RAFT Polymerization Meets Coordination Chemistry: Synthesis of a Polymer-Based Iridium(III) Emitter

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A synthetic approach toward the synthesis of well-defined copolymers with attached phosphorescent iridium(III) emitters is presented. A reactive μ-hydroxy-bridged precursor complex has been utilized to coordinate suitable ligand sites of a methacrylate-based copolymer. The starting copolymer has been synthesized via the reversible addition fragmentation chain transfer (RAFT) polymerization technique. Using a reactive complex species, the coordination reaction at the copolymer could be performed under very mild conditions in the absence of any supporting additives.
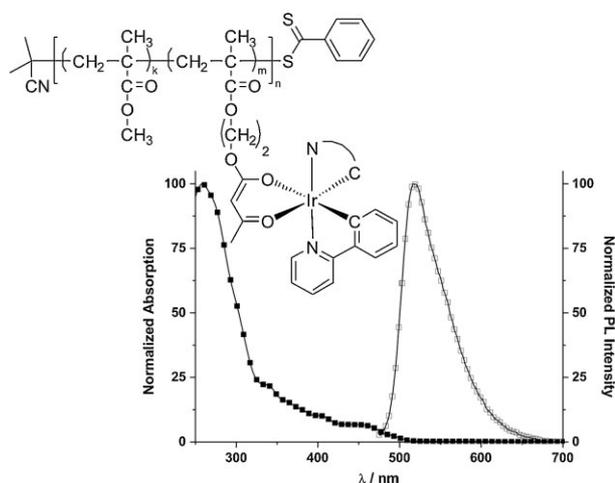
Introduction

For the fabrication of organic light-emitting diodes (OLEDs) mainly two methods are in the focus, vapor deposition and solution processing.[1] Vapor deposition is a very accurate process, which allows designing complicated structures by applying mask techniques, but it is also rather intricate, expensive, and restricted to the handling of small and thermally stable molecules. In contrast, solution processing techniques, such as spin-coating or inkjet printing,[2] are rather low-priced, easily applicable to large areas, and possess much less restrictions regarding the processed materials. Here, polymeric materials are of special interest, with respect to their flexibility and film forming properties.

The combination of suitable polymeric hosts with small emitter molecules, together with additional charge transporting molecules within blends, has become a widespread attempt for the preparation of polymer light-emitting diodes (PLEDs).[3] Blended systems, however, hold the risk of undesired phase separation, aggregation, or crystallization, which can decrease the device performance. Therefore, the design of (co)polymers with multifunctions, such as charge transport and emission, receives an increasing interest.[4,5] Better energy transfer to the emitters, higher efficiency, and higher durability of the device are some of the expected benefits.

There are in principle five general routes to synthesize metal-complex containing polymers.[3] These can be listed as polymerization by complexation (i.e., Ru^II-terpyridine, Zn^II-terpyridine, Fe^II-terpyridine as well as Pt^II-acetylene,

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and Cu[I]-bipyridine polymers),[6–9] "decoration" of (co)polymers with complexes utilizing suitable combinations of functionalities,[10] the complexation of (co)polymers bearing suitable ligands,[11] and polymerization initiated from the metal complex equipped with an initiator functionality.[12,13] However, the most widely employed route to obtain polymers containing phosphorescent Ir[III] complexes is the (co)polymerization[14] or (co)condensation[15] of correspondingly functionalized complexes.

For optical applications, mainly two types of materials are distinguished, which are conjugated and non-conjugated systems. Conjugated polymers are expected to provide better charge transport to the emitter, but devices can suffer from the usually rather low triplet energy level of the polymeric backbone, which increases the probability of energy back transfer from the emitter to the polymer. Non-conjugated polymers usually possess rather high triplet energy levels and can, therefore, be seen as more universal host systems, which are also able to deal with high band gap emitters, i.e., also blue emitters with rather high lowest unoccupied molecular orbital (LUMO) levels.[16]

Radical (co)polymerizations provide an easy access to non-conjugated polymers (i.e., polyvinylcarbazole, PVK), tolerate a large diversity of functionalities, and can be conducted with a variety of monomers under relatively mild conditions. Besides the intensively used free radical polymerization (FRP), controlled radical polymerization techniques, like atom transfer radical polymerization (ATRP),[17] reversible addition fragmentation chain transfer (RAFT) polymerization,[18] and nitroxide mediated polymerization (NMP)[19] gained tremendous interest. These techniques provide control over the molar mass in combination with low polydispersity indices, which allows designing tailor-made (co)polymers.

Previously, we reported on the synthesis and characterization of a new methacrylate-functionalized iridium(III) complex exhibiting orange phosphorescence. This emitter polymer was synthesized under either FRP or ATRP conditions.[20] In continuation of this work, we now followed the complexation of (co)polymers approach. Therefore, a defined methacrylate-based copolymer bearing ligand sites was prepared under controlled radical polymerization conditions applying the RAFT technique. Furthermore, the reactive μ-hydroxy-bridged analog to the common μ-chloro-bridged dimeric Ir[III] precursor species was synthesized. Precursor and copolymer were reacted under mild conditions yielding a phosphorescent polymer. Size exclusion chromatography (SEC) equipped with a photodiode array (PDA) detector was applied to gain clear evidence for the formation of the desired complex-containing polymer. NMR, UV–Vis absorption, and photoluminescence spectroscopy provided further information about these new materials.

Experimental Part

Materials

All chemicals were of reagent grade and used as received unless otherwise specified. The solvents were bought from Biosolve and were dried and distilled according to standard procedures. Methyl methacrylate (MMA) (99%, Aldrich) and acetoacetoxyethyl methacrylate (AAEM) (95%, Aldrich) were passed through neutral aluminum oxide columns prior use to remove the stabilizer. The chain transfer agent 2-cyanobutan-2-yl dithiobenzoate (CBDB) was kindly provided by AGFA. α,α′-Azoisobutyronitrile (AIBN) (98%, Aldrich) was recrystallized from methanol. IrCl$_3 \cdot$3H$_2$O was provided by Heraeus. All reactions involving IrCl$_3 \cdot$3H$_2$O or Ir[III] complexes were conducted under a nitrogen atmosphere. The synthesis and characterization of the *bis*-(2-phenylpyridinato) iridium(III) *n*-butylacetoacetate model complex (**M1**) is reported elsewhere.[21]

Methods

1-D (¹H and ¹³C) and 2-D (¹H-¹H gCOSY) NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer at 298 K. Chemical shifts are given in ppm relative to tetramethylsilane (Me$_4$Si). UV–Vis absorption and emission spectra were recorded on a Perkin Elmer Lambda-45 (1 cm cuvettes, CH$_2$Cl$_2$, at concentrations of about 10^{-5} mol $\cdot$ L^{-1}) and on a Perkin Elmer LS50B Luminescence spectrometer (1 cm cuvettes, CH$_2$Cl$_2$, at concentrations of about 10^{-6} mol $\cdot$ L^{-1}), respectively. Elemental analyses (EAs) were carried out on a EuroVector EuroEA3000 elemental analyzer configured for CHNS. A Waters SEC system consisting of a 717 Plus autosampler, an isocratic pump, a solvent degasser, a column oven, and a Styragel HT 4 SEC column with a precolumn equipped either with a 2 414 refractive-index (RI) or a 2 996 PDA detector was utilized for SEC investigations. Dimethylformamide (DMF) (containing 5×10^{-3} M NH$_4$PF$_6$) was used as eluent at a column temperature of 50 °C and a flow rate of 0.5 mL $\cdot$ min^{-1}. Linear poly(methyl methacrylate) (PMMA) standards have been applied to calculate the molar mass.

Synthesis

Reversible Addition Fragmentation Chain-Transfer (RAFT) Polymerization—(**P1**)

For the synthesis of the copolymer **P1** a mixture of MMA (4.478 mL, 42 mmol, 82 equiv.), AAEM (2 mL, 10.5 mmol, 20.5 equiv.), CBDB (247 mg, 1.05 mmol, 2 equiv.), AIBN (43 mg, 0.256 mmol, 0.5 equiv.), and toluene (6.478 mL, 50 vol.-%) was filled in a pressure-resistant vial equipped with a magnetic stirrer. After the solution was degassed by purging with argon for 30 min, the capped vial was placed for 13 h in a heated oil bath (70 °C). Subsequently, the solution was cooled down and precipitated into methanol to remove residual monomer and solvent.

UV (CH$_2$Cl$_2$): λ_{max} = 232, 303 nm. ¹H NMR (CDCl$_3$): δ (ppm) = 7.80 (m$_c$, H$^{o\text{-RAFT}}$), 7.45 (m$_c$, H$^{p\text{-RAFT}}$), 7.28 (m$_c$, H$^{m\text{-RAFT}}$), 4.45–3.85 (m, H^{2,1}), 3.80–3.15 (m, −O−CH$_3$, H^C), 2.30–0.50 (m, −CH$_3$, −CH$_2$−

polymer backbone, $-CH_3$ initiator, H^A). SEC (5×10^{-3} M NH_4PF_6 in DMF): $\overline{M}_n = 6\,400$ g $\cdot$ mol^{-1}, $\overline{M}_w = 7\,800$ g $\cdot$ mol^{-1}, PDI = 1.22.

Tetrakis(2-phenylpyridinato-N,C²)(µ-dihydroxy) diiridium(III) ([Ir(ppy)₂OH]₂)

A mixture of $IrCl_3 \cdot 3H_2O$ (257 mg, 0.73 mmol), 2-phenyl-pyridine (276 mg, 1.71 mmol), 2-ethoxy-ethanol (9 mL), and water (3 mL) was refluxed under argon for 4.5 h. Subsequently, an excess of NaOH (1.25 g, 0.03 mol) dissolved in H_2O (12.5 mL) was added and the stirring was continued under reflux for 2 h. After cooling to room temperature H_2O (25 mL) was added. An orange-brown precipitate was filtered off, dissolved in CH_2Cl_2 (15 mL), and filtered. The filtrate was treated with NaOH solution (1.68 g, 0.04 mol in 4.5 mL H_2O) at reflux for 6 h. Afterwards, the CH_2Cl_2 was evaporated and H_2O (125 mL) was added. The crude product was filtered off and washed with *n*-pentane (10 mL) and diethyl ether (10 mL). Further purification was achieved by precipitation (CH_2Cl_2 solution) in *n*-pentane yielding [Ir(ppy)₂OH]₂ as a brown powder (295 mg, 78%).

^{1}H NMR (CD_2Cl_2): δ (ppm) = 8.71 (d, 4H, $^3J = 5.7$ Hz, H^k), 7.89 (d, 4H, $^3J = 8.1$ Hz, H^h), 7.63 (dd, 4H, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, H^i), 7.57 (d, 4H, $^3J = 6.5$ Hz, H^e), 6.75 (m$_c$, 4H, H^d), 6.66 (m$_c$, 4H, H^j), 6.54 (m$_c$, 4H, H^c), 5.94 (d, 4H, $^3J = 6.5$ Hz, H^b), −1.45 (s, 2H, H^L). ^{13}C NMR (CD_2Cl_2): δ (ppm) = 118.0, 119.7, 121.1, 123.6, 128.5, 131.3, 135.6, 144.8, 148.3, 150.2, 168.9. $C_{44}H_{34}N_4O_2Ir_2$ (1035.22): Calcd. C 51.05, H 3.31, N 5.41; Found C 50.82, H 3.34, N 5.24.

Preparation of the Phosphorescent Polymer by Coordination—(P2)

The conditions for the coordination reaction were chosen analogous to a known description. The copolymer **P1** (41 mg, ca. 1 equiv. of AAEM units) and a slight excess of precursor [Ir(ppy)₂OH]₂ (41 mg, 0.039 mmol, ca. 0.59 equiv.) were dissolved in degassed CH_2Cl_2 (3 mL) and the solution was kept stirring for 2 d at room temperature. The solution was precipitated in methanol to yield the coordinated polymer **P2**.

UV (CH_2Cl_2): $\lambda_{max} = 259, 337, 365, 402, 456$ nm. Emission (CH_2Cl_2, $\lambda_{ex} = 460$ nm): $\lambda_{max} = 518$ nm. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 8.59 (m$_c$, H^k), 8.22–7.50 (m$_c$, $H^{e,i,h}$, $H^{p,o\text{-RAFT}}$), 7.25 (m$_c$, H^j, $H^{m\text{-RAFT}}$), 7.03–6.60 (m, $H^{c,d}$), 6.26 (m$_c$, H^b), 4.82 (m$_c$, H^C), 4.46 (m$_c$, $H^{1(uc)}$), 4.26–3.27 (m, $-O-CH_3$, $H^{C(uc)}$, $H^{1,2}$, $H^{2(uc)}$), 2.28 (m$_c$, $H^{A(uc)}$), 2.18–0.55 (m, $-CH_3$, $-CH_2-$ polymer backbone, $-CH_3$ initiator, H^A).

Results and Discussion

Synthesis and Characterization

The utilization of acetoacetate (acac) derivatives as ancillary ligands in the coordination of *bis*-cyclometallated iridium(III) complexes was previously reported in literature.[21,22] Commercially available AAEM — combining this class of ligands with a polymerizable unit — was applied as comonomer for the synthesis of a polymer with acac functionalities for subsequent coordination of Ir^{III} centers. For this purpose, MMA and AAEM were copolymerized by RAFT polymerization in a 4 to 1 ratio (Scheme 1). AIBN was

used as radical initiator and CBDB as RAFT agent to perform the copolymerization of both monomers (MMA and AAEM) in a controlled manner. All reactants were dissolved in toluene, degassed by purging with argon, and then reacted at 70 °C for 13 h. The polymer (**P1**) was subsequently purified by precipitation into methanol, and by decantation of the methanol from the polymeric phase.

The ^{1}H NMR spectrum of the MMA–AAEM-copolymer **P1** featured polymer-typical broad and undefined signals (Figure 1). Resonances specific for the RAFT group (at 7.28, 7.45, and 7.80 ppm), and for the AAEM units (at 3.85–4.45 ppm) could be identified. By comparing the integrals, the composition of the copolymer can be determined. Based on the ^{1}H NMR spectroscopic data, the average **P1**-polymer chain contains 14 AAEM units and 55 MMA units per one RAFT agent, respectively. This corresponds to a MMA/AAEM ratio of ≈3.9:1, which is close to the monomer feed (MMA/AAEM = 4:1), and a number average molar mass ($\overline{M}_n$) of about 8 600 g $\cdot$ mol^{-1}.

The synthesis of the reactive µ-hydroxy-bridged Ir^{III} complex [Ir(ppy)₂OH]₂ was conducted in analogy to a stepwise procedure reported in a patent (Scheme 1).[23] A mixture of $IrCl_3 \cdot 3H_2O$, 2-phenyl-pyridine (ppyH), 2-ethoxy-ethanol, and water was refluxed for 4.5 h, an aqueous sodium hydroxide solution was added and heating was continued for another 2 h. After cooling to room temperature, water was added and the precipitate formed was filtered off, washed, and dried. Afterwards the precipitate was dissolved in dichloromethane, mixed with aqueous sodium hydroxide, and refluxed for 6 h. The heating was stopped, the organic solvent (CH_2Cl_2) was evaporated, and the product precipitated from the aqueous phase was filtered off, washed with water, and dried.

The attempt to investigate the precursor [Ir(ppy)₂OH]₂ by MALDI-TOF mass spectrometry failed. However, aside the data from EA, which were in good agreement with the calculated values, NMR spectroscopy gave clear evidence for the formation of the desired precursor complex [Ir(ppy)₂OH]₂. The ^{1}H NMR spectrum was recorded (Figure 1) and compared to the spectrum of the analogous µ-chloro-bridged precursor as well as to the values of a similar precursor. In addition a gCOSY spectrum was recorded to assure the assignment of the signals. The most significant characteristic of the spectrum is the signal of the highly shielded bridging hydroxy-protons ($\delta = -1.4$ ppm). While this finding agrees well with the patent description, it is in contradiction to other reports stating the synthesis of the same ppy-based precursor species.[24] In these reports an alternative synthetic approach was applied and a different NMR-signal at lower field ($\delta = 3.77$ ppm) was observed, which was assigned to the expected hydroxy-protons. Considering the use of methanol as solvent in the precursor-forming step and the chemical shift of the reported signal ($\delta = 3.77$ ppm), the preparation of a µ-
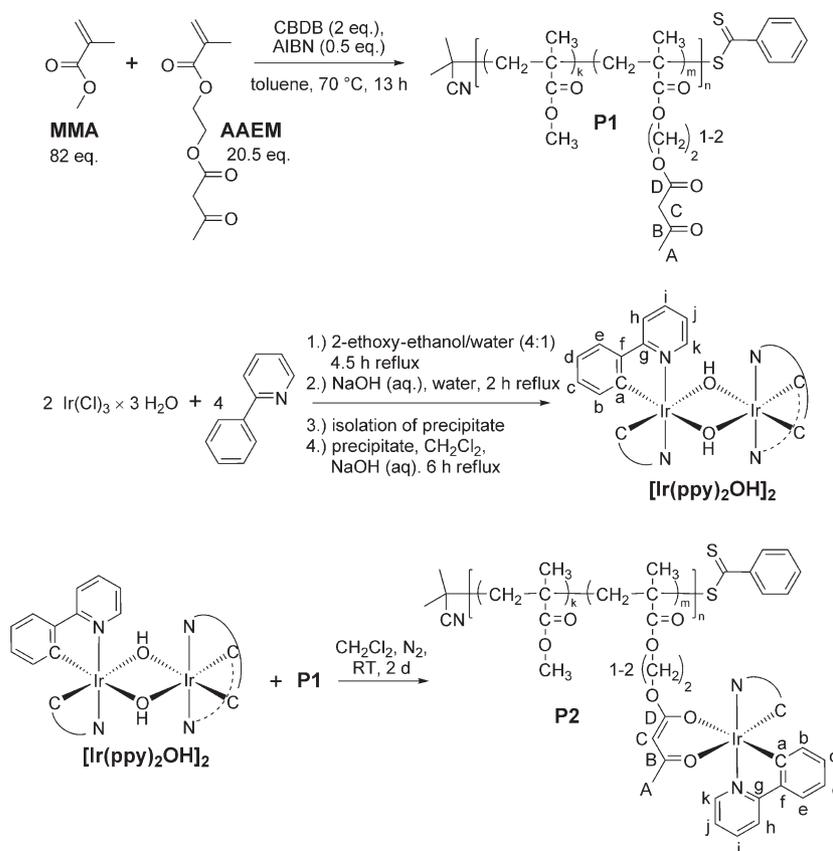
Scheme 1. Schematic representation of the synthesis of **P1** (RAFT polymerization, top), μ-hydroxy-bridged precursor [Ir(ppy)$_2$OH]$_2$ (middle), and Ir^{III}-containing polymer **P2** (bottom).

methoxy-bridged species rather than a μ-hydroxy-bridged complex seems to be likely for these cases.[25]

For the preparation of the metal-containing polymer **P2**, copolymer **P1**, and precursor [Ir(ppy)$_2$OH]$_2$ were dissolved in degassed dichloromethane and the solution was kept

Figure 1. ^{1}H NMR spectra of the copolymer **P1** (in CDCl$_3$), the precursor complex [Ir(ppy)$_2$OH]$_2$ (in CD$_2$Cl$_2$), and the complexed polymer **P2** (in CD$_2$Cl$_2$), as well as the model complex **M1** (in CD$_2$Cl$_2$). For all spectra: 400 MHz, 25 °C.

stirring for 2 d at room temperature.[23] Using the μ-hydroxy-bridged precursor the complexation of the **P1** could be conducted without further additives under these very mild conditions (Scheme 1). The solvent was evaporated and the polymeric material was investigated by ^{1}H NMR, UV–Vis absorption, and emission spectroscopy, as well as SEC combined with a PDA detector.

The ^{1}H NMR spectrum of the coordinated polymer **P2** was compared to the uncomplexed polymer **P1** and the precursor complex [Ir(ppy)$_2$OH]$_2$, as well as an analogous model complex **M1** [bis-(2-phenylpyridinato) iridium(III) n-butylacetoacetate] bearing n-butyl acetoacetate as ancillary ligand (Figure 1). No resonance traces from the precursor complex (in particular, the significant signal of the hydroxy-bridge at around −1.4 ppm) could be detected in the spectrum of **P2**. Besides a broadening and the loss of structure, the signals originating from the 2-phenyl-pyridinato ligands of the copolymer complexes (**P2**) coincide with the corresponding signals in the small model complex (**M1**). The acac site of the complex is represented by signals, which can be attributed to protons at positions H^C, H^2, and H^1, respectively. However, there are also resonance traces present (H^{1f}, H^{2f}, and H^{Af}) which most likely originate from uncomplexed acac sites on the copolymer. According
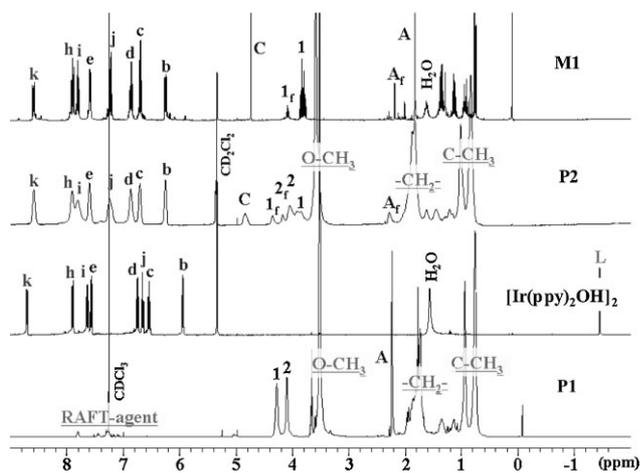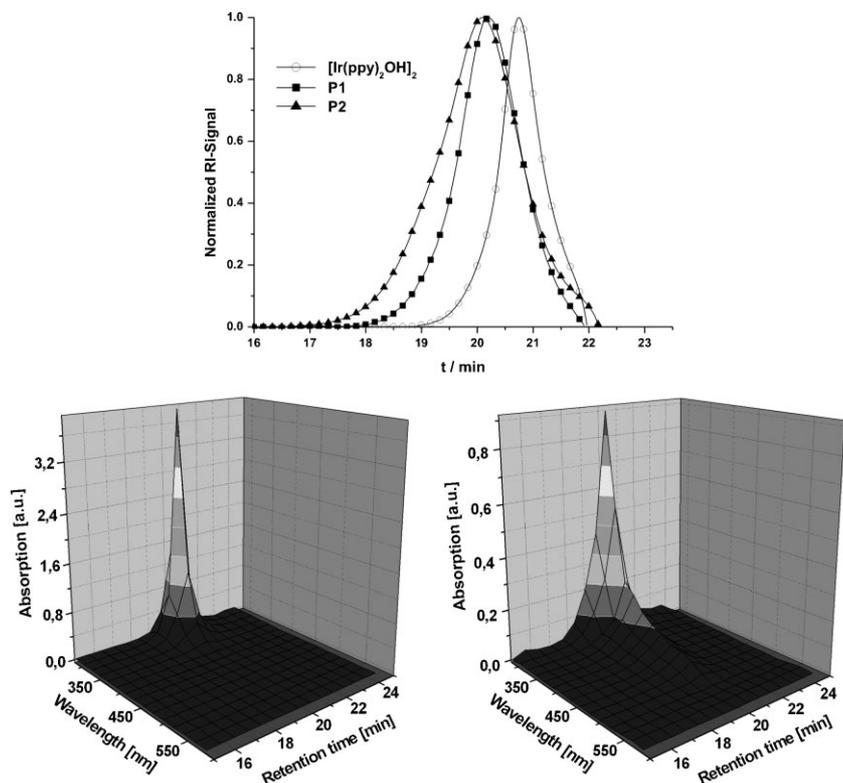
Figure 2. (Top) Normalized SEC–RI traces of the precursor complex [Ir(ppy)$_2$OH]$_2$, the copolymer **P1**, and the coordinated copolymer **P2** (eluent system: DMF with 5×10^{-3} M NH$_4$PF$_6$); (Bottom) SEC-PDA traces of the MMA–AAEM-copolymer before (**P1**, left) and after complexation (**P2**, right).

to the ^{1}H NMR spectrum, $\approx$12% of the polymer-ligand sites appear non-complexed. A complete complexation of all acac units in the copolymer, if not hindered by sterical requirements, might be accomplished by using a larger excess of the reactive precursor in the coordination reaction, but this might also increase the purification efforts.

Additionally, SEC (eluent: DMF with 5×10^{-3} M of NH$_4$PF$_6$) was utilized to investigate the obtained polymeric materials (**P1** and **P2**). Applying a RI detector and a linear PMMA calibration, the characteristics of the MMA–AAEM-copolymer were determined to be: $\overline{M}_n = 6\,400$ g · mol^{-1}, $\overline{M}_w = 7\,800$ g · mol^{-1}, and PDI = 1.22. The discrepancy to the ^{1}H NMR data ($\overline{M}_n = 8\,600$ g · mol^{-1}) might be related to the non-ideal standards (PMMA) used in the SEC experiment. The SEC traces of precursor [Ir(ppy)$_2$OH]$_2$, copolymer **P1** and complexed copolymer **P2** are displayed in Figure 2 (top). Although, the retention time of the precursor is different from the polymeric materials, the coordination of the copolymer **P1** induces no significant changes in the retention time. However, a clear broadening of the trace can be observed. SEC in combination with a PDA detector was conducted to find further evidence for the formation of complexes within the copolymer (Figure 2, bottom). As seen before from the experiments employing a RI detector

(Figure 2, top), no distinct change in the retention time can be observed upon complexation of copolymer **P1**, while a clear broadening of the trace is obvious. However, the PDA detector provides additional information about the UV–Vis absorption behavior of the investigated material(s). Even both samples (**P1** and **P2**) absorb light at short wavelengths, the UV–Vis absorption spectrum of the coordinated copolymer **P2** extends to longer wavelengths (Figure 2, bottom right). This is in full agreement with the photophysical investigations and provides another clear indication for the successful formation of polymer-bound Ir^{III} complexes.

Photophysical Properties

Another proof for the formation of the desired complexes within the copolymer was found by photophysical investigations in solution (i.e., UV–Vis absorption and emission spectroscopy). The copolymer **P1** dissolved in CH$_2$Cl$_2$ (pale pink appearance) exhibited absorption at short wavelengths with two maxima (around 232 and 303 nm) attributed to the RAFT moiety. In contrast, the complexed copolymer **P2** dissolved in CH$_2$Cl$_2$ (dark greenish appearance) shows strong ppy-based absorption (230–350 nm) as well as weak metal-to-ligand charge transfer
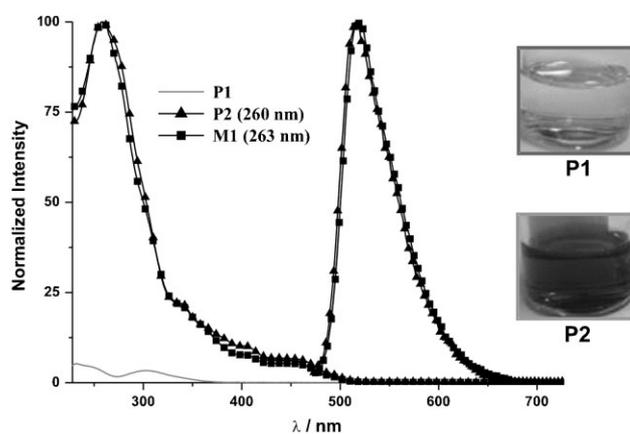

Figure 3. Photophysical investigations in solution (CH$_2$Cl$_2$): Normalized UV–Vis absorption and emission spectra of the coordinated copolymer **P2** and the model complex **M1** (the excitation wavelengths are given in brackets). The UV–Vis absorption of the MMA–AAEM copolymer **P1** is referenced to the spectrum of **P2** recorded at a similar concentration. The images at the right display CH$_2$Cl$_2$ solutions of **P1** and **P2**, respectively.

(MLCT) transitions (400–500 nm) characteristic for this type of *bis*-cyclometallated Ir^{III} complexes (Figure 3). The comparison of the complexed polymer to the analogous small model complex **M1** revealed an almost identical UV–Vis absorption and emission behavior in solution (Figure 3).[26] As expected, the attachment of the Ir^{III} emitter to the polymeric backbone does not seem to effect the absorption and emission properties of the complexes.[27]

Conclusion

A defined copolymer bearing acac-type ligand-sites could be synthesized utilizing a controlled radical polymerization technique (RAFT). Using a reactive, dimeric μ-hydroxy-bridged Ir^{III} precursor the ligand-sites of the copolymer could be coordinated under very mild conditions and without the use of further additives. The formation of complex species at the polymer-bound ligand sites was confirmed by NMR, UV–Vis absorption, and emission spectroscopy as well as SEC. The hydroxy-bridged precursor [Ir(ppy)$_2$OH]$_2$ inheres obviously a significant potential to perform complexation reactions under very mild conditions without any additional supports (i.e., bases, silver salts, etc.) and almost no purification efforts for the obtained complexed materials. In summary, the approach enables the preparation of Ir^{III}-equipped polymers as potential emitters for PLEDs. Furthermore, the protocol could be incorporated into a high-throughput experimentation workflow leading to emissive polymer libraries in a straightforward manner. Besides acacs, further species, such as acetoacetone and picolinic acid, should be efficiently coordinated by such kind of precursors.

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[26] We previously reported on a methacrylate-functionalized iridium(III) complex exhibiting orange phosphorescence and its' copolymerization with MMA (see ref.[20] for details). The UV–Vis absorption maxima had molar extinction coeffi-
cients which were close to the ones obtained for the model complex. Apparently, the photophysical properties of the polymer were hardly influenced by the polymer backbone, neither qualitatively nor quantitatively. Here, the same behavior is concluded also for polymer **P2** and model complex **M1**.

[27] Further investigations are currently focused on the removal of the RAFT moiety prior to complexation. A mild protocol to convert a RAFT to a hydroxy-substituent was recently introduced by Barner-Kowollik and coworkers: T. Gruendling, M. Dietrich, C. Barner-Kowollik, *Aust. J. Chem.* **2009**, *62*, 806.