Copolymers Containing Phosphorescent Iridium(III) Complexes Obtained by Free and Controlled Radical Polymerization Techniques[a]

Christoph Ulbricht, Caglar Remzi Becer, Andreas Winter, Dirk Veldman, Ulrich S. Schubert*

A methacrylate-functionalized phosphorescent Ir(III)-complex has been synthesized, characterized, and applied as a monomer in radical copolymerizations. Together with methyl methacrylate, the complex has been copolymerized under free radical polymerization conditions. Aiming for host-guest-systems, applicable e.g. in organic light emitting devices (OLEDs), the complex was further copolymerized with a methacrylate-functionalized carbazole derivative using the atom transfer radical polymerization technique. Applying gel permeation chromatography, in combination with a photodiode array detector, could clearly prove the formation of the copolymers. The optical properties of the photoactive monomers as well as the copolymers were investigated by absorption and emission spectroscopy (in solution). For the carbazole-copolymer, the emission originates almost exclusively from the complex. This provides evidence of an efficient intrachain energy transfer, which makes the system an interesting candidate for potential OLED applications.
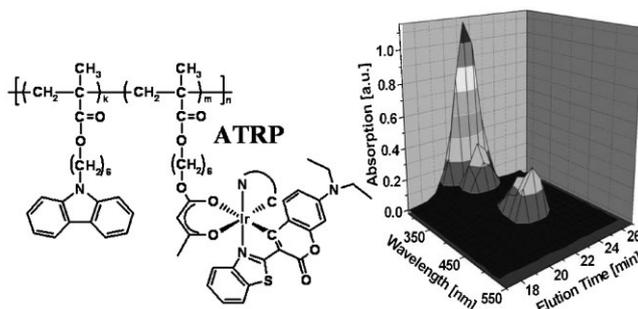
C. Ulbricht, C. R. Becer, A. Winter, U. S. Schubert
Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
Fax: (+31) 40 2474186; E-mail: u.s.schubert@tue.nl
C. Ulbricht, C. R. Becer, A. Winter, U. S. Schubert
Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands
C. R. Becer, U. S. Schubert
Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 10, 07743 Jena, Germany
D. Veldman
Molecular Materials and Nanosystems, Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

[a] ⌨ Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at http://www.mrc-journal.de, or from the author.

Introduction

Phosphorescent transition-metal complexes are attracting significant interest with respect to potential application in organic light emitting devices (OLEDs).[1] While exciton-based electroluminescence from fluorophores cannot exceed a maximum quantum yield of 25%, given by spin statistics, phosphorescent complexes can, in theory, achieve quantum yields up to 100%.[2] Combining phosphorescent emitters with proper host materials and optimized device set-ups can result in high efficient light emitting devices.

In particular promising candidates for multicolor OLEDs are phosphorescent iridium(III)-complexes,[1] with their ligand-based luminescence providing the opportunity to tune the emission color from red to blue by varying the attached ligands.[3,4]

For the fabrication of OLEDs mainly two methods are in the focus, vapor deposition and solution processing. 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,[5] 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). Blended systems, however, inhere the risk of undesired phase separation, aggregation, or crystallization, which can harm the device performance.[6] Therefore, the design of (co)polymers, combining the different functions (charge transport and emission), receives an increasing interest.[7,8] Better energy transfer to the emitters (higher efficiencies) and higher durability of the device are the expected benefits.

For optical applications, two main-types of materials are distinguished, namely conjugated[6c,9–11] and nonconjugated[6a,12,13] 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. Nonconjugated 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., blue emitters with rather high LUMO levels.[14]

Radical (co)polymerizations provide an easy access to nonconjugated polymers [e.g., poly(vinyl carbazole) (PVK)], tolerate a large diversity of functionalities and can be conducted with a variety of monomers under rather mild conditions. Besides the intensively used free radical polymerization (FRP), controlled radical polymerization techniques, like atom transfer radical polymerization (ATRP),[15] reversible addition–fragmentation chain transfer (RAFT) polymerization,[16] and nitroxide mediated polymerization (NMP)[17] gained tremendous interest. Controlling the molar mass of polymers combined with low polydispersity indices (PDI) by using these techniques, allows designing tailor-made polymers.

In this contribution, we report on the synthesis and characterization of a new methacrylate functionalized iridium(III)-complex exhibiting orange phosphorescence. Furthermore, we describe its application in different copolymerization reactions (FRP and ATRP) and the investigation of the resulting polymeric materials. A copolymer consisting of carbazole units and the complex displayed promising emission properties in solution.

Experimental Part

Materials and General Experimental Details

Unless stated otherwise, all reagents were purchased from commercial sources and used without further purification. The solvents were received from Biosolve and were dried and distilled according to standard procedures. All reactions dealing with $IrCl_3 \times 3$ H_2O or Ir-complexes have been conducted under a nitrogen atmosphere. The precursor complex **4** and the carbazole derivative **II** have been synthesized following literature procedures.[18–21] The synthesis of the methacrylate functionalized ancillary ligand **3** was accomplished in two steps adapting literature procedures.[22,23] For further details on all experiments and full characterizations, see the Supporting Information. 1-D (^{1}H and ^{13}C) and 2-D (^{1}H-^{1}H g-COSY) NMR spectra have been recorded on a Varian Mercury 400 MHz spectrometer at 298 K. UV-vis and photoluminescence spectra were obtained on a Perkin Elmer Lambda-45 and a Perkin Elmer LS50B luminescence spectrometer, respectively. For both techniques, dilute CH_2Cl_2 solutions and standard 1 cm path cuvettes were used. MALDI-TOF MS measurements have been conducted on a Voyager-DE^{TM} PRO Biospectrometry^{TM} Workstation (Applied Biosystems) time-of-flight mass spectrometer using the linear operation mode and *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malono-nitrile (DCTB) as matrix. Elemental analyses were carried out on a EuroVector EuroEA3000 elemental analyzer configured for CHNS. A Waters GPC system consisting of a 717 Plus autosampler, an isocratic pump, a solvent degasser, a column oven, and a Styragel HT 4 GPC column with a precolumn equipped either with a 2414 refractive-index (RI) or a 2996 photodiode array (PDA) detector was utilized for size exclusion chromatography investigations. DMF (containing 5×10^{-3} M NH_4PF_6) was used as an eluent at a column temperature of $50\,^{\circ}C$ and a flow rate of 0.5 mL · min^{-1}. Poly(methyl methacrylate) (PMMA) or polystyrene (PS) standards have been applied to determine the molar mass.

Preparation of the Methacrylate-Functionalized Complex 5

The synthesis of complex **5** [iridium(III)*bis*(3-(2-benzothiazolyl)-7-(diethylamino)-coumarinato-N,C4′) (6-(methacryloxy)hexyl acetoacetate)] was conducted adapting a reported complexation procedure.[24,25] The dimeric complex **4** (131 mg, 0.071 mmol) and silver trifluoromethanesulfonate (340 mg, 1.323 mmol) were dissolved in degassed acetone (40 mL) and kept in a nitrogen atmosphere while heating under reflux for 2.5 h. After cooling to room temperature, the acetoacetate derivative **3** (60 mg, 0.222 mmol) and sodium carbonate (130 mg, 0.778 mmol) were added and stirring was continued for 30 h. Thereafter, the solvent was stripped off. The crude material was purified by column chromatography (silica/diethyl ether) and subsequently precipitated in pentane yielding **5** as a red-orange powder (124 mg, 75%).

($C_{54}H_{55}O_9N_4S_2Ir$) 1 160.4041: Calcd. C 55.89, H 4.78, N 4.83, S 5.53; Found C 55.96, H 4.95, N 4.71, S 5.26.
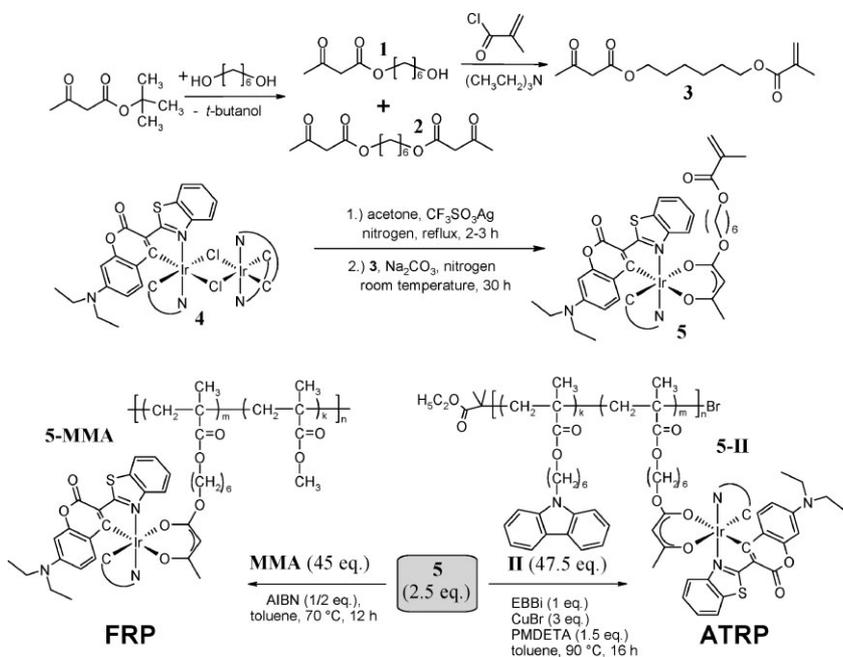
Scheme 1. Schematic representation of the synthesis of the methacrylate functionalized acetoacetate ligand **3** and the iridium(III) complex **5** thereof, as well as the radical copolymerization with MMA (FRP) and the carbazole derivative **II** (ATRP).

UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) = 447 (74 900), 475 nm (82 600 L · mol^{-1} · cm^{-1}).

Photoluminescence (CH$_2$Cl$_2$): $\lambda_{\max}$ = 569 nm (excitation at λ_{ex} = 475 nm).

MALDI-TOF MS (DCTB): m/z = 1 160.4 [C$_{54}$H$_{55}$O$_9$N$_4$S$_2$Ir].

^{1}H NMR (CD$_2$Cl$_2$): δ (ppm) = 1.05 (t, H^a, $J_{a,b}$ = 7.20 Hz); 1.25 (m$_c$, H^3); 1.34 (m$_c$,H^4); 1.46 (m$_c$, H^2); 1.63 (m$_c$, H^5); 1.72 (s, 3H, H^A); 1.93 (s, H^H); 3.25 (m$_c$, H^b); 3.86–4.08 (m, H^1); 4.10 (t, H^6, $J_{6,5}$ = 6.60 Hz,); 4.38 (s, H^C); 5.53–5.54 (m, H$^{G(E)}$); 5.91–5.95 (m, H^d); 6.06–6.11 (m, H$^{G(Z)}$ and H^e); 6.31 (m$_c$, H^h); 7.23–7.32 (m, H^q); 7.33–7.38 (m, H^p); 7.55, 7.74 (d, d, H$^{r,r'}$, $J_{r,q} = J_{r',q'}$ = 8 Hz); 7.92–7.97 (m, H^o).

Polymerizations

Free Radical Polymerization (FRP)

Methyl methacrylate (MMA, 31.8 mg, 0.318 mmol, 90 equiv.), complex **5** (20.4 mg, 0.02 mmol, 5 equiv.), 2,2′-azoisobutylonitrile (AIBN, 0.64 mg, 0.004, 1 equiv.), and toluene (0.5 mL) were placed in a microwave vial equipped with a magnetic stirrer. The vial was capped with a septum and the solution was degassed by purging with nitrogen for 15 min (through cannulae). After stirring the reaction mixture at 70 °C (classical heating, oil bath) for 12 h, the obtained polymer was precipitated twice in methanol.

UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε)^b = 447 (71 700), 475 nm (78 800 L · mol^{-1} · cm^{-1}).

---

^{b} To determine the extinction coefficient (ε) for the copolymer solutions, the molar ratio of the comonomers were calculated from the ^{1}H NMR integrals: M([**5**]$_1$[MMA]$_{16.4}$) = 2 800 g · mol^{-1}; M([**5**]$_1$[**II**]$_{22.2}$) = 8 610 g · mol^{-1}.

Photoluminescence (CH$_2$Cl$_2$): $\lambda_{\max}$ = 569 nm (excitation at λ_{ex} = 475 nm).

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.60–2.20 (m, −CH$_3$, −CH$_2$− polymer backbone, H^{a,2,3,4,5,A,H}); 3.11–3.41 (m, H^b); 3.44–3.70 (m, −O−CH$_3$); 3.80–4.04 (m, H^1 and H^6); 4.35 (s, H^C); 5.85 (m$_c$, H^d); 6.04–6.11 (m, H^e); 6.26–6.32 (m, H^h); 7.15–7.36 (m, H^q and H^p); 7.51, 7.73 (m$_c$, m$_c$, H$^{r,r'}$); 7.89 (m$_c$, H^o).

GPC (RI, PMMA calibration): $\overline{M}_n$ = 19 600 g · mol^{-1}, $\overline{M}_w$ = 31 400 g · mol^{-1}, PDI = 1.60.

Atom Transfer Radical Polymerization (ATRP)

The carbazole derivative **II** (55.7 mg, 0.164 mmol, 47.5 equiv.), **5** (10 mg, 0.009 mmol, 2.5 equiv.), CuBr (1.5 mg, 0.011 mmol, 3 equiv.), and toluene (1 mL from a stock solution) containing *N,N,N′,N′,N″*-pentamethyldiethyl-enetriamine (PMDETA, 0.90 mg, 0.005 mmol, 1.5 equiv.) were placed in a microwave vial equipped with a magnetic stirrer. The vial was capped with a septum and the solution was degassed by purging with nitrogen for 15 min (through cannulae). After the addition of ethyl 2-bromo isobutyrate (EBBi, 0.67 mg, 0.003 mmol, 1 equiv.) the reaction mixture was stirred at 90 °C (classical heating, oil bath) for 16 h. The obtained polymer was precipitated in methanol and diethyl ether, respectively.

UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε)^b = 238 (818 700), 264 (495 000), 295 (341 600), 332 (90 600), 347 (106 100), 447 (77 600), 475 nm (86 600 L · mol^{-1} · cm^{-1}).

Photoluminescence (CH$_2$Cl$_2$): $\lambda_{\max}$ = 569 nm (excitation at λ_{ex} = 475 nm).

^{1}H NMR (CD$_2$Cl$_2$): δ (ppm) = 0.72–2.09 (m, −CH$_3$, −CH$_2$− polymer backbone, H^{a,2,3,4,5,A,H}); 2.99–3.31 (m, H^b); 3.64–3.94 (m, −O−CH$_2$−); 3.96–4.36 (m, −N−CH$_2$−, H^C); 5.83–5.94 (m, H^d); 6.07 (m$_c$, H^e); 6.20–6.33 (m, H^h); 7.04–7.49 (m, H^q, H^p and H^{carbazole}); 7.53, 7.71 (m$_c$, m$_c$, H$^{r,r'}$); 7.83 (m$_c$, H^o); 7.93–8.12 (m, H^{carbazole}).

GPC (RI, PS calibration): $\overline{M}_n$ = 19 500 g · mol^{-1}, $\overline{M}_w$ = 22 000 g · mol^{-1}, PDI = 1.13.

Results and Discussion

The synthesis of the methacrylate functionalized acetoacetate **3** was conducted in two steps: a transesterification reaction of *tert*-butyl acetoacetate[22] with 1,6-hexanediol, yielding 6-hydroxyhexyl acetoacetate was followed up by an esterification with methacryloyl chloride,[23] yielding the desired product **3** (Scheme 1). A procedure, introduced by DeRosa et al.[24] was adapted to synthesize the methacrylate functionalized complex **5** starting from the chloro-bridged dimeric iridium(III) precursor **4**.[18] After treating a precursor **4**/acetone-mixture with silver triflate, while stirring under reflux for 2.5 h, the designated

ligand **3** as well as Na$_2$CO$_3$ were added and stirring was continued at room temperature for 26 h. Purification by column chromatography yielded the desired complex **5** (Scheme 1). The structure and purity were proven by NMR spectroscopy, elemental analysis and MALDI-TOF mass spectrometry. Furthermore, the photophysical properties were investigated by UV-vis absorption and emission spectroscopy in dichloromethane solutions.

The methacrylate-functionalized carbazole monomer **II** (Scheme 1) was synthesized following known procedures.[19–21] For more details regarding the synthesis and analysis, see the Supporting Information. Carbazole derivatives, e.g., PVK, are well-known hole conductors and are widely used as host materials for phosphorescent emitters. Due to the same polymerizable unit (methacrylate) attached via a C6-spacer, both monomers, complex **5** and carbazole **II**, are expected to possess similar reactivity. Moreover, the spacer between carbazole and the polymeric backbone prevents the formation of excimers upon photoexcitation,[26] which occurs e.g., in case of polymerized vinylcarbazole.[27,28]

The subsequent polymerizations were performed as depicted in Scheme 1. The copolymerization of complex **5** (2.5 equiv.) with MMA (45 equiv.) was carried out under free radical conditions, applying AIBN (0.5 equiv.) as initiator. After 12 h stirring at 70 °C, the copolymer **5-MMA** was obtained by precipitation in methanol. Additionally, **5** (2.5 equiv.) and the carbazole monomer **II** (47.5 equiv.) were copolymerized under ATRP conditions, applying EBBi (1 equiv.) as initiator as well as CuBr (3 equiv.) and the ligand PMDETA (1.5 equiv.). After reacting for 16 h at 90 °C the solution was precipitated in methanol and diethyl ether yielding the desired copolymer. The copolymers were investigated by ^{1}H NMR spectroscopy (Figure 1) and size exclusion chromatography (GPC, combined with a PDA detector, Figure 2).

The successful incorporation of the complex into the polymeric structure was confirmed by comparing the ^{1}H NMR spectra of the copolymers to those recorded for the respective monomers. Supported by gCOSY measurements, all signals of the ^{1}H NMR spectra recorded for the synthesized monomers could be assigned (Figure 1).

The depletion of the signals originating from the protons at the double bond in the methacrylate unit (e.g., **5**: G$_Z$, $\delta \approx 6.09$ ppm and G$_E$, $\delta \approx 5.53$ ppm), together with the broadening of the signals and the loss in resolution, indicates the formation of the desired polymers. The monomer ratio within the copolymers calculated from the respective signal intensities in the ^{1}H NMR spectra is close to the applied feed ratio (MMA/**5** ≈ 16, feed ratio: 18 and II/**5** ≈ 22, feed ratio: 19), suggesting a comparable reactivity of the used monomers under the applied conditions.
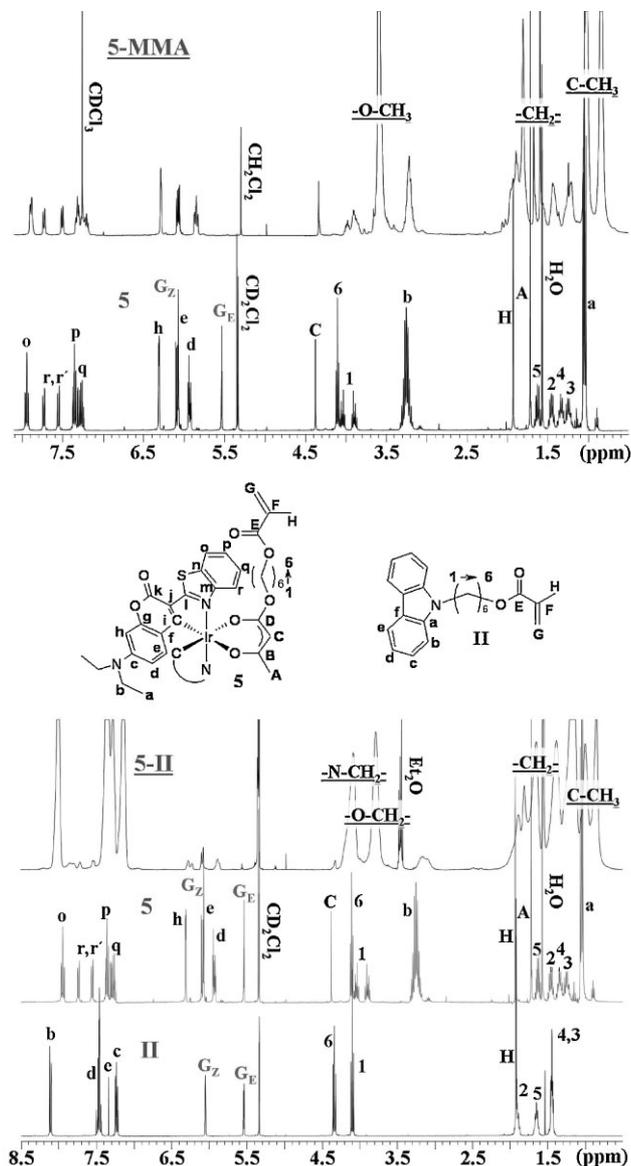

Figure 1. ^{1}H NMR spectra (400 MHz, CD$_2$Cl$_2$). Top: complex **5** (CD$_2$Cl$_2$) and the copolymer with MMA (FRP) **5-MMA** (CDCl$_3$). Bottom: the monomers **II** and **5** as well as the copolymer **5-II** (ATRP). Middle: schematic representation of the monomers **5** and **II** with positional assignment.

Size exclusion chromatography allows the detailed characterization of the synthesized polymers (see Figure 2 for polymer **5-II**) (for the GPC conditions see ref.[29]). By utilizing a PDA detector the absorption spectra of the UV-vis-active monomers **II** (retention time 23.3 min) and **5** (retention time 22.8 min) as well as their combined absorption in the final copolymer **5-II** (retention time 21.2 min) were observed, proving clearly the incorporation of both monomers into the copolymer. Referring the results obtained with the RI detector to PMMA-standard values in the case of **5-MMA** and to PS-standard values for **5-II**, $\overline{M}_n$
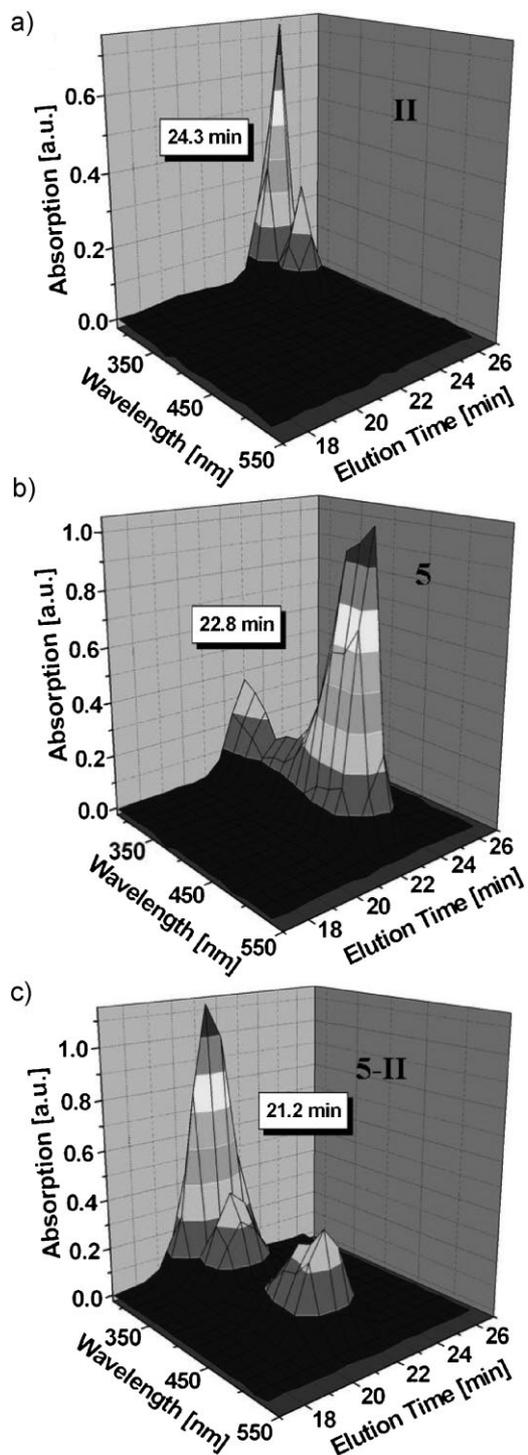
Figure 2. GPC-PDA traces of the monomers **II** (a) and **5** (b) as well as their ATRP-copolymer **5-II** (c).

and $\overline{M}_w$ as well as the PDI values were estimated. Due to the rather bad structural match with the applied standards and the poor solubility of the samples the obtained values represent only a rather rough approximation. The average molar mass of **5-MMA** ($\overline{M}_n = 19\,600$ Da) deviates signifi-

cantly from the theoretical value ($\overline{M}_n = 7\,400$ Da), obtained by assuming a fast initiation by all initiator molecules and a full conversion of the applied monomers. For a FRP the PDI of 1.6 is relatively low and a result of the two precipitation steps, which ensured the removal of low molar mass materials. The observed molar mass and PDI value reflect the restrictions of FRP. A fast initiation by a few of the designated initiator molecules is followed by a rapid propagation leading to the formation of high molar mass polymers already at the beginning of the polymerization. The number of polymer chains correlates with the half life time of the applied initiator under the given conditions (in particular the temperature). A relatively high amount of free radical chain ends and depletion of monomers promotes termination reactions, like recombination and disproportionation, further broadening the molar mass distribution.

In the case of the ATRP polymer **5-II**, the estimated average molar mass ($\overline{M}_n = 19\,500$ Da) was close to the theoretical value ($\overline{M}_n = 18\,800$ Da) for full conversion. The low PDI (1.13) suggests a high degree of control for the conducted polymerization. Taking the data from ^{1}H NMR and GPC the average monomer composition of the polymers can be determined — **5-MMA**: $(5)_7(\mathbf{MMA})_{114.8}$ [feed: $(5)_{2.5}(\mathbf{MMA})_{45}$]; **5-II**: $(5)_{2.3}(\mathbf{II})_{51}$ [feed: $(5)_{2.5}(\mathbf{II})_{47.5}$].

Initial investigations of the optical properties were performed in dichloromethane solutions (Figure 3). Absorption and emission of the complex **5** are in analogy to reports describing similar coumarin6-based iridium(III) complexes.[3,24,25] Coumarin6, functioning as cyclometalating ligand, has a dominant impact on the photophysical properties of the complex **5**. A solution of **5** in dichloromethane shows two distinct absorption maxima at 447 ($\varepsilon \approx 74\,900$) and 475 nm ($\varepsilon \approx 82\,600$ L·mol^{-1}·cm^{-1}), respectively. Excitation of **5** into the absorption band results in an emission maximum at 569 nm with a clear vibronic progression at 612 nm (Figure 3a and c).

The copolymer **5-MMA** shows almost identical absorption and emission characteristics as the complex monomer **5** (Figure 3a). Based on the monomer ratio, obtained from the integrals of the ^{1}H NMR spectrum, molar extinction coefficients were calculated to 71 700 L·mol^{-1}·cm^{-1} (447 nm) and 78 800 L·mol^{-1}·cm^{-1} (475 nm), which are close to the values for **5**. Assuming a minimal influence from the MMA-units on the optical properties of the embedded complex, the molar ratio of the monomers in the copolymer can be calculated via the molar extinction coefficient, as well. The good agreement of the values from both methods (NMR and UV-vis spectroscopy) confirms the reliability of the monomer ratio.

The UV-vis spectrum of the complex-carbazole-copolymer **5-II** reveals the combined absorptions of both monomers **5** and **II** (Figure 3b). Also for this copolymer the monomer composition obtained from NMR spectroscopy is
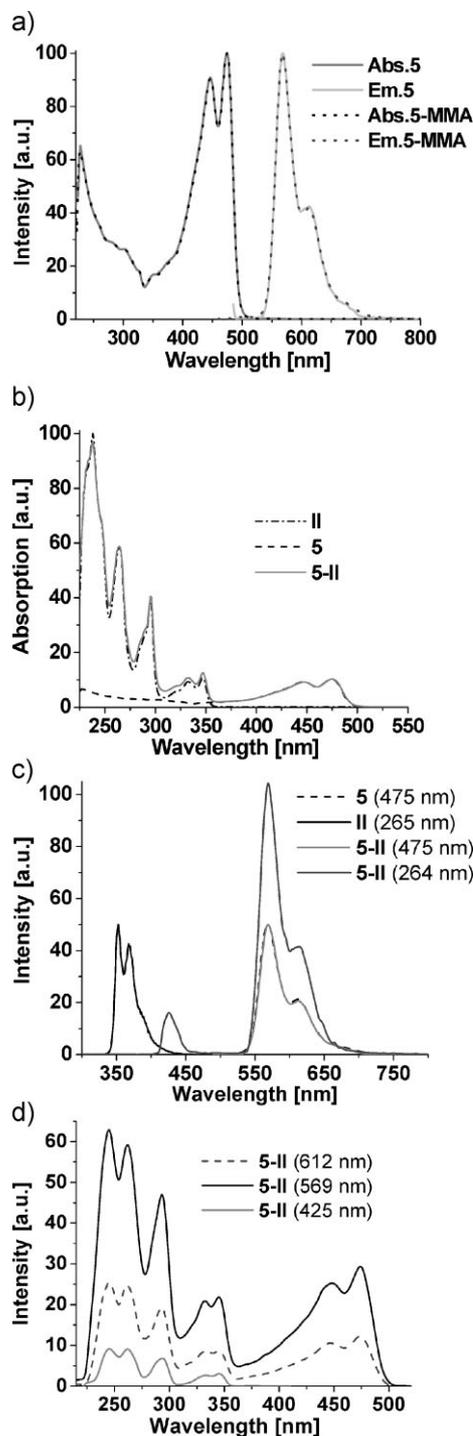
Figure 3. Optical investigations in solution (CH₂Cl₂): (a) absorption and emission ($\lambda_{ex} = 475$ nm) spectra (normalized) of the methacrylate-functionalized complex **5** and the copolymer **5-MMA**. (b) Absorption spectra (normalized) of the monomers **5** and **II** as well as the copolymer **5-II**. (c) Emission spectra (normalized) of the monomers **5** and **II** as well as the copolymer **5-II**. The excitation wavelengths are given in brackets. The emissions of the copolymer **5-II** after excitation at 475 and 264 nm, respectively, are in the found proportion. (d) Excitation spectra of the copolymer **5-II** for the different emission maxima, given in brackets.

confirmed by the high resemblance of the molar extinction coefficients, 77 600 $L \cdot mol^{-1} \cdot cm^{-1}$ (447 nm) and 86 600 $L \cdot mol^{-1} \cdot cm^{-1}$ (475 nm), to the values obtained for **5**.

The emission of **5-II** originates almost exclusively from the complex, independently from the applied excitation wavelength (Figure 3c). Direct excitation of the complex ($\lambda_{ex} = 475$ nm) as well as excitation in the carbazole absorption band ($\lambda_{ex} = 264$ nm) results in complex emission ($\lambda_{max} = 569$ nm) without monomeric carbazole emission ($\lambda = 353$, 368 nm) being present. However, besides the complex emission, a new emission with a maximum around 425 nm occurs upon excitations in the carbazole absorption band, which might be attributed to excimer emission.[27] The carbazole absorption bands dominate the excitation spectra at each emission wavelength (425, 569, and 612 nm) (Figure 3d). The strong complex emission upon excitation of the carbazole units provides evidence for an efficient energy transfer to the complex, already occurring in solution at rather low complex content (**5/5-II** ≤ 0.05).[11] Due to the high dilution of the investigated solution ($\approx 10^{-7}$ mol $\cdot$ L^{-1}, relating to complex moieties), the occurrence of interchain energy transfer processes is very unlikely.[11] Hence, the complete quenching of the monomeric carbazole emission in solution gives further evidence that all carbazole polymer chains possess complex moieties, which harvest the energy via intrachain energy transfer processes.

A composition according to the monomer feed, a low PDI value suggesting a rather defined system, and a host-guest-energy transfer upon photoexcitation already occurring in solution make the system **5-II** an interesting candidate for the application in phosphorescent OLEDs.

Conclusion and Outlook

We presented the synthesis and characterization of a new methacrylate functionalized phosphorescent iridium(III)-complex as well as its application in radical copolymerizations. FRP as well as ATRP conditions have proven to be suitable methods for the copolymerization of complex monomer **5**. The copolymerization of **5** and **II** represents, to the best of our knowledge, the first polymerization conducted under the conditions of controlled radical polymerization (here: ATRP) involving an iridium(III) complex monomer species. Upon photoexcitation of the host, the copolymer **5-II** possessing a rather low complex loading (**5/5-II** ≤ 0.05) efficiently transfers energy to the incorporated phosphorescent emitter via an intrachain mechanism. This renders the system a promising candidate for the construction of efficient phosphorescent OLEDs.

In follow-up studies, the redox properties of the monomers as well as the photo- and electro-optical

properties of the polymers will be investigated in more detail. OLEDs will be prepared and investigated. Further polymers with different monomer ratios and molar weights will be synthesized to find the optimum and the boundaries of the system. Copolymer- and blend-based films will be compared in terms of morphology (homogeneity) and performance upon photo- and electro-excitation to investigate the benefits of covalently anchoring the designated emitter within the polymeric host.

[1] E. Holder, B. M. W. Langeveld, U. S. Schubert, *Adv. Mater.* **2005**, *17*, 1109.

[2] Y. Kawamura, K. Goushi, J. Brooks, J. J. Brown, H. Sasabe, C. Adachi, *Appl. Phys. Lett.* **2005**, *86*, 071104.

[3] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2001**, *123*, 4304.

[4] Y. You, Y. Park, *J. Am. Chem. Soc.* **2005**, *127*, 12438.

[5] [5a] B.-J. de Gans, P. C. Duineveld, U. S. Schubert, *Adv. Mater.* **2004**, *16*, 203; [5b] E. Tekin, P. J. Smith, U. S. Schubert, *Soft Matter* **2008**, *4*, 703; [5c] E. Tekin, E. Holder, V. Marin, B.-J. de Gans, U. S. Schubert, *Macromol. Rapid Commun.* **2005**, *26*, 293; [5d] E. Tekin, B.-J. de Gans, U. S. Schubert, *J. Mater. Chem.* **2004**, *14*, 2627; [5e] B.-J. de Gans, U. S. Schubert, *Macromol. Rapid Commun.* **2003**, *24*, 659.

[6] [6a] Y. You, S. H. Kim, H. K. Jung, S. Y. Park, *Macromolecules* **2006**, *39*, 349; [6b] Y. Deng, S.-J. Liu, Q.-L. Fan, C. Fang, R. Zhu, K.-Y. Pu, L.-H. Yuwen, L.-H. Wang, W. Huang, *Synth. Met.* **2007**, *157*, 813; [6c] H. Zhen, C. Luo, W. Yang, W. Song, B. Du, J. Jiang, C. Jiang, Y. Zhang, Y. Cao, *Macromolecules* **2006**, *39*, 1693.

[7] J. Jian, W. Yang, Y. Cao, *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 37.

[8] V. Marin, E. Holder, R. Hoogenboom, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 618.

[9] X. Chen, J.-L. Liao, Y. Liang, M. O. Ahmed, H.-E. Tseng, S.-A. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 636.

[10] J. Langecker, M. Rehahn, *Macromol. Chem. Phys.* **2008**, *209*, 258.

[11] S.-J. Liu, Q. Zhao, R.-F. Chen, Y. Deng, Q.-L. Fan, F.-Y. Li, L.-H. Wang, C.-H. Huang, W. Huang, *Chem. Eur. J.* **2006**, *12*, 4351.

[12] X.-Y. Wang, A. Kimyonok, M. Weck, *Chem. Commun.* **2006**, 3933.

[13] L. Deng, P. T. Furuta, S. Garon, J. Li, D. Kavulak, M. E. Thompson, J. M. J. Fréchet, *Chem. Mater.* **2006**, *18*, 386.

[14] M. Sudhakar, P. I. Djurovich, T. E. Hogen-Esch, M. E. Thompson, *J. Am. Chem. Soc.* **2003**, *125*, 7796.

[15] [15a] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721; [15b] J. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614.

[16] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moa, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, *31*, 5559.

[17] C. J. Hawker, G. G. Barclay, A. Orellana, J. Dao, W. Devonport, *Macromolecules* **1996**, *29*, 5245.

[18] [18a] S. Sprouse, K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1984**, *106*, 6647; [18b] E. Holder, V. Marin, A. Alexeev, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2765; [18c] K. K.-W. Lo, C.-K. Chung, N. Zhu, *Chem. Eur. J.* **2003**, *9*, 475.

[19] A. A. Farah, W. J. Pietro, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 6057.

[20] R. Lygaitis, A. Matoliukstyte, N. Kreiveniene, J. V. Grazulevicius, *J. Photochem. Photobiol. A: Chem.* **2004**, *167*, 163.

[21] A. A. Farah, W. J. Pietro, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 679.

[22] J. S. Witzeman, W. D. Nottingham, *J. Org. Chem.* **1991**, *56*, 1713.

[23] V. Marin, E. Holder, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 374.

[24] M. C. DeRosa, D. J. Hodgson, G. D. Enright, B. Dawson, C. E. B. Evans, R. J. Crutchley, *J. Am. Chem. Soc.* **2004**, *126*, 7619.

[25] N. Rehmann, C. Ulbricht, A. Kähnen, P. Zacharias, M. C. Gather, D. Hertel, E. Holder, K. Meerholz, U. S. Schubert, *Adv. Mater.* **2008**, *20*, 129.

[26] A. Ledwith, N. J. Rowley, S. M. Walker, *Polymer* **1981**, *22*, 435.

[27] G. E. Johnson, *J. Chem. Phys.* **1975**, *62*, 4697.

[28] J. V. Grazulevicius, P. Strohriegl, J. Pielichowski, K. Pielichowski, *Prog. Polym. Sci.* **2003**, *28*, 1297.

[29] M. A. R. Meier, B. G. G. Lohmeijer, *Macromol. Rapid Commun.* **2003**, *24*, 852.