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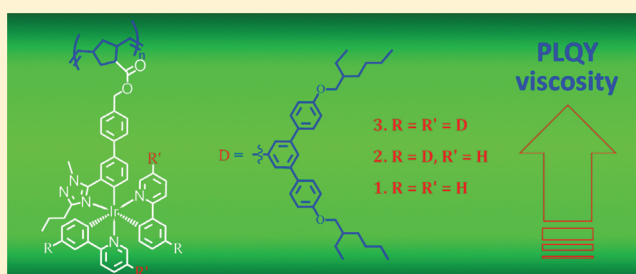
Poly(dendrimers) with Phosphorescent Iridium(III) Complex-Based Side Chains Prepared via Ring-Opening Metathesis Polymerization

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ABSTRACT: Phosphorescent poly(dendrimers) with a norbornene-derived backbone have been synthesized using ring-opening metathesis polymerization with the Grubbs III catalyst. The dendrimers are comprised of a heteroleptic iridium(III) complex core with two 2-phenylpyridyl ligands and a phenyltriazolyl ligand, biphenyl-based dendrons, and 2-ethylhexyloxy surface groups. The phenyltriazolyl ligand provides the attachment point to the polymer backbone, and the two poly(dendrimers) differ in the number of dendrons attached to the 2-phenylpyridyl ligands. The poly(dendrimer) with one and two dendrons per ligand are termed mono- and doubly dendronized. The mono- and doubly dendronized poly(dendrimers) were found to have relatively narrow polydispersities, around 1.4, viscosities approaching those required for inkjet printing, and could be solution processed to form thin films. The dendrons played an important role in controlling the photophysical properties of the materials. The parent homopolymer with the same iridium(III) complex but no dendrons attached to the ligands had a solution photoluminescence quantum yield (PLQY) of 48%. The solution PLQY was found to increase with increasing number of dendrons with the mono- and doubly dendronized materials having solution PLQYs of 65% and 71%, respectively. The increase in PLQY is due to decreased intrachain interchromophore interactions. A similar trend was observed in the solid state with the parent, mono-, and doubly dendronized polymers having film PLQYs of 2%, 44%, and 58%, respectively, demonstrating that both intra- and interchain interactions are controlled by the dendrons.



INTRODUCTION

Organic light-emitting diodes (OLEDs) offer a number of important properties for large-area displays and lighting including low driving voltage, high efficiency, light weight, and fast switching times. Tremendous advances have been achieved in OLEDs containing light-emitting small molecules,¹ polymers,² and dendrimers.^{3,4} Iridium(III) complexes have so far proven to be the most promising candidates as emissive materials in the development of OLEDs because of their high efficiency, relatively short excited state lifetime, and color tunability.^{5–7} The strong spin–orbit coupling of the heavy metal allows efficient intersystem crossing that enables harvesting both the singlet and triplet excitons formed in the OLEDs to give internal quantum efficiencies as high as 100%.^{5b,c} Small molecules are primarily processed by thermal evaporation, while dendrimers and polymers are generally processed from solution at room temperature. Solution processing of materials is desirable since it can simplify the fabrication of large-area OLEDs and lower the cost. However, the ability to combine the high efficiency of iridium(III) complex emitters with processing by printing techniques has continued to prove challenging. Phosphorescent dendrimers are solution processable and have given rise to very efficient

monochrome devices prepared by spin-coating. Inkjet printing is an attractive technique for large area fabrication of pixelated structures on flexible plastic electronics⁸ as it allows more than one material to be deposited at a time, thus limiting the number of processing steps, and it is compatible with roll-to-roll production.⁹ However, the viscosity of dendrimer solutions used for spin-coating is normally similar to that of the solvent itself at the concentrations used,¹⁰ and is not compatible with large-area inkjet printing.

“Light-emitting inks” for inkjet printed OLEDs require good solution processability and suitable viscosity and should give efficient phosphorescence in the solid state. While there has been some effort on polymeric materials containing iridium(III) side chains the main focus has been on random copolymers with low levels of small molecule iridium(III) complexes attached as side chains.^{11–23} The low level of complexes attached to the copolymer is to avoid triplet–triplet annihilation.²⁴ However, the viscosity of the polymers and their potential for printing has not generally been considered. Our

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approach to developing “light-emitting” inks has been to combine the excellent photophysical properties of light-emitting dendrimers with the viscosity imparted by a polymer backbone.²⁵

In this contribution, we demonstrate that ring-opening metathesis polymerization (ROMP) can be used to form sterically encumbered poly(dendrimers) with a relatively narrow poly(dispersity). The structures of poly(dendrimers) are shown in Figure 1, and they are comprised of a norbornenyl

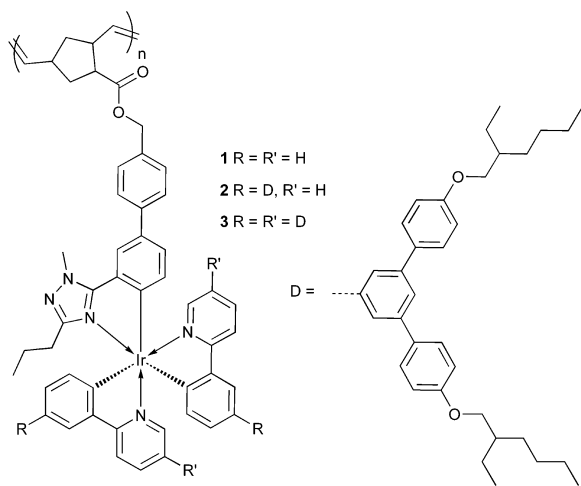


Figure 1. Structures of parent homopolymer **1** and poly(dendrimers) **2** and **3**.

derived backbone and dendrimer “side chains”. The dendrimer side chains have a heteroleptic iridium(III) complex core that utilizes a phenyltriazole ligand as the attachment point to the polymer backbone, and the dendrons are attached to the two 2-phenylpyridyl ligands. We compare the physical and optoelectronic properties of the parent polymer that has the simple small molecule complex (no dendrons) attached to each “monomer unit” (**1** in Figure 1) and two poly(dendrimers) (**2** and **3**, Figure 1). **2** has one first generation biphenyl-based dendron with 2-ethylhexyloxy surface groups attached to each ligand while **3** has two.

RESULTS AND DISCUSSION

Synthesis. The synthetic route to all three polymers followed the same three steps as shown in Scheme 1. The “macromonomer” route was chosen to ensure that every monomer unit in the final polymer had a phosphorescent side chain attached. The syntheses all start from the brominated heteroleptic complexes, **4**, **5**, and **6**, which have been previously reported.^{27–29} Coupling of the heteroleptic iridium(III) complexes **4**, **5**, and **6** with 4-formylphenylboronic acid under Suzuki conditions³⁰ gave compounds **7**, **8**, and **9** in yields of 97%, 77%, and 79%, respectively. The aldehyde group of each compound was then reduced to the corresponding alcohol using lithium aluminum hydride, and subsequent esterification with exo-5-norbornene-2-carboxylic acid gave “macromonomers” **10**, **11**, and **12** in excellent yields of 91%, 100%, and 86%, respectively, over the two steps. “Macromonomers” **10**, **11**, and **12** were then polymerized in chloroform (for **10** and THF for **11** and **12**) at room temperature using the Grubbs III catalyst.³¹ The polymerizations were left for 20 min and quenched by the addition of ethyl vinyl ether. The target

polymers were purified and collected by reprecipitation to give **1**, **2**, and **3** in yields of 94%, 94%, and 94%, respectively.

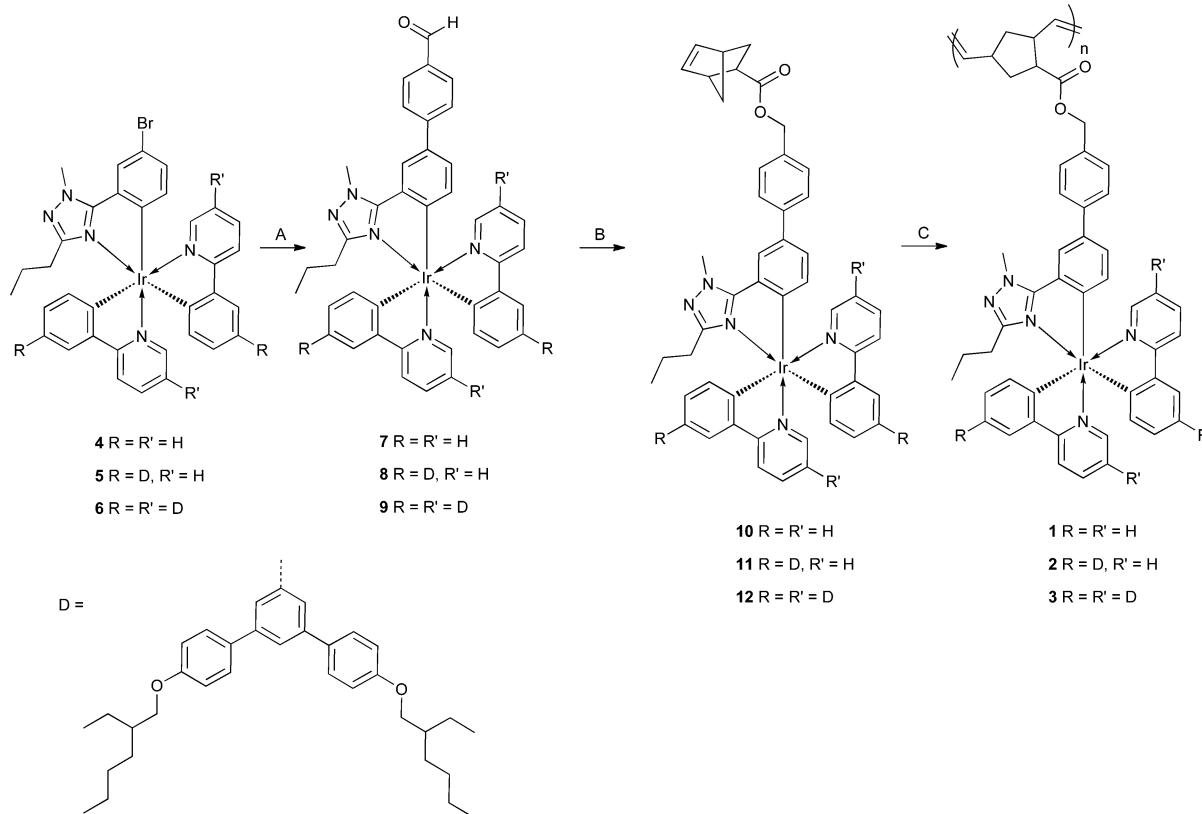
Physical Properties. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards. Polymer **1** had an \bar{M}_w of 14 kDa and a polydispersity of 1.5 while poly(dendrimers) **2** and **3** had \bar{M}_w s of 74 and 65 kDa and polydispersities of 1.3 and 1.4, respectively. It is worthwhile to note that GPC can underestimate the molecular weights by a factor of around 3–4 as found in our previous work.¹⁰ Nevertheless, the low polydispersity of the polymers indicates good control of the polymerizations under the ROMP conditions. The polymers were soluble in common organic solvents such as dichloromethane, chloroform, dichlorobenzene, and tetrahydrofuran, and good-quality films could be formed by spin-coating.

One of the reasons for designing the poly(dendrimers) was to increase their solution viscosity relative to the simple dendrimers. The viscosity of poly(dendrimer) **2** and its corresponding monomer **11** were evaluated at different concentrations in 1,2-dichlorobenzene at 20 °C with deionized freshly distilled water used as the reference³² (1.00 cSt at 20 °C). 1,2-Dichlorobenzene was determined to have a viscosity of 1.06 cSt. At a concentration of 10 mg/mL “macromonomer” **11** had a viscosity of 1.14 cSt while the viscosity of poly(dendrimer) **2** at the same concentration was 1.30 cSt, a 14% increase. At a concentration of 25 mg/mL, the viscosity of **2** increased to 1.41 cSt. At the same concentration (25 mg/mL), a viscosity of 1.50 cSt was determined for poly(dendrimer) **3** (the doubly dendronized material), which is suitable for inkjet printing.²⁹

The final step in the analysis of the physical properties of the materials was a study on their thermal properties. Thermal gravimetric analysis of parent polymer **1** showed a 5% weight loss at 365 °C, whereas poly(dendrimers) **2** and **3** were more stable with similar weight losses not seen until 405 and 421 °C, respectively. Thus, dendronization improves the thermal stability. Differential scanning calorimetry of the three polymers showed no thermal transitions, indicating that the materials were amorphous.

Optoelectronic Properties. The first step in studying the optoelectronic properties of the three polymers was determination of their oxidation potentials using cyclic voltammetry. Parent polymer **1** had an oxidation potential of 0.22 V against the ferrocenium/ferrocene couple. As was expected, addition of the dendrons on the phenyl group of the ligand *para* to the phenyl–iridium(III) bond had little effect on the oxidation potential, which was 0.26 V for poly(dendrimer) **2**. Similarly, the oxidation potential for the doubly dendronized poly(dendrimer) **3** was 0.29 V, which again shows a minimal effect of dendronization is small when the $E^{1/2}(\text{ox})$ is compared with the parent polymer **1**.

The solution absorption spectra of polymers **1**, **2**, and **3** are shown in Figure 2. Each spectrum is comprised of two main regions: at wavelengths greater than 350 nm the relatively weak absorptions are mainly due to the so-called metal-to-ligand charge transfer (MLCT) transitions,³³ while those at shorter wavelengths are dominated by the $\pi-\pi^*$ transitions of the ligands and in the case of poly(dendrimers) **2** and **3** there is also additional absorption due to the chromophores in the dendrons. For poly(dendrimer) **3**, the onset to the absorption was found at about 544 nm, which is about 30 nm red-shifted compared to those of **1** and **2**. The red shift in the onset of absorption indicates a slightly narrower optical gap in **3**, which

Scheme 1^a

^aReagents and conditions: (A) 4-formylphenylboronic acid, Pd(PPh₃)₄, 2 M K₂CO_{3(aq)}, THF (for 8 and 9, and EtOH and toluene for 7), heat, Ar_(g); (B) LiAlH₄, THF then H₂O, rt, Ar_(g), and then *exo*-5-norbornene-2-carboxylic acid, 4-(*N,N*-dimethylamino)pyridine, dicyclohexylcarbodiimide, CH₂Cl₂, rt, Ar_(g); (C) Grubbs III initiator, CHCl₃, rt, Ar_(g).

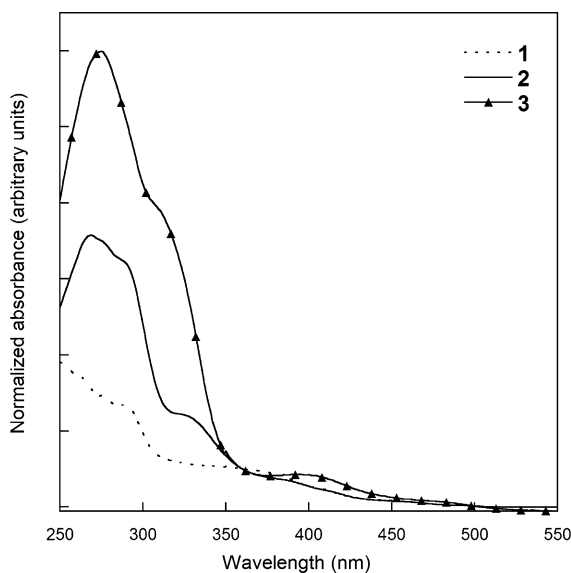


Figure 2. UV-vis absorption spectra of parent polymer 1 and poly(dendrimers) 2 and 3 in dichloromethane, normalized at 360 nm.

is due to the dendron attached to the pyridine moiety of the 2-phenylpyridyl ligand extending the conjugation of the ligand.^{7e}

Figure 3a shows the solution spectra for polymers 1, 2, and 3. In solution, the PL spectra of parent polymer 1 and monodendronized polymer 2 are similar with emission maxima at 514 and 517 nm, respectively. This again reflects the fact that

when the dendron is attached *para* to the phenyl-iridium bond, the conjugation length of the ligand is not significantly increased. In contrast, the solution PL of the doubly dendronized poly(dendrimer) 3 is red-shifted (with an emission maximum at 550 nm) with respect to 1 and 2. As discussed for the absorption spectrum, this is because the first phenyl ring of the dendron attached to the pyridyl ring is now in conjugation with the ligand phenyl ring.

The film PL spectra are shown in Figure 3b. For polymers 2 and 3, the spectra are similar to the solution spectra of the same polymers. However, for small molecule parent polymer 1, the film spectrum is broader than that in solution with a pronounced shoulder and tail on the long wavelength side of the emission, which is attributed to aggregate or excimer emission arising from interchromophore interactions.

To probe the photophysical properties more closely and the role of interchromophore interactions (both intra- and interchain), we measured the PLQYs and PL lifetimes (Figure 4) in solution and the solid-state for the three polymers with the results summarized in Tables 1 and 2. The solution PLQY of the parent complex (Scheme 1, compound 4 but Br = H)²⁸ was 82%. In contrast, polymer 1, which has a complex on every "monomer" unit only has a solution PLQY of 48%. In other systems this has been attributed to intrachain interchromophore interactions.²⁷ In contrast, poly(dendrimer) 2 had a solution PLQY of 65%, which indicates that the dendrons are significantly reducing the intrachain interchromophore interactions. Doubly dendronizing the ligands led to a slight increase in the solution PLQY for poly(dendrimer) 3 to 71%. On the

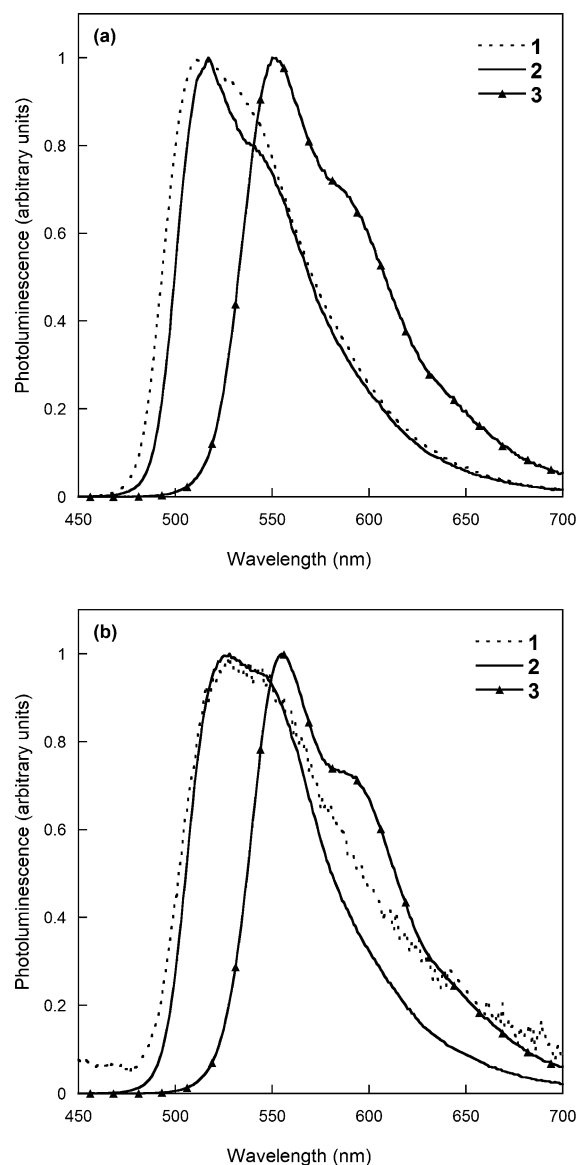


Figure 3. (a) Normalized solution PL spectra of **1**, **2**, and **3**. (b) Normalized film PL spectra of **1**, **2**, and **3**. Excitation wavelength 360 nm for solution and 325 nm for films.

basis of the solution PL measurements and spectra, it might be thought that having one dendron per ligand would be sufficient to control the interactions that govern the photophysical properties of the materials. However, in moving from the solution to the solid state, there is an important difference. For polymer **1**, the neat film is almost nonluminescent with a PLQY of only 2%. The low PLQY for **1** is due to strong intra- and interchain interchromophore interactions. That is, in addition to the intrachain interchromophore interactions seen in solution, there are now interchain interchromophore interactions leading to further pathways for PL deactivation. Addition of a dendron to each 2-phenylpyridyl ligand in poly(dendrimer) **2** partially controls the interchain interchromophore interactions. There is a decrease in PLQY in moving from solution (65%) to the film (44%), but it is much smaller decrease than that of polymer **1**. Finally, the film PLQY of poly(dendrimer) **3** was found to be 58%. This is the highest of all three polymers and demonstrates that the double dendron

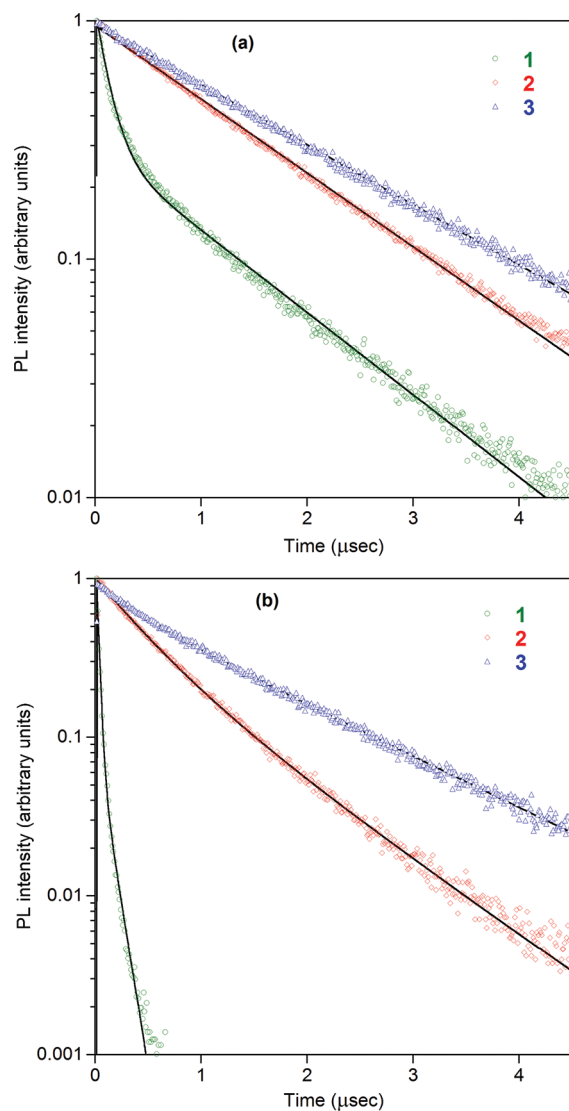


Figure 4. Time-resolved PL intensity of materials **1**, **2**, and **3** in (a) solutions and (b) films. The samples were excited at 393 nm. The emission is collected in each case at the peak of the PL spectra.

strategy is the best in controlling both intra- and interchain interchromophore interactions.

Similar trends are seen in the time-resolved PL (TRPL) measurements. As the light-emitting chromophores are very similar in the three polymers, differences in lifetime are likely to arise from differences in nonradiative decay rate; i.e., faster decay implies more quenching of PL (as a result of interchromophore interactions). The TRPL results for solutions are shown in Figure 4a. The PL decay of **1** is significantly faster than that of **2**, which decays slightly faster than that of **3**. This is consistent with the observed solution PLQYs of these materials. The single-exponential decay of **2** and **3** indicates a single emitting chromophore. Namely, in solution interchromophore interactions are negligible as a result of the presence of the dendrons. This is not the case for **1**, where the biexponential decay indicates more than one emissive species is present as a result of interchromophore interactions.

The film TRPL data are shown in Figure 4b. It can be seen that the decay of **1** is very much faster than in solution, indicating strong quenching in the solid state for this material.

Table 1. Solution PLQYs and PL Lifetime Measurements for the Three Polymers

| polymer | detection wavelength (nm) | PLQYs (%) | A_1 (μ s) | τ_1 | A_2 | τ_2 (μ s) | radiative lifetime (μ s) |
|---------|---------------------------|-----------|------------------|----------|-------|---------------------|-------------------------------|
| 1 | 514 | 48 | 0.20 | 0.12 | 0.80 | 1.26 | |
| 2 | 517 | 65 | 1 | 1.40 | | | 2.15 |
| 3 | 550 | 71 | 1 | 1.72 | | | 2.42 |

Table 2. Film PLQYs and PL Lifetime Measurements for the Three Polymers

| polymer | detection wavelength (nm) | PLQYs (%) | A_1 | τ_1 (μ s) | A_2 | τ_2 (μ s) |
|---------|---------------------------|-----------|-------|---------------------|-------|---------------------|
| 1 | 530 | 2 | 0.69 | 0.022 | 0.31 | 0.102 |
| 2 | 530 | 44 | 0.37 | 0.415 | 0.63 | 0.916 |
| 3 | 550 | 58 | 0.10 | 0.434 | 0.90 | 1.34 |

In fact, for the fast decay component for polymer 1, this is the major part of the PL decay in the film TRPL, which is reflected to the poor film PLQY (2%). The PL decays of 2 and 3 are slightly faster than in solution. However, the very much longer-lived PL than for 1 shows the effectiveness of dendrons for stopping quenching by intermolecular interactions, and the longer lifetime for 3 shows that the double dendron approach is more effective than a single dendron.

Finally, the high film PLQYs of poly(dendrimers) 2 and 3 enable the formation of efficient OLEDs. The detailed OLED study is reported elsewhere but in summary devices with an architecture of indium tin oxide/poly(dendrimer)/1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene/LiF/Al achieved 100 cd/m² at 4.1 and 5.5 V for 2 and 3, respectively, with concomitant efficiencies of 11.9% (42 cd/A) and 11.7% (38 cd/A), respectively.³⁴

CONCLUSION

Three homopolymers with a norbornene-derived backbone have been prepared using the Grubbs III catalyst. The polymers all contain heteroleptic iridium(III) complex emissive chromophores as side chains. The ROMP conditions enabled polymers of low polydispersity to be formed, and the polymers had higher viscosities compared to the simple “monomer” units. The position and number of dendrons were vital for controlling the optoelectronic properties. By increasing the number of dendrons attached to the ligands of the iridium(III) complex, both intra- and interchain interchromophore interactions could be controlled, leading to high film PLQYs. The homopolymer approach gives control of the intrachain and interchain interchromophore interactions. It also has the advantage over (random) copolymer architectures³⁵ of being simpler to reproduce and having a well-defined structure. We have therefore achieved our goal of forming highly luminescent materials with increased viscosity as an approach towards inkjet printing phosphorescent materials for OLEDs.

EXPERIMENTAL SECTION

Measurements. All commercial reagents were used as received unless otherwise noted. Tetrahydrofuran was distilled from sodium and benzophenone under a nitrogen atmosphere before use. ¹H and ¹³C NMR spectra were recorded using a 300, 400, or 500 MHz Bruker spectrometer, in deuterated chloroform solution; EH = 2-ethylhexyl, Pr = *n*-propyl, NB = norbornenyl, CP = cyclopentanyl, V = vinyl, LH = ligand phenyl/pyridyl and/or phenyltriazole H, LPH = phenyl H attached to phenyltriazole ligand, G1-BPH = branch phenyl H, SPH = surface phenyl H. All coupling constants (*J*) are in Hertz and quoted to the nearest 0.5 Hz. Gel permeation chromatography (GPC) was

carried out using either a Polymer Laboratories PL-GPC 50 using PLgel Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories, calibrated with polystyrene narrow standards ($\bar{M}_p = 162$ to 6.04×10^6 g/mol) (for 10–12) or a 1515 isocratic pump (Waters), a 717 autosampler (Waters), Styragel HT 3 and Styragel HT 6E columns (Waters) (300 mm + 300 mm lengths, 7.8 mm diameter), calibrated with polystyrene standards (Waters) ($\bar{M}_p = 1.06 \times 10^3$ to 1.32×10^6 g/mol) (for 1–3) and run in series in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran pumped at a rate of 1 cm³/min at 40 °C. Microanalyses were carried out at the School of Chemistry & Molecular Biosciences, The University of Queensland. UV–vis absorption measurements were recorded with a Cary Varian 5000 UV–vis–NIR spectrophotometer; sh = shoulder. Melting points were measured in a glass capillary on a BÜCHI melting point B-545 and are uncorrected. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer STA6000, and the differential scanning calorimetry was performed using a Perkin-Elmer Diamond DSC. Mass spectra were recorded on an Applied Biosystems Voyager matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) from 2-[(2-*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) or 2,5-dihydroxybenzoic acid (DHB) in positive reflection mode.

Viscosities of the poly(dendrimers) at different concentrations in 1,2-dichlorobenzene were determined on a homemade OSTWALD viscometer at a constant temperature of 20 °C. Deionized freshly distilled water with viscosity of 1.00 cSt at 20 °C was used as the reference.³²

Electrochemistry was performed using a BAS Epsilon electrochemistry station using a glassy carbon working, 0.1 M AgNO₃ in acetonitrile reference, and platinum counter electrodes. All measurements were made at room temperature on samples at a 1 mM concentration in dichloromethane (HPLC grade), with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the electrolyte. The solutions were deoxygenated with argon, and the ferricenium/ferrocene (Fc⁺/Fc) couple was used as the standard.³⁶ The scan rate was 100 mV s^{−1}, and in all cases several scans were carried out to confirm the chemical reversibility of the redox processes.

Solution PLQYs were measured by a relative method using quinine sulfate in 0.5 M sulfuric acid, which has a PLQY of 0.546, as the standard.³⁷ Materials were dissolved in dichloromethane and freeze–pump–thaw degassed. Photoluminescence spectra were recorded in a JY Horiba Fluoromax 2 fluorimeter, with the solutions excited at 360 nm. The optical densities of the standard and sample were similar and small (~0.1). The accuracy of these measurements is estimated to be ±10% of the stated value. Time-resolved luminescence measurements were performed using the time-correlated single photon counting technique, with excitation at 393 nm from a pulsed Picoquant GaN laser diode and an instrument response of 250 ps. The PL decay in each case was measured at a wavelength corresponding to the peak of the emission spectrum. Solid-state PLQY measurements were measured in an integrating sphere under a nitrogen purge³⁸ using a Hamamatsu C9920-02 luminescence measurement system.

Synthesis of 7. A mixture of 4²⁷ (250 mg, 0.321 mmol) and 4-formylphenylboronic acid (120 mg, 0.802 mmol), tetrakis-(triphenylphosphine)palladium(0) (56 mg, 0.048 mmol), aqueous potassium carbonate (2 M, 1.6 mL), ethanol (1.6 mL), and toluene (4.8 mL) was deoxygenated (by placing under vacuum and backfilling with argon) before being heated at reflux under argon for 21 h. The mixture was allowed to cool to room temperature, and then water (25 mL) was added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (4 × 25 mL). The organic portions were combined and dried over anhydrous magnesium sulfate

and filtered. The filtrate was collected, and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane/hexane (7:3 to 1:0) and then dichloromethane/ethyl acetate (24:1) as eluent to give **7** as a bright yellow solid (251 mg, 97%); mp 322 °C (decomp). Found: C, 60.9; H, 4.2; N, 8.8. $C_{41}H_{34}IrN_5O$ requires C, 61.2; H, 4.3; N, 8.7%. $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1688 (C=O); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 248 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.74), 264 sh (4.70), 279 (4.70), 369 (4.43), 406 sh (4.26), 482 sh (3.01). ^1H NMR (400 MHz, CDCl_3): δ 0.58 (3H, t, $J = 7.5$, Pr CH_3), 1.20–1.43 (2H, m, Pr CH_2), 1.79–1.94 (2H, m, Pr CH_2), 4.29 (3H, s, NCH₃), 6.78–7.03 (9H, m, LH), 7.13–7.14 (1H, dd, $J = 2$ and 8, LH), 7.53–7.59 (2H, m, LH), 7.6–7.720 (3H, m, LH), 7.74 and 7.90 (4H, AA'BB', LPH), 7.78 (1H, d, $J = 2$, LH), 7.82–7.96 (3H, m, LH), 10.02 (1H, s, CHO). ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 21.7, 28.7, 38.0, 118.4, 118.9, 119.9, 120.0, 121.4, 122.0, 122.2, 123.9, 124.0, 126.5, 128.5, 129.9, 130.0, 130.4, 130.9, 133.4, 134.2, 135.9, 136.16, 136.20, 136.6, 139.0, 143.5, 143.9, 147.7, 148.1, 159.1, 160.3, 161.3, 163.0, 163.7, 166.5, 167.1, 191.9. m/z (MALDI: DHB): calcd for $C_{41}H_{34}IrN_5O$, 803.2 (56%), 804.2 (27%), 805.2 (100%), 806.2 (46%), 807.2 (11%), 808.2 (2%); found, 803.2 (56%), 804.2 (31%), 805.2 (100%), 806.2 (51%), 807.2 (16%), 808.2 (5%).

Synthesis of 10. Lithium aluminum hydride (5.5 mg, 0.145 mmol) was added to a solution of **7** (90 mg, 0.112 mmol) dissolved in tetrahydrofuran (3.7 mL). The reaction was stirred at ambient temperature for 1.5 h and then quenched with water (25 mL). The mixture was extracted with dichloromethane (7 \times 25 mL). The extracts were combined, dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed to give the crude alcohol (90 mg), which was used without further purification. A mixture of the crude alcohol (90 mg), *exo*-5-norbornene-2-carboxylic acid (18.5 mg, 0.134 mmol), and (*N,N*-dimethylamino)pyridine (7.2 mg, 0.059 mmol) in dichloromethane (4.5 mL) was added to a solution of dicyclohexylcarbodiimide (29 mg, 0.141 mmol) in dichloromethane (0.7 mL). The reaction was stirred under argon at ambient temperature for 24 h. The solvent was evaporated, and the residue was purified by column chromatography over silica using dichloromethane/hexane (2.3:1 to 19:1) as eluent to give **10** as a bright yellow powder (94 mg, 91% for the two steps); mp 163–165 °C. Found: C, 63.3; H, 4.9; N, 7.3. $C_{49}H_{44}IrN_5O_2$ requires C, 63.5; H, 4.8; N, 7.55%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1725 (C=O); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 247 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.78), 264 sh (4.71), 275 (4.67), 288 (4.63), 340 sh (4.25), 369 sh (4.18), 406 sh (3.88), 452 sh (3.41), 479 sh (3.00). ^1H NMR (400 MHz, CDCl_3): δ 0.58 (3H, t, $J = 7$, Pr CH_3), 1.20–1.48 (3H, m, Pr H_2 , NB CH), 1.59–1.60 (2H, m, NB CH_2), 1.75–2.03 (3H, m, Pr H_2 , NB CH), 2.30–2.36 (1H, m, NB H), 2.95 (1H, s, NB H), 3.10 (1H, m, NB H), 4.27 (3H, m, NCH₃), 5.17 (2H, s, COOCH₂), 6.10–6.19 (2H, m, V H), 6.78–7.03 (9H, m, LH), 7.08–7.12 (1H, m, LH), 7.40 and 7.58 (4H, AA'BB', LPH), 7.51–7.60 (2H, m, LH), 7.61–7.71 (3H, m, LH), 7.74–7.78 (1H, m, LH), 7.83–7.97 (3H, m, LH). ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 21.7, 28.7, 29.7, 30.4, 38.0, 41.7, 43.2, 46.4, 46.6, 66.2, 118.4, 118.8, 119.8, 119.9, 121.4, 121.9, 122.2, 123.85, 123.9, 126.4, 128.6, 128.7, 129.9, 130.0, 132.0, 133.0, 134.0, 135.7, 136.0, 136.3, 136.6, 138.1, 138.7, 141.9, 143.5, 144.0, 147.7, 159.5, 160.6, 160.9, 161.2, 163.3, 166.5, 167.2, 176.1. m/z (MALDI: DHB): calcd for $C_{49}H_{44}IrN_5O_2$, 925.3 (54%), 926.3 (31%), 927.3 (100%), 928.3 (53%), 929.3 (15%), 930.3 (3%); found: 925.4 (56%), 926.4 (37%), 927.3 (100%), 928.3 (61%), 929.3 (22%), 930.3 (6%).

Synthesis of 1. A solution of Grubbs III catalyst in chloroform (0.05 M, 11.7 μL) was added to a solution of **10** (27 mg, 0.03 mmol) in chloroform (3 mL). The reaction mixture was stirred at ambient temperature under argon for 20 min. The reaction was quenched by the addition of ethyl vinyl ether (0.3 mL). The mixture was concentrated and precipitated into methanol (20 mL). The resulting solid was collected by filtration, redissolved in dichloromethane (2 mL), and reprecipitated into methanol (20 mL). This procedure was repeated until the methanol solution was clear to yield **1** as a powder (26 mg, 94%); TGA_(5%) 365 °C; Found: C, 63.2; H, 4.6; N, 7.45. ($C_{49}H_{44}IrN_5O_2$)_n requires C, 63.5; H, 4.8; N, 7.55%; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1728 (C=O); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 248, 263 sh, 276, 290, 386 sh, 405

sh, 446 sh, 484 sh. ^1H NMR (400 MHz, CDCl_3): δ 0.43–0.59 (br, Pr CH_3), 0.84–1.38 (brm, Pr CH_2 , 1/2CP CH_2), 1.65–2.80 (brm, Pr CH_2 , 1/2CP CH_2 , CP CH_2 , CP CH), 2.80–3.24 (brm, OCOCH), 3.80–4.19 (br, NCH₃), 4.83–5.42 (br, COOCH₂, V H), 6.64–7.10 (brm, LH), 7.12–7.28 (br, LPH), 7.29–7.65 (brm, LPH, LH), 7.66–7.87 (brm, LH). GPC: $\bar{M}_w = 14\,185$; $\bar{M}_n = 9435$; polydispersity = 1.5. $E^{1/2}(\text{ox}) = 0.22 \text{ V}$ vs Fc^+/Fc .

Synthesis of 8. A mixture of S^{27} (200 mg, 0.114 mmol) and 4-formylphenylboronic acid (43 mg, 0.287 mmol), tetrakis-(triphenylphosphine)palladium(0) (13 mg, 0.011 mmol), aqueous potassium carbonate (2 M, 0.3 mL), and tetrahydrofuran (2 mL) was deoxygenated (by placing under vacuum and backfilling with argon) before being heated at reflux under argon for 24 h. The mixture was allowed to cool to room temperature, and water (30 mL) was added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 \times 10 mL). All the organic portions were combined and dried over anhydrous magnesium sulfate and filtered. The filtrate was collected and the solvent removed. The residue was purified by column chromatography over silica using dichloromethane as eluent to give **8** as a bright yellow solid (157 mg, 77%); mp 148.5–150.5 °C. Found: C, 73.6; H, 6.9; N, 3.8. $C_{109}H_{122}IrN_5O_5$ requires C, 73.8; H, 6.9; N, 3.95%; $\lambda_{\max}(\text{solid})/\text{cm}^{-1}$ 1695 (C=O); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 274 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 5.15), 326 (4.63), 391 sh (4.40), 491 sh (2.99). ^1H NMR (500 MHz, CDCl_3): δ 0.63 (3H, t, $J = 7.5$, Pr CH_3), 0.94–1.02 (24H, m, EH CH_3), 1.30–1.64 (34H, m, EH CH_2 , Pr CH_2), 1.75–1.86 (4H, m, EH CH), 1.89–2.02 (2H, m, Pr CH_2), 3.93–3.95 (8H, m, OCH₂), 4.32 (3H, s, NCH₃), 6.84–6.90 (1H, m, LH), 6.99 (1H, d, $J = 8$, LH), 7.00–7.08 (10H, m, SPH, LH), 7.13 (1H, d, $J = 8$, LH), 7.20 (1H, dd, $J = 2$ and 8, LH), 7.27 (1H, dd, $J = 2$ and 8, LH), 7.31 (1H, dd, $J = 2$ and 8, LH), 7.56–7.63 (1H, m, LH), 7.65–7.73 (12H, m, SPH, LH), 7.76 and 7.92 (4H, AA'BB', LPH), 7.78 (2H, d, $J = 1.5$, G1-BPH), 7.81 (2H, d, $J = 2$, G1-BPH), 7.85 (1H, d, $J = 2$, LH), 7.95 (1H, d, $J = 1$, LH), 8.01–8.08 (4H, m, G1-BPH, LH), 10.04 (1H, s, CHO). m/z (MALDI: DCTB): calcd for $C_{109}H_{122}IrN_5O_5$, 1771.9 (40%), 1772.9 (50%), 1773.9 (100%), 1774.9 (99%), 1775.9 (58%), 1776.9 (24%), 1777.9 (9%); found, 1771.9 (38%), 1772.9 (44%), 1773.9 (81%), 1774.9 (100%), 1775.8 (38%), 1776.9 (22%), 1777.8 (5%). GPC: $\bar{M}_w = 1990$; $\bar{M}_n = 1984$; polydispersity = 1.0.

Synthesis of 11. Lithium aluminum hydride (3.3 mg, 0.087 mmol) was added to a solution of **8** (120 mg, 0.068 mmol) in tetrahydrofuran (5.5 mL). The reaction mixture was stirred at ambient temperature under argon for 45 min and then quenched carefully with water (5 mL). The crude was extracted with dichloromethane (3 \times 10 mL), washed with water (30 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected, and the solvent was removed to give crude alcohol (~135 mg), which was used without further purification. A solution of dicyclohexylcarbodiimide (20 mg, 0.095 mmol) in dichloromethane (0.5 mL) was added to a solution of the crude alcohol (~135 mg), *exo*-5-norbornene-2-carboxylic acid (13 mg, 0.091 mmol), and (*N,N*-dimethylamino)pyridine (5 mg, 0.04 mmol) in dichloromethane (3 mL). The reaction was stirred at ambient temperature under argon for 24 h. The solvent was removed, and the residue was purified by column chromatography over silica using dichloromethane/hexane (2:1) as eluent to give **11** as a green-yellow powder (128 mg, 100% for the two steps); mp 97–99 °C. Found: C, 73.85; H, 7.0; N, 3.65. $C_{117}H_{132}IrN_5O_6$ requires C, 74.1; H, 7.0; N, 3.7%; $\nu_{\max}(\text{solid})/\text{cm}^{-1}$ 1728 (C=O); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 269 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 5.25), 288 sh (5.22), 325 (4.80), 386 (4.23), 409 (4.03), 494 (2.99). ^1H NMR (400 MHz, CDCl_3): δ 0.65 (3H, t, $J = 7.5$, Pr CH_3), 0.97–1.07 (24H, m, EH CH_3), 1.35–1.66 (37H, m, EH CH_2 , Pr CH_2 , NB CH_2 , 1/2NB CH_2), 1.78–2.08 (7H, m, EH CH, Pr CH_2 , 1/2NB CH_2), 2.34–2.39 (1H, m, NB CH), 2.99 (1H, s, NB CH), 3.15 (1H, s, NB CH), 3.94–4.03 (8H, m, EH OCH₂), 4.32 (3H, s, NCH₃), 5.22 (2H, s, COOCH₂), 6.14–6.25 (2H, m, V H), 6.89 (1H, t, $J = 7$, LH), 7.03–7.15 (12H, m, SPH, LH), 7.18–7.23 (1H, m, LH), 7.30–7.38 (2H, m, LH), 7.46 and 7.65 (4H, AA'BB', $J = 8$, LPH), 7.60 (1H, t, $J = 8$, LH), 7.56–7.77 (12H, m, SPH, LH), 7.82–7.88 (5H, m, G1-BPH), 7.98–8.10 (5H, m, G1-BPH, LH). m/z (MALDI: DCTB): calcd for $C_{117}H_{132}IrN_5O_6$, 1894.0 (38%), 1895.0 (52%),

1896.0 (97%), 1897.0 (100%), 1898.0 (63%), 1899.0 (29%), 1900.0 (9%); found, 1894.0 (24%), 1895.1 (46%), 1896.0 (78%), 1897.0 (100%), 1898.1 (51%), 1899.0 (22%), 1900.0 (11%). GPC: $\bar{M}_w = 2112$; $\bar{M}_n = 2106$; polydispersity = 1.0. $E^{1/2}(\text{ox}) = 0.22 \text{ V vs Fc}^+/\text{Fc}$.

Synthesis of 2. Deoxygenated **11** (71 mg, 0.037 mmol) (by placing under high vacuum and backfilling with argon three times) was dissolved in dry tetrahydrofuran (0.35 mL). Grubbs III catalyst (3.8 mM, 100 μL) was rapidly injected. After stirring at ambient temperature under argon for 20 min, the reaction mixture was quenched by the addition of ethyl vinyl ether (0.3 mL). The resulting solution was added to methanol (20 mL) that was being stirred to precipitate the polymer. The precipitate was filtered, washed with methanol (20 mL), and dried under high vacuum to give **2** as a powder (67 mg, 94%); mp > 230 °C; TGA_(5%) 405 °C. Found: C, 73.75; H, 6.9; N, 3.6. ($\text{C}_{117}\text{H}_{132}\text{IrN}_5\text{O}_6$)_n requires C, 74.1; H, 7.0; N, 3.7%; $\nu_{\text{max}}(\text{solid})/\text{cm}^{-1}$ 1732 (C=O); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 269, 276 sh, 287 sh, 326 sh, 350 sh, 384 sh, 441 sh, 458 sh, 493 sh. ^1H NMR (400 MHz, CDCl_3): δ 0.36–0.54 (br, Pr CH_3), 0.75–1.00 (br, EH CH_3), 1.10–1.53 (brm, EH CH_2 , 1/2CP CH_2), 1.64–2.55 (brm, EH CH , Pr CH_2 , CP CH_2), 2.57–3.25 (br, OCOCH), 3.75–4.20 (brm, OCH₂, NCH₃), 4.56–5.40 (brm, COOCH₂, V H), 6.57–6.73 (br, LH), 6.74–6.83 (brm, LH), 6.84–6.97 (br, SPH), 6.98–7.08 (brm, LH), 7.11–7.26 (brm, LPH, LH), 7.32–7.46 (brm, LPH, LH), 7.48–7.62 (brm, SPH, LH), 7.63–7.73 (brm, G1-BPH), 7.74–8.02 (brm, G1-BPH, LH). GPC: $\bar{M}_w = 73\,663$; $\bar{M}_n = 57\,290$; polydispersity = 1.3. $E^{1/2}(\text{ox}) = 0.26 \text{ V vs Fc}^+/\text{Fc}$.

Synthesis of 9. A mixture of **6**²⁹ (200 mg, 0.074 mmol), 4-formylphenylboronic acid (28 mg, 0.184 mmol), tetrakis-(triphenylphosphine)palladium(0) (8.5 mg, 7.36 μmol), aqueous potassium carbonate (2 M, 0.2 mL), and tetrahydrofuran (1 mL) was deoxygenated (by placing under vacuum and backfilling with argon) before being heated at reflux under argon for 24 h. The mixture was allowed to cool to room temperature before water (10 mL) was added. The organic layer was separated. The aqueous layer was extracted with dichloromethane (2 \times 10 mL). The organic portions were combined and dried over anhydrous magnesium sulfate and filtered. The filtrate was collected and the solvent removed. The residue was purified by column chromatography over silica using dichloromethane/hexane (1:1) as eluent to give **9** as an orange-yellow solid (159 mg, 79%); mp 158 °C. Found: C, 77.15; H, 7.8; N, 2.6. ($\text{C}_{177}\text{H}_{210}\text{IrN}_5\text{O}_9$)_n requires C, 77.5; H, 7.7; N, 2.55%; $\nu_{\text{max}}(\text{solid})/\text{cm}^{-1}$ 1697 (C=O); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 276 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 5.46), 307 sh (5.26), 397 (4.57), 474 sh (3.77). ^1H NMR (500 MHz, CDCl_3): δ 0.56 (3H, t, $J = 7.0$, Pr CH_3), 0.93–1.09 (48H, m, EH CH_3), 1.30–1.68 (66H, m, EH CH_2 , Pr CH_2), 1.69–1.78 (2H, m, EH CH), 1.79–1.90 (6H, m, EH CH), 1.99–2.06 (1H, m, 1/2Pr CH_2), 2.07–2.17 (1H, m, 1/2Pr CH_2), 3.75–3.83 (4H, m, OCH₂), 3.90–4.03 (12H, m, OCH₂), 4.32 (3H, s, NCH₃), 6.82 (4H, d, $J = 8$, SPH), 7.02 (4H, d, $J = 8.5$, SPH), 7.05 (4H, d, $J = 8.5$, SPH), 7.09 (4H, d, $J = 9$, SPH), 7.14 (1H, d, $J = 7.5$, LH), 7.23–7.28 (1H, m, LH), 7.28–7.35 (2H, m, LH), 7.35–7.41 (2H, m, LH), 7.42–7.56 (10H, m, G1-BPH, SPH), 7.60 (2H, s, G1-BPH), 7.65–7.77 (12H, m, LH, SPH), 7.80 and 7.95 (4H, AA'BB', LPH), 7.78–7.92 (6H, m, G1-BPH, LH), 8.00–8.06 (1H, m, LH), 8.07–8.25 (5H, m, G1-BPH, LH), 8.53 (1H, s, G1-BPH), 10.06 (1H, s, CHO). m/z (MALDI: DHB): calcd for $\text{C}_{177}\text{H}_{210}\text{IrN}_5\text{O}_9$, 2740.6 (22%), 2741.6 (43%), 2742.6 (78%), 2743.6 (100%), 2744.6 (86%), 2745.6 (55%), 2746.6 (27%), 2747.6 (12%), 2748.6 (4%); found, 2740.7 (24%), 2741.7 (43%), 2742.7 (81%), 2743.7 (100%), 2744.7 (83%), 2745.7 (52%), 2746.7 (30%), 2747.7 (13%), 2748.7 (8%). GPC: $\bar{M}_w = 2974$; $\bar{M}_n = 2961$; polydispersity = 1.0.

Synthesis of 12. Lithium aluminum hydride (2.7 mg, 0.071 mmol) was added to a solution of **9** (150 mg, 0.055 mmol) in tetrahydrofuran (3.5 mL). The reaction mixture was stirred at ambient temperature under argon for 45 min and then quenched carefully with water (5 mL). The crude mixture was extracted with dichloromethane (3 \times 10 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected, and the solvent was removed to give the crude alcohol (~150 mg), which was used without further purification. A solution of dicyclohexylcarbodiimide (14 mg, 0.068 mmol) in dichloromethane

(0.35 mL) was added to a solution of the alcohol (~150 mg), *exo*-5-norbornene-2-carboxylic acid (9 mg, 0.066 mmol), and (*N,N*-dimethylamino)pyridine (3.5 mg, 0.029 mmol) in dichloromethane (2 mL). The reaction was stirred under argon at ambient temperature for 24 h. The solvent was removed, and the residue was purified by column chromatography over silica using a dichloromethane/hexane (1:1) as eluent to give **12** as an orange-yellow powder (135 mg, 86% for the two steps); mp 151 °C. Found: C, 77.3; H, 7.9; N, 2.25. ($\text{C}_{185}\text{H}_{220}\text{IrN}_5\text{O}_{10}$)_n requires C, 77.5; H, 7.7; N, 2.4%; $\nu_{\text{max}}(\text{solid})/\text{cm}^{-1}$ 1729 (C=O); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 275 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 5.62), 308 sh (5.46), 393 (4.46), 472 sh (3.89); ^1H NMR (300 MHz, CDCl_3): δ 0.57 (3H, t, $J = 7$, Pr CH_3), 0.91–1.09 (48H, m, EH CH_3), 1.29–1.66 (70H, m, EH CH_2 , Pr CH_2 , NB CH_2), 1.67–1.76 (2H, m, EH CH), 1.77–1.92 (6H, m, EH CH), 1.96–2.16 (2H, m, Pr CH_2), 2.32–2.40 (1H, m, NB CH), 2.99 (1H, s, NB CH), 3.15 (1H, s, NB CH), 3.73–3.86 (4H, m, EH OCH₂), 3.88–4.07 (12H, m, EH OCH₂), 4.32 (3H, s, NCH₃), 5.22 (2H, s, COOCH₂), 6.13–6.24 (2H, m, V H), 6.83 (4H, d, $J = 8.5$, SPH), 6.99–7.17 (14H, m, LH, SPH), 7.23–7.31 (2H, m, LH), 7.34–7.41 (2H, m, LH), 7.42–7.57 (13H, m, LH, LPH, G1-BPH, SPH), 7.58–7.63 (2H, m, G-BPH), 7.66 (2H, 1/2AA'BB', LPH), 7.68–7.81 (12H, m, LH, SPH), 7.82–7.92 (5H, m, G1-BPH, LH), 8.00–8.27 (6H, m, LH, G1-BPH), 8.51–8.57 (1H, m, G1-BPH). m/z (MALDI: DHB): calcd for $\text{C}_{185}\text{H}_{220}\text{IrN}_5\text{O}_{10}$, 2862.6 (19%), 2863.6 (41%), 2864.6 (77%), 2865.6 (100%), 2866.6 (91%), 2867.6 (58%), 2868.6 (30%), 2869.6 (13%), 2870.6 (6%), 2871.6 (2%); found, 2862.7 (17%), 2863.7 (37%), 2864.7 (64%), 2865.7 (100%), 2866.7 (97%), 2867.7 (70%), 2868.7 (42%), 2869.7 (20%), 2870.7 (12%), 2871.7 (9%). GPC: $\bar{M}_w = 3137$; $\bar{M}_n = 3124$; polydispersity = 1.0. $E^{1/2}(\text{ox}) = 0.28 \text{ V vs Fc}^+/\text{Fc}$.

Synthesis of 3. Deoxygenated **12** (97 mg, 0.034 mmol) (by placing under high vacuum and backfilling with argon three times) was dissolved in dry tetrahydrofuran (0.2 mL). Grubbs III catalyst (3.8 mM, 100 μL) was rapidly injected. After stirring at ambient temperature under argon for 1.5 h, the reaction mixture was quenched by the addition of ethyl vinyl ether (0.3 mL). The resulting solution was added to methanol (20 mL) that was being stirred to precipitate the polymer. The precipitate was filtered, washed with methanol (20 mL), and dried under high vacuum to give **3** as a powder (91 mg, 94%); mp > 240 °C. TGA_(5%) 421 °C; Found: C, 77.2; H, 7.6; N, 2.5. ($\text{C}_{185}\text{H}_{220}\text{IrN}_5\text{O}_{10}$)_n requires C, 77.5; H, 7.7; N, 2.4%; $\nu_{\text{max}}(\text{solid})/\text{cm}^{-1}$ 1732 (C=O); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 270, 308 sh, 398, 482 sh; ^1H NMR (400 MHz, CDCl_3): δ 0.30–0.48 (br, Pr CH_3), 0.75–0.98 (br, EH CH_3), 1.15–1.50 (brm, EH, Pr CH_2 , 1/2CP CH_2), 1.56–1.72 (brm, EH CH), 1.79–2.80 (brm, Pr CH_2 , CP CH_2 , CP CH), 2.90–3.20 (br, OCOCH), 3.52–4.20 (brm, EH OCH₂, NCH₃), 4.74–5.42 (brm, COOCH₂, V H), 6.61–6.98 (brm, SPH, LH), 7.00–7.68 (brm, LPH, G1-BPH, LH), 7.80–8.18 (brm, G1-BPH, LH), 8.30–8.48 (br, G1-BPH). GPC: $\bar{M}_w = 64\,890$; $\bar{M}_n = 47\,417$; polydispersity = 1.4. $E^{1/2}(\text{ox}) = 0.29 \text{ V vs Fc}^+/\text{Fc}$.

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Notes

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REFERENCES

- (1) (a) Tang, C. W.; van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151. (c) Holder, E.; Langeveld, B. M. W.; Schubert, U. S. *Adv. Mater.* **2005**, *17*, 1109. (d) Huang, Q.; Walzer, K.; Pfeiffer, M.; Lyssenko, V.; He, G.; Leo, K. *Appl. Phys. Lett.* **2006**, *88*, 113515.
- (2) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2007**, *107*, 1097. (c) Wang, X.-Y.; Kimyonok, A.; Weck, M. *Chem. Commun.* **2006**, 3933.
- (3) (a) Burn, P. L.; Lo, S.-C.; Samuel, I. D. W. *Adv. Mater.* **2007**, *19*, 1675. (b) Lo, S.-C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097. (c) Harding, R. E.; Lo, S.-C.; Burn, P. L.; Samuel, I. D. W. *Org. Electron.* **2008**, *9*, 377. (d) Lo, S.-C.; Harding, R. E.; Brightman, E.; Burn, P. L.; Samuel, I. D. W. *J. Mater. Chem.* **2009**, *19*, 3213.
- (4) (a) Tsuzuki, T.; Shirasawa, N.; Suzuki, T.; Tokito, S. *Jpn. J. Appl. Phys.* **2005**, *44*, 4151. (b) Lo, S.-C.; Namdas, E. B.; Shipley, C. P.; Markham, J.; Anthopoulos, T. D.; Burn, P. L.; Samuel, I. D. W. *Org. Electron.* **2006**, *7*, 85. (c) Ding, J.; Gao, J.; Cheng, Y.; Xie, Z.; Wang, L.; Ma, D.; Jing, X.; Wong, F. *Adv. Funct. Mater.* **2006**, *16*, 575. (d) Velusamy, M.; Thomas, J. K. R.; Chen, C.-H.; Lin, J. T.; Wen, Y. S.; Hsieh, W.-T.; Lai, C.-H.; Chou, P.-T. *Dalton Trans.* **2007**, 3025. (e) Huang, W.-S.; Lin, J. T.; Lin, H.-C. *Org. Electron.* **2008**, *9*, 557.
- (5) (a) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Nature* **2000**, *403*, 750. (b) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, *90*, 5048. (c) Ikai, M.; Tokito, S.; Sakamoto, Y.; Suzuki, T.; Taga, Y. *Appl. Phys. Lett.* **2001**, *79*, 156. (d) Yang, X.; Müller, D. C.; Neher, D.; Meerholz, K. *Adv. Mater.* **2006**, *18*, 948. (e) You, Y.; Park, S.-Y. *Dalton Trans.* **2009**, 1267. (f) Ulbricht, C.; Beyer, B.; Friebe, C.; Winter, A.; Schubert, U. S. *Adv. Mater.* **2009**, *21*, 4418. (g) Chi, Y.; Chou, P.-T. *Chem. Soc. Rev.* **2010**, *39*, 381. (h) Xiao, L.; Chen, Z.; Qu, B.; Luo, J.; Kong, S.; Gong, Q.; Kido, J. *Adv. Mater.* **2011**, *23*, 926.
- (6) (a) Nazeeruddin, M. K.; Humphry-Baker, R.; Berner, D.; Rivier, S.; Zuppiroli, L.; Grätzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 8790. (b) Gong, X.; Ma, W. L.; Ostrowski, J. C.; Bazan, G. C.; Moses, D.; Heeger, A. J. *Adv. Mater.* **2004**, *16*, 615. (c) Coppo, P.; Plummer, E. A.; De Cola, L. *Chem. Commun.* **2004**, 1774. (d) Yang, C.-H.; Cheng, Y.-M.; Chi, Y.; Hsu, C.-J.; Fang, F.-C.; Wong, K.-T.; Chou, P.-T.; Chang, C.-H.; Tsai, M.-H.; Wu, C.-C. *Angew. Chem., Int. Ed.* **2007**, *46*, 2418. (e) Chang, C.-F.; Cheng, Y.-M.; Chi, Y.; Chiu, Y.-C.; Lin, C.-C.; Lee, G.-H.; Chou, P.-T.; Chen, C.-C.; Chang, C.-H.; Wu, C.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 4542.
- (7) (a) Lo, S.-C.; Male, N. A. H.; Markham, J.; Magennis, S. W.; Burn, P. L.; Salata, O. V.; Samuel, I. D. W. *Adv. Mater.* **2002**, *14*, 975. (b) Frampton, M. J.; Namdas, E. B.; Lo, S.-C.; Burn, P. L.; Samuel, I. D. W. *J. Mater. Chem.* **2004**, *14*, 2881. (c) Lo, S.-C.; Richards, G. J.; Markham, J.; Namdas, E. B.; Sharma, S.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2005**, *15*, 1451. (d) Lo, S.-C.; Anthopoulos, T. D.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater.* **2005**, *17*, 1945. (e) Knights, K. A.; Stevenson, S. G.; Shipley, C. P.; Lo, S.-C.; Olsen, S.; Harding, R. E.; Gambion, S.; Burn, P. L.; Samuel, I. D. W. *J. Mater. Chem.* **2008**, *18*, 2121. (f) Lo, S.-C.; Harding, R. E.; Shipley, C. P.; Stevenson, S. G.; Burn, P. L.; Samuel, I. D. W. *J. Am. Chem. Soc.* **2009**, *131*, 16681. (g) Gambino, S.; Lo, S.-C.; Liu, Z. H.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2012**, *22*, 157.
- (8) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. *Science* **2000**, *290*, 2123.
- (9) De Gans, B. J.; Duineveld, P. C.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 203.
- (10) Gunning, J. P.; Levell, J. W.; Wyatt, M. F.; Burn, P. L.; Robertson, J.; Samuel, I. D. W. *Polym. Chem.* **2010**, *1*, 730.
- (11) Sandee, A. J.; Williams, C. K.; Evans, N. R.; Davies, J. E.; Boothby, C.; Kohler, A.; Friend, R. H.; Holmes, A. B. *J. Am. Chem. Soc.* **2004**, *126*, 7041.
- (12) (a) Tokito, S.; Suzuki, M.; Sato, F. *Thin Solid Films* **2003**, *445*, 353. (b) Tokito, S.; Suzuki, M.; Sato, F.; Kamachi, M.; Shirane, K. *Org. Electron.* **2003**, *4*, 105. (c) Suzuki, M.; Tokito, S.; Sato, F.; Igarashi, T.; Kondo, K.; Koyama, T.; Yamaguchi, T. *Appl. Phys. Lett.* **2005**, *86*, 103507. (d) Wang, X.-Y.; Prabhu, R. N.; Schmehl, R. H.; Weck, M. *Macromolecules* **2006**, *39*, 3140. (e) Haldi, A.; Kimyonok, A.; Domercq, B.; Hayden, L. E.; Jones, S. C.; Marder, S. R.; Weck, M.; Kippelen, B. *Adv. Funct. Mater.* **2008**, *18*, 3056.
- (13) (a) Chen, X.; Liao, J. L.; Liang, Y.; Ahmed, M. O.; Tseng, H.; Chen, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 636. (b) Zhen, H. Y.; Luo, C.; Yang, W.; Song, W. Y.; Du, B.; Jiang, J. X.; Jiang, C. Y.; Zhang, Y.; Cao, Y. *Macromolecules* **2006**, *39*, 1693. (c) Liu, S. J.; Zhao, Q.; Xia, Y. J.; Deng, Y.; Lin, J.; Fan, Q. L.; Wang, L. H.; Huang, W. J. *Phys. Chem. C* **2007**, *111*, 1166. (d) Jiang, J.; Jiang, C.; Yang, W.; Zhen, H.; Huang, F.; Cao, Y. *Macromolecules* **2005**, *38*, 4072. (e) Yang, W.; Zhen, H. Y.; Jiang, C. Y.; Su, L. J.; Jiang, J. X.; Shi, H. H.; Cao, Y. *Synth. Met.* **2005**, *153*, 189.
- (14) Liu, S. J.; Zhao, Q.; Chen, R. F.; Deng, Y.; Fan, Q. L.; Li, F. Y.; Wang, L. H.; Huang, C. H.; Huang, W. *Chem.—Eur. J.* **2006**, *12*, 4351.
- (15) (a) Deng, L.; Furuta, P. T.; Garon, S.; Li, J.; Kavulak, D.; Thompson, M. E.; Fréchet, J. M. J. *Chem. Mater.* **2006**, *18*, 386. (b) Furuta, P. T.; Deng, L.; Garon, S.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15388.
- (16) Kimyonok, A.; Domercq, B.; Haldi, A.; Cho, J.-Y.; Carlise, J. R.; Wang, X.-Y.; Hayden, L. E.; Jones, S. C.; Barlow, S.; Marder, S. R.; Kippelen, B.; Weck, M. *Chem. Mater.* **2007**, *19*, 5602.
- (17) (a) Marin, V.; Holder, E.; Hoogenboom, R.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4153. (b) Ito, T.; Suzuki, S.; Kido, J. *Polym. Adv. Technol.* **2005**, *16*, 480.
- (18) Carlise, J. R.; Wang, X.-Y.; Weck, M. *Macromolecules* **2005**, *38*, 9000.
- (19) Holder, E.; Marin, V.; Alexeev, A.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2765.
- (20) Tekin, E.; Holder, E.; Marin, V.; de Gans, B. J.; Schubert, U. S. *Macromol. Rapid Commun.* **2005**, *26*, 293.
- (21) (a) Lee, C. L.; Kang, N. G.; Cho, Y. S.; Lee, J. S.; Kim, J. J. *Opt. Mater.* **2002**, *21*, 119. (b) You, Y.; Kim, S. H.; Jung, H. K.; Park, S. Y. *Macromolecules* **2006**, *39*, 349.
- (22) Schulz, G. L.; Chen, X. W.; Chen, S. A.; Holdcroft, S. *Macromolecules* **2006**, *39*, 9157.
- (23) (a) Park, M.-J.; Lee, J.; Kwak, J.; Jung, I. H.; Park, J.-H.; Kong, H.; Lee, C.; Hwang, D.-H.; Shim, H.-K. *Macromolecules* **2009**, *42*, 5551. (b) Park, M.-J.; Kwak, J.; Lee, J.; Jung, I. H.; Kong, H.; Lee, C.; Hwang, D.-H.; Shim, H.-K. *Macromolecules* **2010**, *43*, 1379.
- (24) Poulsen, D. A.; Kim, B. J.; Ma, B.; Zonté, C. S.; Fréchet, J. M. J. *Adv. Mater.* **2010**, *22*, 77.
- (25) (a) Lai, W.-Y.; Levell, J. W.; Burn, P. L.; Lo, S.-C.; Samuel, I. D. W. *J. Mater. Chem.* **2009**, *19*, 4952. (b) Lai, W.-Y.; Cavaye, H.; Wang, X.; Lo, S.-C.; Meredith, P.; Burn, P. L. *Polym. Prepr.* **2009**, *50*, 296.
- (26) Furuta, P.; Brooks, J.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2003**, *125*, 13165.
- (27) Lai, W.-Y.; Levell, J. W.; Jackson, A. C.; Lo, S.-C.; Bernhardt, P. V.; Samuel, I. D. W.; Burn, P. L. *Macromolecules* **2010**, *43*, 6986.
- (28) Levell, J. W.; Lai, W.-Y.; Lo, S.-C.; Burn, P. L.; Samuel, I. D. W. *Polym. Prepr.* **2011**, *52*, 884.
- (29) Lai, W.-Y.; Levell, J. W.; Balfour, M. N.; Lo, S.-C.; Burn, P. L.; Samuel, I. D. W. *Polym. Chem.* **2012**, *3*, 734.
- (30) (a) Lo, S.-C.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **2003**, *36*, 9721. (b) Lo, S.-C.; Bera, R. N.; Harding, R. E.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2008**, *18*, 3080. (c) Cavaye, H.; Shaw, P. E.; Wang, X.; Burn, P. L.; Lo, S.-C.; Meredith, P. *Macromolecules* **2010**, *43*, 10253.

- (31) (a) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035. (b) Choi, T.-L.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1743.
- (32) (a) Swindells, J. F.; Coe, J. R.; Godfrey, T. B. *J. Res. Natl. Bur. Std.* **1952**, *48*, RP2279. (b) Korosi, A.; Fabuss, B. M. *Anal. Chem.* **1968**, *40*, 157.
- (33) (a) Schmid, B.; Garces, F. O.; Watts, R. J. *Inorg. Chem.* **1994**, *33*, 9. (b) Hofbeck, T.; Yersin, H. *Inorg. Chem.* **2010**, *49*, 9290.
- (34) Levell, J. W.; Zhang, S.; Lai, W.-Y.; Lo, S.-C.; Burn, P. L.; Samuel, I. D. W. *Opt. Express* **2012**, *20*, A213.
- (35) (a) Levell, J. W.; Lai, W.-Y.; Borthwick, R. J.; Lo, S.-C.; Burn, P. L.; Samuel, I. D. W. *J. Phys. Chem. C* **2011**, *115*, 25464. (b) Levell, J. W.; Lai, W.-Y.; Borthwick, R. J.; Burn, P. L.; Lo, S.-C.; Samuel, I. D. W. *New J. Chem.* **2012**, *36*, 407.
- (36) Gritzner, G.; Kuta, J. *Electrochim. Acta* **1984**, *29*, 869.
- (37) Demas, J. N.; Crosby, G. A. J. *J. Phys. Chem.* **1971**, *75*, 991.
- (38) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89.