual proton solvent. Mass spectral analyses were provided by the Georgia Tech Mass Spectrometry Facility using a VG-70se spectrometer. Gel permeation chromatography (GPC) analyses were carried out using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector with methylene chloride as an eluant on American Polymer Standards 10 μm particle size, linear mixed bed packing columns. All GPCs were calibrated using poly(styrene) standards. Atlantic Microlabs, Norcross, GA, performed all elemental analyses. UV/vis absorption measurements were taken on a Shimadzu UV-2401 PC recording spectrophotometer. Emission measurements were acquired using a Shimadzu RF-5301 PC spectrofluorophotometer. Lifetime measurements were taken using a PTI model C-72 fluorescence laser spectrophotometer with a PTI GL-3300 nitrogen laser. DSC data were collected using a Seiko model DSC 220C. TGA data were collected using a Seiko model TG/DTA 320.

***exo*-Bis(2-phenyl-pyridine)iridium(III) Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 1-Methyl-3-(3-methyl-[2,3′]bipyridinyl-4′-yl)propyl Ester Hexafluorophosphate (1).** Compound **5** (910 mg, 2.51 mmol) and $[Ir(ppy)_2Cl]_2$ (615 mg, 1.14 mmol Ir) were combined in degassed ethylene glycol (10 mL) and refluxed for 24 h under an argon atmosphere. The reaction mixture was then removed from the heat and allowed to cool to room temperature followed by the addition of NH_4PF_6 (1.7 mL of a 1.0 mM aqueous solution). The reaction mixture was then extracted with methylene chloride and washed three times with water and dried with $MgSO_4$, and the solvent was removed to give crude **1**, which was purified via column chromatography (silica, 98:2 CH_2Cl_2/EtOH) to give compound **1** as a bright yellow powder (830 mg, 0.82 mmol, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.48$ (m, 2H); 7.91 (s, br, 1H); 7.88 (s, br, 1H); 7.80−7.71 (m, 4H); 7.66 (d, 2H, $J = 7.5$ Hz); 7.54−7.49 (m, 2H); 7.21−7.17 (m, 2H); 7.06−7.02 (m, 2H); 6.99 (dt, 2H, $J_1 = 7.4$ Hz, $J_2 = 0.9$ Hz); 6.88 (dt, 2H, $J_1 = 7.5$ Hz, $J_2 = 1.1$ Hz); 6.29 (dd, 2H, $J_1 = 7.4$ Hz, $J_2 = 3.8$ Hz); 6.13−6.08 (m, 2H); 4.93 (m, 1H); 3.02 (s, 1H); 2.90 (m, 3H); 2.57 (s, 3H); 2.08−1.96 (m, 2H); 1.92−1.85 (m, 1H); 1.70 (s, br, 1H); 1.49 (m, 1H); 1.36 (m, 2H); 1.28 (dt, 3H, $J_1 = 6.2$ Hz, $J_2 = 1.7$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 176.2$, 168.0, 167.9, 156.0, 155.5, 155.4, 152.5, 150.8, 150.0, 149.8, 148.8, 143.8, 138.3, 138.2, 136.0, 132.0, 131.9, 130.9, 129.1, 128.3, 128.3, 126.1, 125.2, 124.9, 123.6, 122.7, 119.8, 70.0, 46.9, 46.6, 46.5, 43.6, 41.9, 41.8, 35.7, 31.4, 30.6, 30.6, 21.6, 20.0. MS (ESI) 863.3 (M − loss of PF_6^-). Elemental analysis for $C_{45}H_{42}F_6IrN_4O_2P$: Calcd: C, 53.62; H, 4.20; N, 5.56. Found: C, 53.63; H, 4.21; N, 5.42.

***mer-exo*-Bis(2-phenyl-pyridine)iridium(II) Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 4-Pyridin-2-yl-benzyl Ester (*mer*-2).** $[Ir(ppy)_2Cl]_2$ (100 mg, 0.187 mmol Ir) was treated with silver triflate in 5 mL of refluxing acetone for 2 h in the dark. The reaction mixture was then filtered, and the filtrate was combined with compound **7** (114 mg, 0.37 mmol). Immediately, 0.1 mL of triethylamine was added, causing the reaction to turn instantly from light yellow to deep orange and turbid. The reaction was left to stir under argon at ambient temperature overnight. Then the solvent was removed, and the residue was purified via column chromatography (neutral alumina, 1:1 hexane/dichloromethane) to give *mer*-**2** in 43% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.08$ (d, 1H, $J = 5.8$ Hz); 7.92 (m, 1H); 7.78 (m, 2H); 7.63 (m, 2H); 7.63 (m, 1H); 7.57 (m, 1H); 7.49 (m, 2H); 6.93 (m, 3H); 6.81 (m, 1H); 6.71 (m, 1H); 6.60 (m, 1H); 6.39 (m, 1H); 6.11 (m, 2H); 4.95 (m, 2H); 2.97 (s, br, 1H); 2.89 (s, br, 1H); 2.18 (m, 1H); 1.89 (m, 1H); 1.34 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 167.0$, 166.5, 161.7, 161.3, 161.0, 147.3, 147.2, 143.9, 143.8, 137.5, 137.4, 137.3, 136.2, 136.1, 136.0, 133.1, 130.1, 130.0, 124.1, 124.0, 122.2, 122.1, 120.1, 120.0, 119.4, 119.0, 118.9, 66.6, 49.8, 45.9, 43.5, 42.8, 29.4. Elemental analysis for $C_{42}H_{43}IrN_3O_2$: Calcd: C, 62.67; H, 4.26; N, 5.22. Found: C, 62.19; H, 4.35; N, 4.89.

***fac-exo*-Bis(2-phenyl-pyridine)iridium(II) Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 4-Pyridin-2-yl-benzyl Ester (*fac*-2).** Compound **8** (200 mg, 0.24 mmol), *exo*-5-norbornene-2-carboxylic acid (40 mg, 0.24 mmol), and dimethylaminopyridine (DMAP) (17 mg, 0.12 mmol) were combined in 15 mL of dichloromethane. A solution of dicyclohexylcarbodiimide (DCC) (60 mg, 0.24 mmol) in 5 mL of dichloromethane was added, and the reaction was stirred under argon at ambient temperature for 24 h. The solvent was evaporated, and the residue was purified via column chromatography (neutral alumina, 1:1 hexane/dichloromethane) to give *fac*-**2** as a bright yellow powder in 40% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta =$ 7.79−7.75 (m, 3H); 7.64−7.59 (m, 3H); 7.50−7.39 (m, 6H); 6.92−6.85 (m, 8H); 6.83−6.77 (m, 3H); 6.17−6.08 (m, 2H); 4.98 (d, 1H, $J = 12.8$ Hz); 4.92 (dd, 1H, $J_1 = 12.7$ Hz, $J_2 = 1.8$ Hz); 2.99 (s, br, 1H); 2.90 (s, br, 1H); 2.20 (dd, 1H, $J_1 = 10.1$ Hz, $J_2 = 4.4$ Hz); 1.93−1.86 (m, 1H); 1.56 (m, 1H); 1.47 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 176.3$, 166.8, 166.4, 161.8, 161.3, 161.0, 147.2, 144.0, 143.9, 138.4, 138.2, 137.4, 137.3, 137.3, 136.2, 135.9, 130.1, 130.0, 129.9, 128.9, 124.1, 122.3, 122.2, 120.2, 120.1, 119.5, 119.0, 67.0, 64.1, 46.9, 46.7, 43.5, 43.4, 41.9, 30.7, 30.6, 30.5, 27.2. Elemental analysis for $C_{42}H_{43}IrN_3O_2$: Calcd: C, 62.67; H, 4.26; N, 5.22. Found: C, 62.30; H, 4.36; N, 4.88.

4-(Methyl-[2,3′]bipyridinyl-4′-yl)-butan-2-ol (4). Diisopropylamine (1.41 g, 13.9 mmol) was dissolved in 30 mL of dry THF under argon and cooled to 0 °C. *n*-Butyllithium (10 M solution in hexanes, 1.39 mL, 13.9 mmol) was added, and the reaction was stirred for 20 min. The resulting in-situ-generated lithium diisopropylamide was then cooled to −78 °C, and a solution of 4,4′-dimethyl-2,2′-dipyridyl (2.5 g, 13.6 mmol) was added dropwise over a period of 10 min. The reaction was stirred for 30 min, allowed to warm to 0 °C, and then cooled to −20 °C. A solution of propylene oxide (788 mg, 13.6 mmol) in 70 mL of THF was added dropwise over a period of 30 min, and the reaction was stirred for 1 h. The reaction mixture was quenched by slow addition of 10 mL of water, followed by 70 mL of aqueous pH 7 phosphate buffer. The mixture was extracted three times with diethyl ether, the combined organic layers dried with $MgSO_4$, the solvent removed, and the resulting residue subject to column chromatography (neutral alumina, 1:1 hexane/EtOAc) to remove less polar impurities (r_f 0.5), while the product remained on the baseline. Pure **4** was subsequently eluted (r_f 0.5) by flushing the column with a 20:1 mixture of EtOAc/EtOH to give 2.40 g (9.90 mmol, 73%) of the target compound as a slightly yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.49$ (dd, 2H, $J_1 = 8.1$ Hz, $J_2 = 5.0$ Hz); 8.18 (d, 2H, $J = 4.2$ Hz); 7.09 (dt, 2H, $J_1 = 4.9$ Hz, $J_2 = 1.6$ Hz); 3.78 (sextet, 1H, $J = 6.1$ Hz); 2.76 (m, 2H); 2.39 (s, 3H); 1.80 (m, 2H), 1.17 (d, 3H, $J = 6.2$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 156.3$, 156.2, 152.6, 149.3, 149.1, 148.5, 124.9, 124.2, 122.3, 121.6, 67.2, 39.8, 31.9, 24.0, 21.4. MS (ESI) 243.1 (M + 1).

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 1-Methyl-3-(3-Bicyclo-[2,3′]bipyridinyl-4′-yl)propyl Ester (5).** Compound **4** (2.00 g, 8.25 mmol), *exo*-5-norbornene-2-carboxylic acid (1.14 g, 8.25 mmol), and DMAP (50 mg, 0.41 mmol) were combined in 50 mL of dichloromethane at ambient temperature under argon. A solution of DCC (1.74 g, 8.42 mmol) in 30 mL of dichloromethane was added, and the reaction mixture was stirred overnight. The resulting white precipitate was filtered off, and the solvent was removed. The residue was purified using column chromatography (neutral alumina, 5:1 hexane/EtOAc) to yield two distinct compounds that eluted together. The impurity was removed by repeated reprecipitation from hot hexanes, while pure **5** remained fully soluble. Compound **5** was collected as a slightly yellow oil (1.27 g, 3.50 mmol, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.55$ (m, 2H); 8.23 (s, br, 2H); 7.13 (m, 2H); 6.13 (m, 2H); 4.98 (sextet, 1H, $J = 6.3$ Hz); 3.03 (d, br, 1H, $J = 4.5$ Hz); 2.92 (s, br, 1H), 2.75

(m, 2H); 2.44 (s, 3H); 2.20 (m, 1H); 1.96 (m, 3H); 1.52 (m, 1H), 1.39 (m, 2H); 1.27 (dd, 3H, $J_1 = 6.3$ Hz, $J_2 = 1.1$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 175.9$, 156.4, 156.0, 151.8, 149.3, 149.0, 148.3, 138.2, 135.9, 124.9, 124.0, 122.2, 121.1, 70.4, 47.0, 46.7, 43.8, 43.7, 42.0, 37.0, 36.9, 31.9, 30.7, 21.6, 20.5. MS (ESI) 363.2 (M + 1). Elemental analysis for $C_{23}H_{26}N_2O_2$: Calcd: C, 76.21; H, 7.23; N, 7.73. Found: C, 75.56; H, 7.38; N, 7.73.

(4-Pyridin-2-yl-phenyl)methanol (6). A solution of 4-pyridin-2-yl-benzaldehyde (2.00 g, 10.9 mmol) in 20 mL of dry THF was added dropwise over a period of 10 min to a stirred suspension of lithium aluminum hydride (829 mg, 21.8 mmol) in 80 mL of dry THF at 0 °C under an argon atmosphere. After complete addition, the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The solution was then cooled again to 0 °C, and the reaction mixture was carefully quenched by the slow addition of 10 mL of 1 N HCl. The mixture was diluted with diethyl ether, washed twice with neutral phosphate buffer (pH 7.0) and once with brine, and dried over $MgSO_4$, the solvent was removed, and the residue was purified by column chromatography (silica gel, ethyl acetate/hexanes 1:2) to yield **6** as a slightly yellow oil (1.90 g, 10.2 mmol, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.66$ (ddd, 1H, $J_1 = 4.9$ Hz, $J_2 = 1.7$ Hz, $J_3 = 0.9$ Hz); 7.91 (d, 2H, $J =$ 8.3 Hz); 7.72 (m, 2H); 7.41 (d, 2H, $J = 8.4$ Hz); 7.22 (ddd, 1H, $J_1 = 6.9$ Hz, $J_2 = 4.8$ Hz, $J_3 = 1.6$ Hz); 4.71 (s, 2H); 2.82 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 157.4$, 149.6, 142.3, 142.2, 138.5, 138.4, 137.1, 127.4, 127.2, 122.3, 121.0, 64.9. MS (ESI) 185.9 (M + 1).

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 4-Pyridin-2-ylbenzyl Ester (7).** Compound **6** (1.50 g, 8.10 mmol), *exo*-5-norbornene-2-carboxylic acid (1.12 g, 8.10 mmol), and DMAP (10 mg, 0.081 mmol) were combined in 50 mL of dichloromethane under argon. Then a solution of DCC (1.68 g, 8.18 mmol) in 30 mL of dichloromethane was added, and the reaction mixture was stirred overnight at ambient temperatures. A white precipitate formed during the reaction which was filtered off. The solvent was removed and the residue subject to column chromatography (basic alumina, 7:1 hexane/EtOAc) to yield **7** as a clear oil (1.98 g, 6.48 mmol, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.69$ (ddd, 1H, $J_1 = 4.8$ Hz, $J_2 = 1.7$ Hz, $J_3 = 1.0$ Hz); 8.00 (d, 2H, $J = 8.4$ Hz); 7.74 (m, 2H); 7.45 (d, 2H, $J = 8.4$ Hz); 7.23 (ddd, 1H, $J_1 = 7.1$ Hz, $J_2 = 4.9$ Hz, $J_3 = 2.2$ Hz); 6.12 (m, 2H); 5.19 (s, 2H); 3.08 (s, 1H); 2.93 (s, 1H); 2.30 (m, 1H); 1.95 (dt, 1H, $J_1 = 11.8$ Hz, J_2 = 3.6 Hz); 1.54 (m, 1H); 1.39 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 176.1$, 157.1, 149.9, 139.4, 138.3, 137.2, 137.0, 135.9, 128.6, 127.3, 122.4, 120.7, 66.2, 47.0, 46.7, 43.5, 42.0, 30.8. MS (ESI) 306.1 (M + 1). Elemental analysis for $C_{20}H_{19}NO_2$: Calcd: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.35; H, 6.36; N, 4.63.

***fac*-Bis(2-phenylpyridine)-*p*-hydroxymethyl-2-(pyridyl)-benzene Iridium (III) (8).** *fac*-Ir(ppy)$_2$(fppy) (0.20 mg, 0.29 mmol) was dissolved in 30 mL of tetrahydrofuran (THF), and 8.8 mL (3-fold excess) of lithium aluminum hydride (0.1 M solution in THF) was added dropwise, upon which the solution turned immediately from bright orange-red to yellow-green. The reaction mixture was stirred at ambient temperatures for 1 h and then quenched by the addition of ethyl acetate. The crude material, which showed no remaining aldehyde signal by ^{1}H NMR, was dissolved in dichloromethane and washed three times with water, dried with $MgSO_4$, and used without further purification.

General Polymerization Procedure. Polymerizations were carried out under argon, at ambient temperatures, in dichloromethane, at concentrations of 0.2 M in monomer. All polymers were synthesized on an ~50 mg scale with a monomer-to-catalyst ratio of 50:1. All polymers were purified by precipitation into either methanol or diethyl ether.

Poly-1. ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 8.44$ (m, 2H); 7.93−7.74 (m, 8H); 7.53 (m, 2H); 7.23 (m, 3H); 7.02 (m, 5H); 6.91 (m, 1H); 6.34 (m, 2H); 5.45−5.16 (m, 2H); 4.91 (m, 1H); 3.21−2.71 (m, 4H); 2.56 (m, 5H); 1.97 (m, 3H); 1.66 (m, 2H); 1.23 (m, 5H). ^{13}C NMR (CD_2Cl_2, 100 MHz): $\delta = 167.9$, 155.9, 155.6, 152.3, 150.8, 150.3, 150.0, 148.8, 144.0, 138.4, 131.9, 130.7, 129.2, 128.4, 125.7, 125.0, 124.9, 123.6, 122.7, 120.0, 65.9, 37.3, 35.8, 31.5, 21.4, 21.3, 20.1, 19.9, 19.8.

Poly-1-*co*-3 (1:2). ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 8.42$ (m, 0.6H); 7.95 (m, 0.6H); 7.87−7.73 (m, 1.3H); 7.53 (m, 0.6H); 7.25 (m, 0.6H); 7.03 (m, 0.9H); 6.94 (m, 0.6H); 6.34 (m, 0.6H); 5.50−5.15 (m, 2H); 4.95 (m, 0.4H); 3.99 (m, 1.2H); 3.16 (0.6H); 2.90−2.65 (m, 1.8H); 2.41 (m, 1.5H), 1.97 (m, 2H); 1.82−1.48 (m, 2H); 1.30 (m, 5.5H); 0.91 (m, 1.9H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 175.7$, 174.8, 168.0, 156.0, 155.5, 152.3, 150.7, 150.4, 150.1, 148.8, 144.0, 138.3, 134.7, 133.6, 132.9, 131.9, 130.8, 129.2, 128.4, 125.7, 125.0, 124.7, 123.5, 122.7, 120.0, 64.4, 48.7, 41.5, 36.8, 32.0, 31.4, 29.4, 28.9, 26.3, 26.2, 22.9, 21.4, 15.3, 14.1.

Poly-*mer*-2. ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 9.27$ (d, 1H, $J = 5.7$ Hz); 8.05 (m, 1H); 7.97−7.88 (m, 2H); 7.82 (t, 1H, $J =$ 7.7 Hz); 7.68 (m, 2H); 7.58 (d, 2H, $J = 7.8$ Hz); 7.46−7.07 (m, 2H); 7.00−6.71 (m, 7H); 6.65−6.50 (m, 3H); 6.38 (m, 1H); 5.90 (d, 1H, $J = 7.7$ Hz); 5.40−4.81 (m, 2H); 3.13 (m, 2H); 2.73−2.31 (m, 2H); 2.10−1.78 (m, 2H); 1.62 (m, 2H); 1.18 (m, 1H). ^{13}C NMR (CD_2Cl_2, 100 MHz): $\delta = 168.2$, 151.7, 145.0, 144.2, 136.9, 130.6, 129.3, 124.4, 123.9, 122.8, 121.6, 118.9, 47.1, 8.7.

Poly-*mer*-2-*co*-3 (1:2). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta =$ 9.22 (d, 0.3H, $J = 5.5$ Hz); 8.08 (m, 0.2H); 7.87 (m, 0.4H); 7.73 (m, 0.5H); 7.54 (m, 0.6H); 7.22 (m, 0.4H); 6.95−6.68 (m, 1.2H); 6.55 (m, 0.3H); 6.37 (m, 0.2H); 5.92 (d, 0.2H, $J = 7.8$ Hz); 5.50−4.79 (m, 2H); 3.99 (m, 1.3H); 3.06 (m, 0.8H); 2.85 (m, 0.9H); 2.50 (m, 0.5H); 1.98 (m, 1H); 1.74 (m, 0.4H); 1.60 (m, 1.1H); 1.32 (m, 7.1H); 0.88 (m, 1.8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 174.8, 168.7, 153.4, 151.8, 145.5, 143.9, 137.4, 136.5, 134.7, 133.5, 132.9, 130.8, 130.2, 129.9, 129.3, 126.5, 124.4, 123.9, 122.4, 121.5, 118.8, 118.6, 64.6, 48.7, 47.0, 43.1, 40.8, 36.3, 32.0, 29.4, 28.9, 26.3, 26.2, 22.9, 14.4, 8.9.

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Supporting Information Available: Absorption spectra for all functionalized polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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