Functional ruthenium(II)- and iridium(III)-containing polymers for potential electro-optical applications†

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The need for novel materials with luminescent properties and advanced processing features requires reliable and reproducible synthetic routes for the design of suitable materials, such as *e.g.* polypyridyl ruthenium(II) and iridium(III)-containing polymers. The most popular ligand for those purposes is the 4,4′-functionalized bipyridine unit. Therefore, several synthetic strategies for the derivatization of the 4,4′-dimethyl-2,2′-bipyridine are highlighted, and in particular functionalities, which enable further covalent linkage to polymeric structures, are discussed in this *critical review*. Subsequently, the different synthetic strategies for the preparation of polymeric metal-complexes are described, either starting from small functionalized complexes (later covalently attached to the polymer), or from macroligands (subsequently coordinated to the metal ions). The designed materials reveal good processing properties using spin coating and inkjet printing, as well as beneficial electro-optical properties for potential thin functional film applications, such as light-emitting electrochemical cells.

1. Introduction

Nowadays, new functional materials with tailor-made properties, good processing features and straightforward synthesis are of central importance in light-emitting devices, in particular in large area applications such as lighting.[1] Furthermore, labelling of well-known polymers with light-emitting systems represents an interesting topic, and in particular luminescent and redox active transition metal-containing systems are highly appealing due to their special photochemical and electrochemical properties.[2] The use of

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Veronica Marin was born in 1975 in Harsova (Romania). She graduated in 2001 from the "Politehnica" University of Bucharest. During her last year of study she was employed as research assistant at the National Highfield NMR Laboratory of the "C.D. Nenitescu" Organic Chemistry Institute in Bucharest, Romania. In the middle of 2002, she started her PhD thesis as part of the Dutch Polymer Institute program (project #324, Polymer-Polymer Photovoltaics) in the group of Prof. Dr Ulrich S. Schubert, Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, the Netherlands. Her work focuses on synthesis of novel functional materials based on ruthenium(II) and iridium(III) polypyridyl complexes for potential electro-optical applications.

Elisabeth Holder

Elisabeth Holder studied Chemistry at the "Eberhard-Karls Universität" in Tübingen, Germany and received her PhD in 2001 in the laboratory of Prof. E. Lindner. Thereafter, she enjoyed a postdoctoral stay at the "University of Maryland" in the "Center for Fluorescence Spectroscopy" with Prof. J. R. Lakowicz (Baltimore, USA). Subsequently, she pursued a postdoctoral stay at the "Technische Universiteit Eindhoven", the Netherlands in the laboratory of Prof. U. S. Schubert. Since April 2006 she heads the "Functional Polymers Group" at the "University of Wuppertal", Germany. Her research interests are based on the synthesis and characterization of new functional polymers involving metal–ligand complexes, organic–inorganic hybrid materials and composites for applications in light-emitting devices, solar cells and sensors. Her focus in materials development is on engineering energy and electron transfer processes.

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non-covalent metal–ligand (coordination) interactions[3,4] offers some additional advantages. The coordination bond is highly directional, the ligand structures can be varied in a desired manner by established organic chemistry, and the thermodynamic and kinetic stability can be fine-tuned with the appropriate type of ligand and/or metal ions.[5] In addition, the metal–ligand interaction introduces new electrochemical, photochemical and photophysical properties to the whole material (*e.g.* ligand-centred and metal-centred absorption bands, redox behaviour, metal-to-ligand or ligand-to-metal charge-transfer bands). Metal coordinating units can be introduced into macromolecules *via* polymerization of functional monomers, end group or side group modification, and *via* functional initiators.[6–11]

Currently, novel polymeric materials based on d^6 transition metal complexes, especially using ruthenium(II) and iridium(III) ions, gained special attention due to their potential applications in light-emitting devices supported by improved processing features.[1,12] Even more important, the properties of the materials can be strongly influenced by the choice of the utilized metal ions, as well as by the chelating ligand and the polymer backbone. The covalent linkage of the complexes to a polymer leads to materials that reveal the advantage of preventing the aggregation of metal complexes as observed in polymer blends, while still maintaining the properties of the individual complexes. This approach ensures the processing features of the materials by spin coating and inkjet printing.[13,14] Furthermore, quick degradation on the electrode surface of the emitters might be prevented by making use of this concept.[15,16]

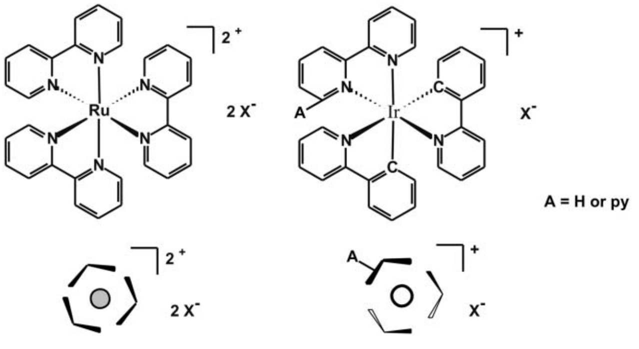

Fig. 1 Chemical structures and sketch of 2,2′-bipyridine, heteroleptic ruthenium(II) and iridium(III) complexes.

The general target of current research is to develop new synthetic pathways for an easy access to a variety of functionalized-bipyridine ligands which enable further covalent linkage to polymers, opening the way to advanced processing methods for potential device applications. The functionalization of 4,4′-dimethyl-2,2′-bipyridine ligands, followed by incorporation of these ligands and/or of the corresponding pre-formed complexes into polymeric architectures, will be discussed in this article. In addition, we address the ruthenium(II) and iridium(III) transition metal ions since they are suitable for device application due to appropriate photophysical and electrochemical properties, and their versatility to form homo- and heteroleptic complexes (Fig. 1). Charged ruthenium(II) and iridium(III)[17–20] complexes based on chelating ligands such as 2,2′-bipyridine and terpyridine

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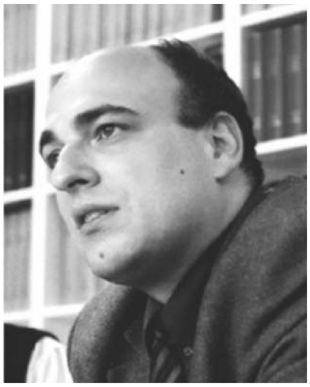
Richard Hoogenboom

Richard Hoogenboom was born in 1978 in Rotterdam (The Netherlands). In 2001 he obtained his M.Sc. degree in chemical engineering at the Eindhoven University of Technology, whereby his undergraduate research was performed in the group of Bert Meijer (Eindhoven, The Netherlands). During the studies, he performed an internship within the group of Andrew Holmes (Cambridge, United Kingdom). In 2005, he obtained his PhD under supervision of Ulrich Schubert (Eindhoven, The Netherlands) focusing on supramolecular initiators for controlled polymerization techniques, automated parallel synthesis of well-defined polymers and microwave irradiation in polymer chemistry. Currently, he is working as project leader for the Dutch Polymer Institute (DPI) with a major focus on the use of high-throughput experimentation and microwave irradiation for living/controlled polymerization techniques.



Ulrich S. Schubert

Ulrich S. Schubert was born in Tübingen in 1969. He studied chemistry at the Universities of Frankfurt and Bayreuth (both Germany) and the Virginia Commonwealth University, Richmond (USA). His PhD was performed under the supervision of Professor Eisenbach (Bayreuth, Germany) and Professor Newkome (Florida, USA). In 1995 he obtained his doctorate with Prof. Eisenbach. After a postdoctoral training with Professor Lehn at the Université Strasbourg (France) he moved to the Technische Universität München (Germany) to obtain his habilitation in 1999 (with Professor Nuyken). From 1999 to spring 2000 he held a temporal position as a professor at the Center for NanoScience at the Universität München (Germany). Since Summer 2000 he is Full-Professor at the Eindhoven University of Technology (Chair for Macromolecular Chemistry and Nanoscience). From 2003 on he is member of the management team of the Dutch Poymer Institute. His awards include the Bayerischen Habilitations-Förderpreis, the Habilitandenpreis of the GDCh (Makromolekulare Chemie), the Heisenberg-Stipendium of the DFG, the Dozenten-Stipendium of the Fonds der Chemischen Industrie and a VICI award of NWO. The major focus of the research interest of his relates to organic heterocyclic chemistry, supramolecular materials, combinatorial material research, nanoscience and tailor-made macromolecules.

systems have been already successfully applied in light-emitting electrochemical cells (LECs)[1] due to their high quantum yields and counter ion induced high conduction properties.

2. Synthetic strategies

Polypyridyl-based ligands such as 2,2′-bipyridines (abbreviated as bpy) and 2,2′-6′,2″-terpyridines (abbreviated as tpy) are well-known as heterocyclic entities. They gained significant attention for their excellent complexation chemistry towards metal ions. Bipyridines consist of two pyridine rings which can coordinate d^6 metal ions *e.g.* Ru(II) or Ir(III) in an octahedral fashion. Using bipyridines as ligands leads to the formation of the two primary σ-dative interactions that are further enhanced by the opportunities for overlap between the aromatic π-system and the d-orbitals of coordinated metal ions.[21] Terpyridines consist of three pyridine rings and the complexation to iridium(II) dimers allows the participation of only two rings, resulting in a bipyridine-like complexation (Fig. 1).

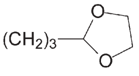
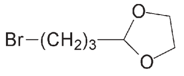
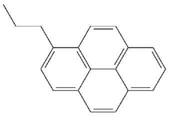
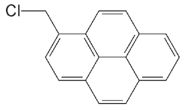
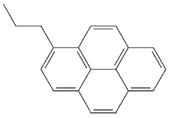
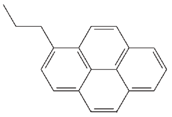
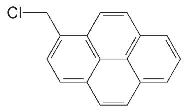
2,2′-Bipyridines and their analogues can be synthesized in many ways. A recent review[22] evaluates improved and modern synthetic methodologies to prepare these bidentate ligands. Finding synthetic approaches to link bipyridine ligands and/or their corresponding complexes to a variety of molecules or to polymeric substrates is highly desirable for many applications. Moreover, the use of transition metal complexes as light-emitter, in combination with polymers that enable advanced processing features as *e.g.* inkjet printing, became very attractive in research areas targeting device technology applications. As a consequence reliable routes towards functionalized bipyridines are required.

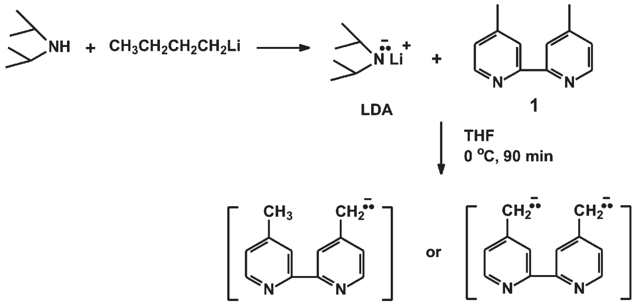
2.1 Derivatization of 4,4′-dimethyl-2,2′-bipyridine by direct or sequential functionalization routes

A popular starting material is 4,4′-dimethyl-2,2′-bipyridine (dMbpy), since it is a versatile, inexpensive and easily accessible commercial source of 2,2′-bipyridine derivatives. Several synthetic strategies have been described for the direct synthesis of dMbpy *via* homocoupling of substituted pyridine in the presence of a Raney nickel[23] or a palladium catalyst,[24] as well as by Stille-type cross coupling reaction of halo-pyridines in toluene in the presence of tetrakis(triphenyl-phosphine) palladium(0) in rather good yields.[25]

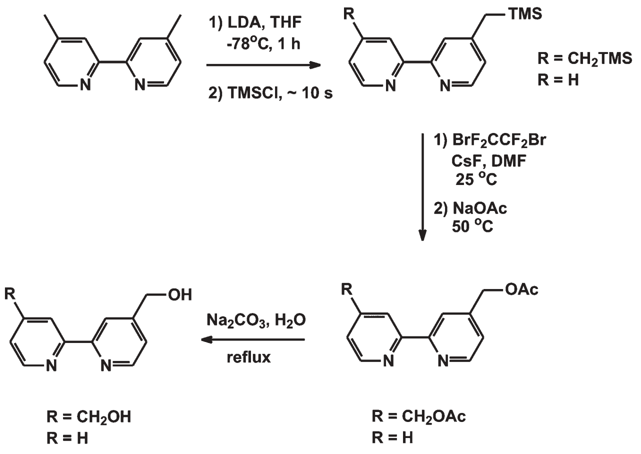
The most versatile method to introduce various functionalities onto dMbpy is employing the lithium di-isopropylamine (LDA) procedure (Table 1).[26–37] LDA is generated by treatment of di-isopropylamine with *n*-butyl lithium in THF under an inert atmosphere at −78 °C and it can successfully mono- or bis-lithiate the methyl groups on the 4,4′-dimethyl-2,2′-bipyridine ligand depending on the stoichiometry (Scheme 1).

Table 1 Selected examples of mono- and bis-functionalities introduced by derivatization of 4,4′-dimethyl-2,2′-bipyridine *via* the LDA procedure

R_1	R_2	Reagent	***Ref.***
CH_3	$(CH_2)_nCH_3$, n = 3, 10, 11, 12, 14, 18	$Br(CH_2)nCH_3$	26
$(CH_2)_nCH_3$	$(CH_2)_nCH_3$	$Br(CH_2)_nCH_3$	
n = 6	n = 6		27
n = 9	n = 9		23
n = 11	n = 11		26
$(CH_2)_n$–CH=CH_2	$(CH_2)_n$–CH=CH_2	$X(CH_2)_n$–CH=CH_2, X = I, OTs	28
CH_3	$(CH_2)_nBr$	$Br(CH_2)_nBr$	
	n = 3–7		29
	n = 16		30
CH_3	$(CH_2)_nOH$		
	n = 2	HCHO	24
	n = 5	(1) Dioxolane; (2) H_2O; (3) $NaBH_4$	32
CH_3			32
CH_2X (X = Br, Cl)	CH_2 X (X = Br, Cl)	(1) TMSCl; (2) BrF_2CCF_2Br or Cl_3CCCl_3	33
CH_3	$(CH_2)_nCN$		
	n = 2	$ClCH_2CN$	34
	n = 7	(1) $Br(CH_2)_6Br$; (2) $HO(CH_2)_2NH_2$, $Cd(OAc)_2$	35
CH_3			36
			36

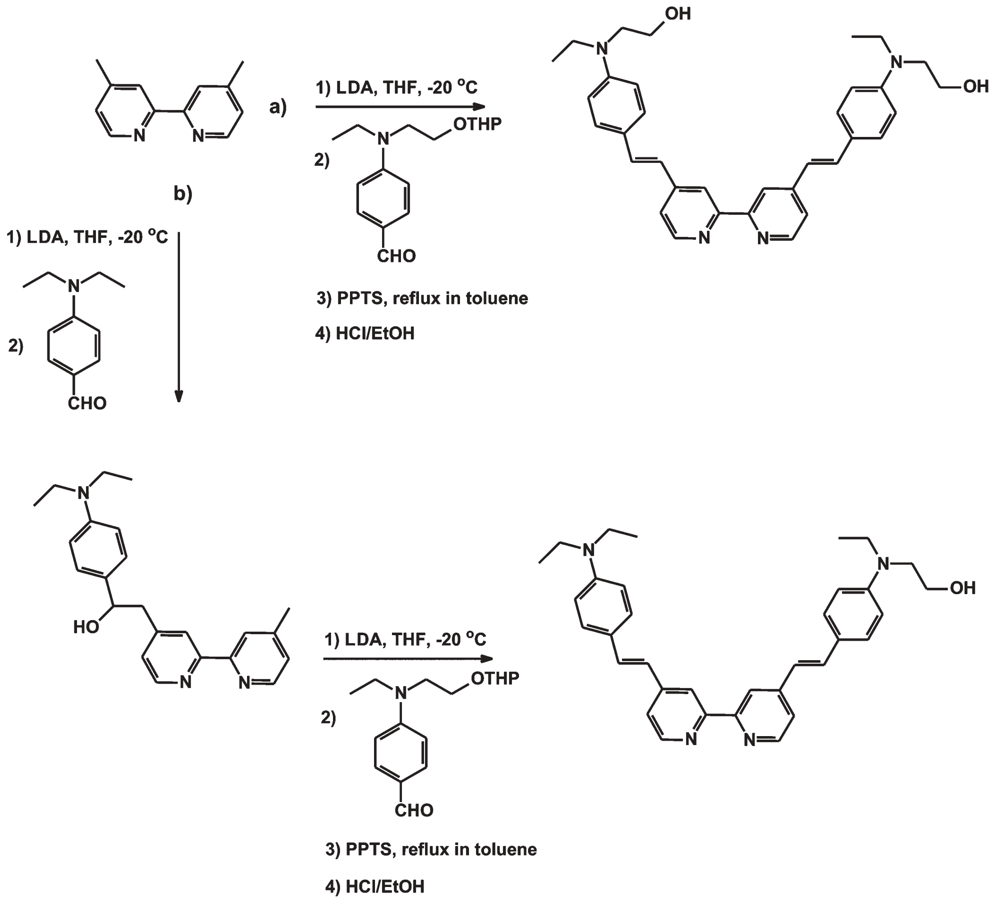


Scheme 1 Schematic representation of the LDA procedure and examples of functionalities introduced following this procedure.[26–37]

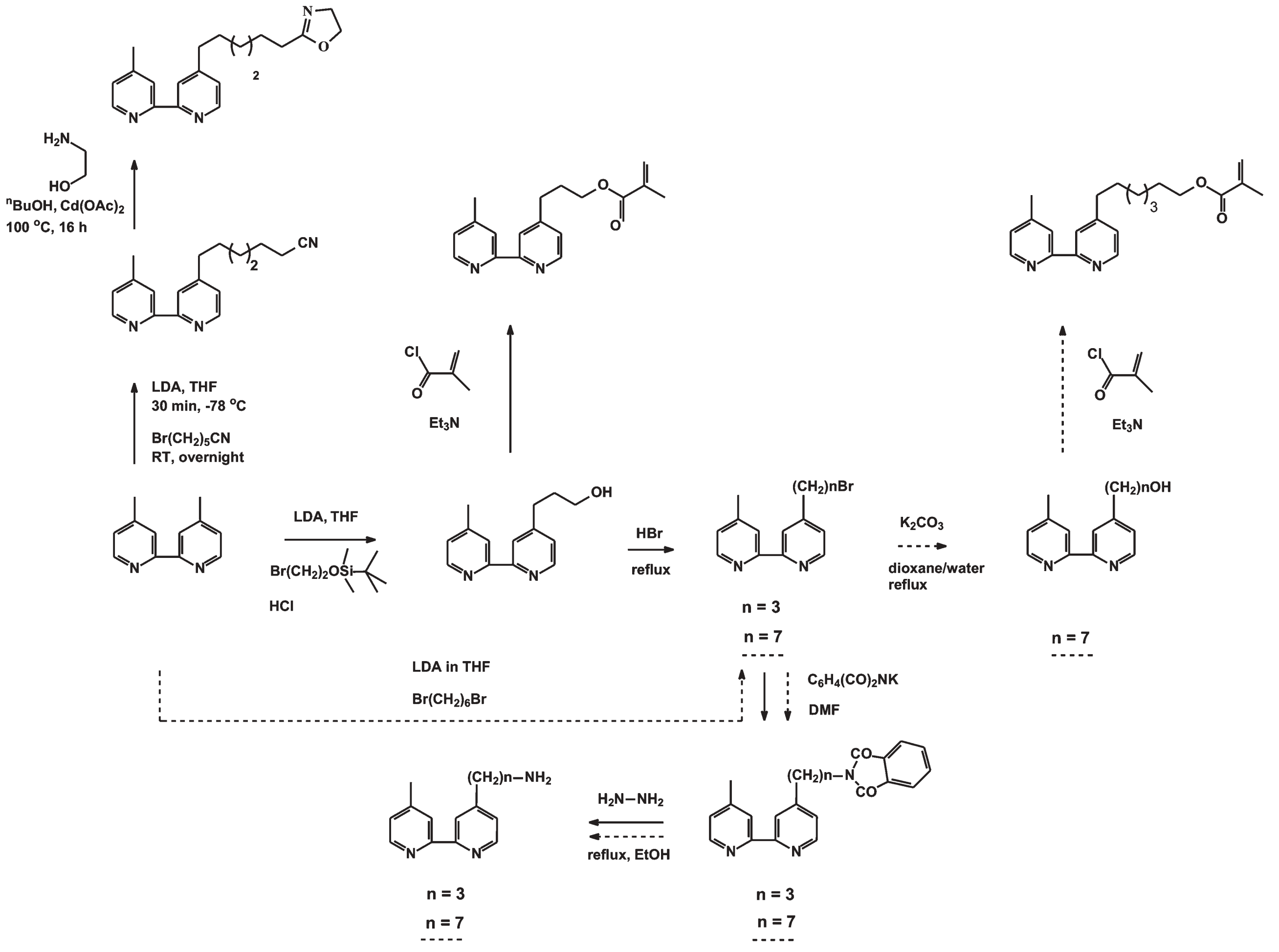


Scheme 3 Synthesis of mono- and bis-hydroxymethyl-substituted bipyridines.[33]

One of the most attractive functional groups for further derivatization[32,37,38] or polymerization[39] is the hydroxy-group. Several synthetic routes were described towards hydroxy-functionalized bipyridines in the 4 and/or 4′-positions. For instance Le Bozec *et al.*[40] applied successfully the LDA procedure in the preparation of symmetrical and unsymmetrical hydroxy-functionalized bipyridines by reacting the monolithiated species of 4,4′-dimethyl-2,2′-bipyridine with a tetrahydropyranyl-protected (THP) hydroxy-functionalized (dialkylamino)-benzaldehyde (Scheme 2). After deprotection, symmetrical and unsymmetrical hydroxy-functionalized bipyridines could be synthesized up to multigram scale in very good yields (>90%). Although the yields are very promising, the synthetic pathway involves a disadvantageous three-step synthesis to the precursor (the THP-protected benzaldehyde). Using 4,4′-dimethyl-2,2′-bipyridine as starting materials, Fraser *et al.*[33] developed a new and improved route to hydroxymethyl-functionalized bipyridine derivatives in good overall yields (Scheme 3). Deprotonation of dMbpy with LDA followed by trapping with trimethylsilyl chloride (TMSCl) leads to TMS substituted intermediates. Bromination of the unsymmetrical or symmetrical TMS-intermediates, followed



Scheme 2 Synthesis of symmetrical (a) and unsymmetrical (b) bipyridine ligands.[40]



Scheme 4 Overview on the synthesized 2,2′-bipyridine ligands.[35,37,38]

by treatment with sodium acetate and hydrolysis with aqueous sodium carbonate in THF, resulted in the formation of the mono-hydroxymethyl-substituted bipyridine in 70% yield, whereas the bis-hydroxymethyl substituted bipyridine was isolated in 85%.

In contrast, we were interested to develop a versatile synthetic route to a mono-hydroxy-functionalized bpy with a flexible alkyl spacer between the functionality and the pyridine ring. In this way, a wide spectrum of binding reactions is accessible, whereas the spacer allows an unhindered metal complexation reaction, as well as mobility of the complex bound to macromolecules. Consistent pathways for sequential derivatization of dMbpy with different functionalities of two different spacer lengths could be developed according to Scheme 4 (C_3 route: solid line arrows *via* a bromo-intermediate; C_7 route: dashed lines arrows *via* a silylated-intermediate).[37] For the synthesis of the hydroxy-bipyridine with a C_3 spacer, a commercially available silyl-protected hydroxy-alkyl bromide was employed, followed by cleavage of the Si–O bond in a strong acidic medium, whereas for the hydroxy-bipyridine with a C_7 spacer, a bromo-intermediate was isolated first. The advantage of the C_3 spacer route lies in the fact that no purification was necessary for the intermediate, whereas the bromo-bipyridine has to be isolated by column chromatography. The approach *via* the silylated intermediate drastically reduced the overall preparation time and generates products in higher yields compared to the synthetic routes *via* dibromo-alkanes. Moreover, several grams could be easily prepared in one batch. Therefore, only the C_3 spacer ligands were utilized for further derivatization reactions or for the incorporation of the bipyridine into polymers. The methyl methacrylate functionalities were prepared by esterification reactions with methyl methacroyl chlorides,[37] while the amino-functionalities have been prepared following a Gabriel protocol.[38] In addition, an oxazoline-functionalized-bipyridine was prepared by monoalkylation of dMbpy in the presence of LDA with 1-bromo-6-cyano-pentane, leading to a cyano-functionality, which is subsequently subjected to a general *Witte and Seeliger* procedure[41] employing 2-aminoethanol and cadmium acetate. This route follows previous work by Nuyken *et al.*[35] who prepared a poly(oxazoline)-based amphiphilic block copolymer (*i.e.* a water-soluble poly(2-methyloxazoline) block and a hydrophobic block with bipyridine ligands in the side chain), useful as ligand system for the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA).

In summary, the here discussed straightforward and reliable synthetic routes for the side chain modification of dMbpy represent an essential step for the preparation of bipyridine-containing macromolecules.

3. Ruthenium(II)-containing polymers

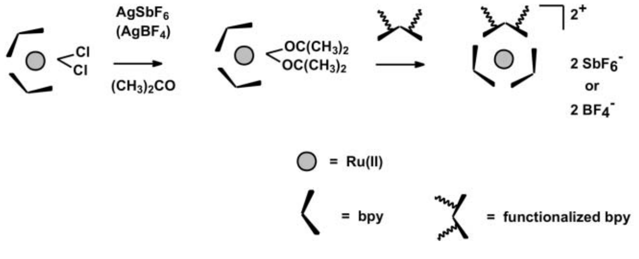
Generally, functionalized metal-containing polymers can be synthesized *via* different polymerization techniques (whereby the polypyridyl compounds can act either as monomers or initiators) or *via* end group coupling procedures. The nature and properties of the resulting polymers can be easily fine-tuned by utilizing different combination of monomers. In general, ruthenium(II)-containing polymers[3,4] can be prepared either starting from small heteroleptic ruthenium(II) complexes, which are subsequently covalently linked to polymeric architectures, or from polymers with bipyridine units in the side chains or in the polymer backbone, later coordinated to metal ions.

There are only a few widely used synthetic strategies for the complexation of bipyridine ligands and macroligands, and they all include the use of a bis-chloro bis-pyridyl ruthenium(II) precursor complex (*e.g.* Rubpy$_2$Cl$_2$) that is prepared *a priori*.[42] The synthesis of the tris-bipyridine ruthenium(II) complex is straightforward and it is performed by stirring the ruthenium(II) precursor complex with silver hexafluoroantimonate in acetone at room temperature. Dehalogenation takes place and acetone ligands are coordinated to the metal sphere to generate a red ruthenium(II) synthon. After careful filtration of the formed AgCl, the intermediate is reacted in a second step with the desired bipyridine (Scheme 5).[43]

3.1 Polymers with bipyridines in the side chains

The synthesis of metal-containing polymers with bipyridines in the side chain involves the use of functional bipyridines and/or ruthenium(II) bipyridine complexes as monomers in copolymerization processes with "classical" monomers. Polymers with 4,4′-functionalized bipyridines in the side chain could be successfully synthesized by free radical (FRP),[37,44,45] cationic ring-opening polymerization (CROP),[46] as well as ring-opening methatesis polymerization techniques (ROMP).[47]

Fréchet *et al.*[44] prepared luminescent polymers containing Ru(II) chromophores and coumarin laser dyes *via* free radical copolymerization procedures (FRP). The resulting polymers exhibited light-harvesting properties and could undergo energy transfer and function as light harvesting antennae. A series of coumarin-2–Ru(II)bpy copolymers (Fig. 2) was prepared through two different chemical approaches: (1) copolymerization of coumarin-2 and bipyridine functionalized styrene monomers followed by complexation with a Ru(dMbpy)$_2$(MeOH)$_2$·2PF$_6$ intermediate, and (2) preparation of the ruthenium(II)-containing monomers followed by copolymerization with the respective coumarin derivatives. The grafting approach led to polymers that displayed low solubility which could not be improved by either the addition of styrene into the polymer backbone or the placement of a spacer between the backbone and the acceptor chromophore. However, the solubility was enhanced by copolymerising the donor monomers with a Ru(II) acceptor monomer.



Scheme 5 General synthetic strategy for preparation of heteroleptic tris-bipyridine ruthenium(II) complexes.[42,43]

Meyer *et al.*[6] synthesized an amide-linked polypyridyl ruthenium-derivatized polystyrene *via* a trimethylsilyl-protected (amino-ethyl)styrene prepared *a priori* by applying the living anionic polymerization of a vinyl monomer bearing a protected amine using *sec*-BuLi as initiator. Subsequently, the amino-functionalized polymer was coupled to a carboxy-functionalized ruthenium(II) complex *via* an amido-moiety in the presence of the [tris(dimethylamino)phosphonium hexafluorophosphate (BOP)/4-(dimethylamino)pyridine (DMAP)/4-methylmorpholine (NMM)/1-hydroxybenzotriazole hydrate (HOBT)] coupling system, followed by protection of unreacted amines with acetic anhydride (Scheme 6).

In our work, we have also used free radical polymerization processes since the required methyl methacrylate- and acrylate-based monomers can be prepared in a straightforward manner. In addition, the polymerization mechanism is compatible with the bipyridine ligand. A methyl methacrylate-modified bipyridine was used as comonomer in the free radical copolymerization of methyl methacrylate (MMA) with 2,2′-azoisobutyronitrile (AIBN) as the initiator (Scheme 7a).[37] Subsequent grafting of ruthenium(II) polypyridyl precursor complexes onto the PMMA copolymer with bipyridine units in the side chain allowed the formation of a class of graft copolymers which reveal the optical properties of a tris-polypyridyl species, demonstrating that the PMMA backbone does not influence the photophysical and electrochemical properties. In addition, the solubility and processing properties of the polymer are retained. In a second approach, a pre-formed methyl methacrylate ruthenium(II) complex was used as comonomer in the free radical polymerization of MMA using AIBN as the initiator (Scheme 7b).[45] By using a different molar ratio of monomer to initiator, the metal content within the polymer could be varied from 1.3 to 22%. Nevertheless, the UV-vis absorption and emission properties of the corresponding polymers with copolymerized methyl methacrylate ruthenium(II) complexes revealed similar UV-vis activity. Moreover, the luminescence properties were not influenced, indicating that self-quenching of the complexes is prevented by the incorporation into the polymer. Due to the higher content of the metal complex, the copolymer with the highest metal content showed an increased absolute MLCT band with a maximum at 455 nm. In addition, the electrochemical properties (obtained by cyclic voltammetry) were preserved, guaranteeing good charge mobility and thus electrical conductivity. Processing of the films, either by spin coating or by inkjet printing, revealed beneficial film forming features, even for the higher ruthenium content polymer, with no aggregation of the ruthenium complexes. Comparing the two synthetic routes towards poly(methyl methcrylate)-containing ruthenium(II) complexes, it was found that the second approach *via* FRP of a pre-made ruthenium(II) complex with a

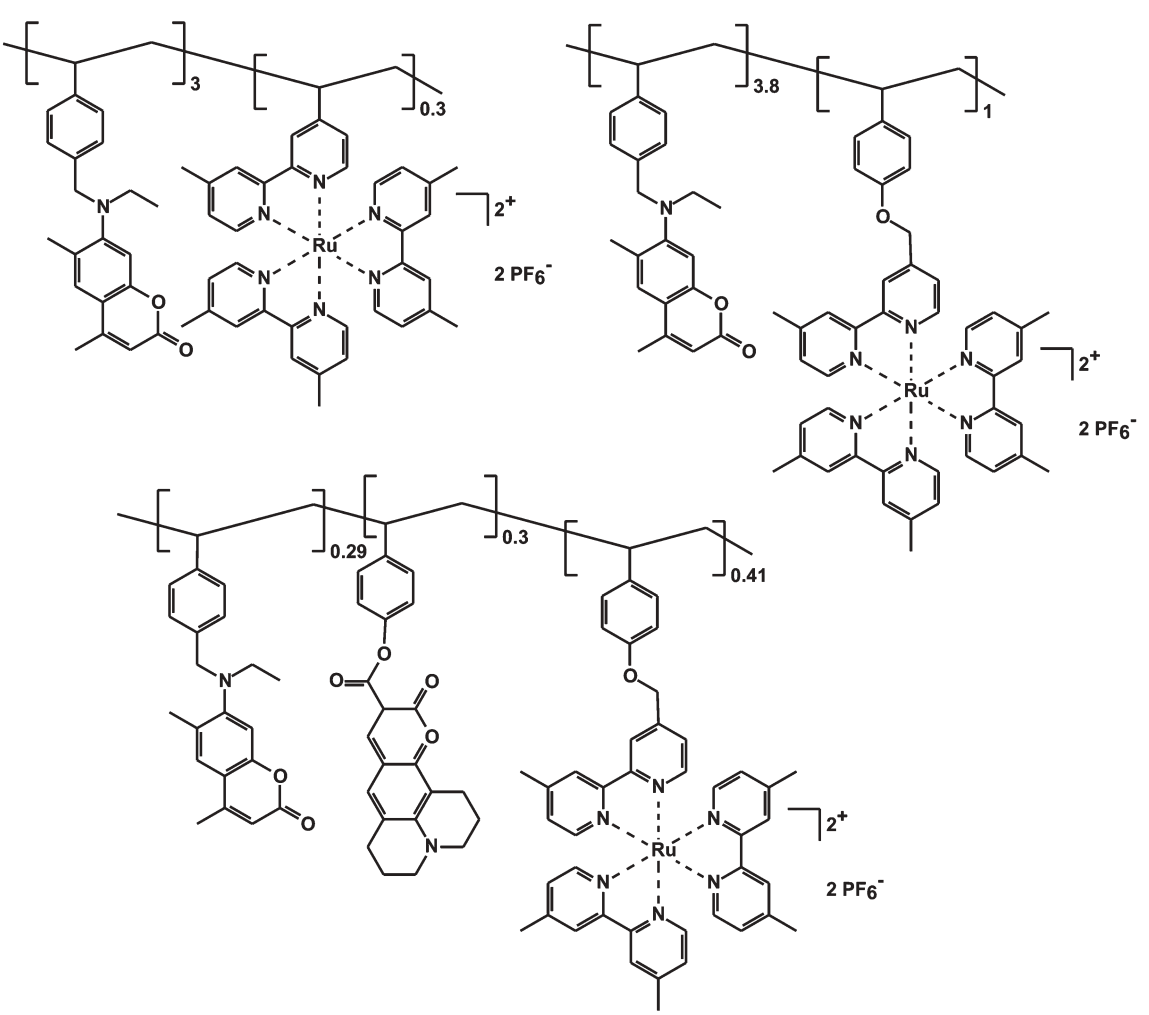


Fig. 2 Graft copolymers containing ruthenium(II) chromophores and coumarin dyes.[44]

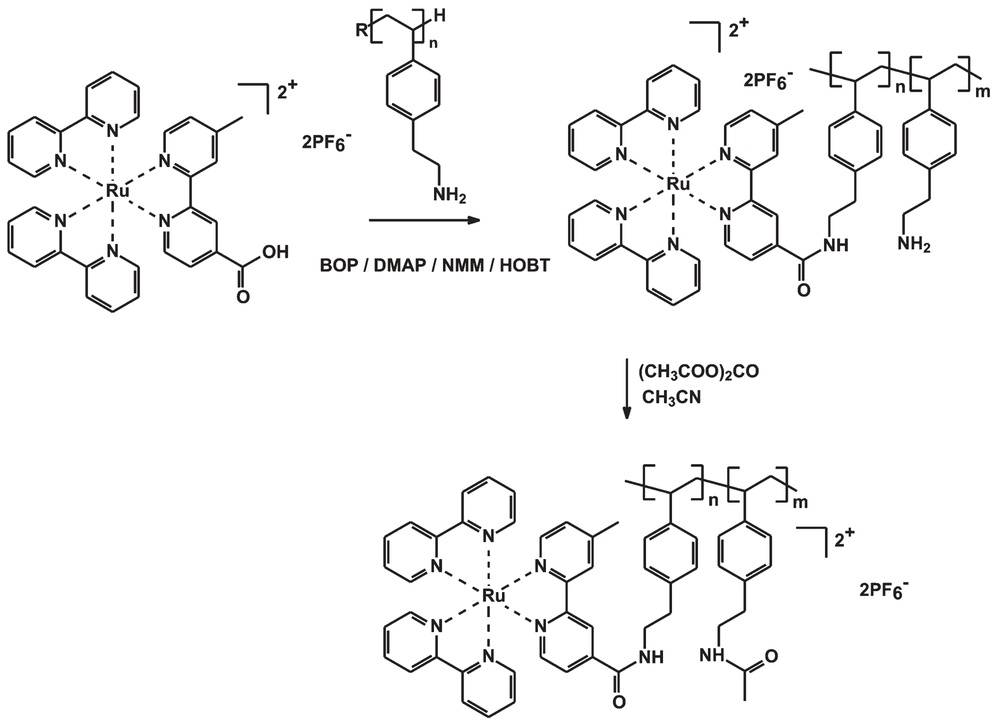
methacrylate-functionality proved to be beneficial compared to the grafting approach due to the easier purification. Moreover, the metal content in the polymer could be easily varied.

In addition to the free radical polymerization approach, the CROP of 2-ethyl-2-oxazoline was used to create polymeric structures with bipyridine units in the side chains, whereby a ruthenium(II) complex with an oxazoline functionality was used as comonomer. The living cationic ring-opening polymerization of 2-oxazolines is a well-established polymerization technique for the synthesis of tailor-made amphiphilic block, graft and star-shaped polymers.[48] Tris-bipyridine ruthenium(II) chromophores functionalized in the 4,4′-positions have been introduced into the backbone of poly(oxazoline) architectures in a controlled way *via* a "metallo-initiation" approach by Fraser *et al.*[46] The authors described a variety of bromo-, chloro- and iodomethyl difunctionalized ruthenium(II) complexes, which were used as initiators in the ring-opening polymerization of 2-oxazolines. A wide range of star-shaped architectures is accessible by varying the number of pendent initiator sites on the ligands.[49] In addition, two other strategies can be applied for incorporation of ruthenium(II) bipyridine complexes into poly(oxazoline): (1) either by post-analogous coordination of the appropriate bipyridine functionalized copoly(oxazoline) with the corresponding ruthenium(II) metal ions,[50] or (2) by using the appropriate oxazoline-functionalized ruthenium(II) monomer.[51]

3.2 Polymers bearing bipyridine units at the chain ends

The 4,4′-functionalized bipyridine ligands and complexes were successfully applied in initiation and end functionalization reactions, and as chain transfer agents. A recent tutorial review summarises the use of metallo-supramolecular initiators for the preparation of end-functionalized metallo-supramolecular polymers.[9]

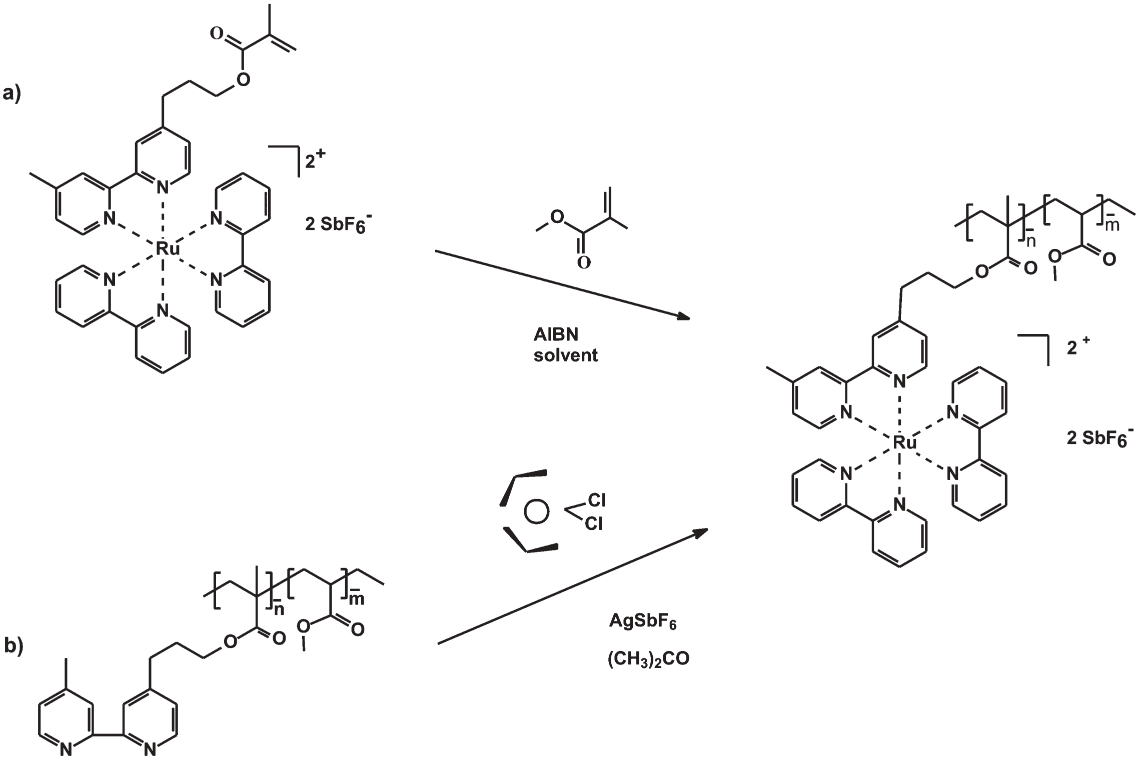
Polyethylene glycol (PEG) has been attached to bipyridine ligands by coupling reactions to end-functionalized polymers. For instance Chujo *et al.*[52] coupled a tosylate-functionalized poly(propylene glycol) mono-butyl-ether to a mono-lithiated 4,4′-dimethyl-2,2′-bipyridine in low yields (10%). In another example, Fraser introduced a bipyridine to the PEG backbone by coupling reactions of bis-chloromethyl functionalized bipyridines to alkoxy-PEG nucleophiles in the presence of sodium hydride (Scheme 8).[10] Recently, the same group described that hydroxy-functionalized bipyridines can initiate the anionic polymerization of ethylene oxide in the presence of



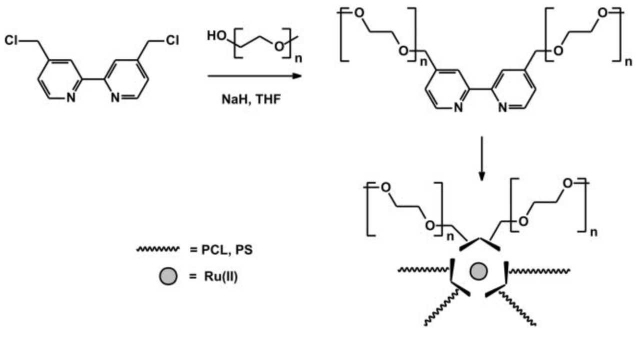
Scheme 6 Synthesis of polystyrene polymers functionalized with ruthenium(II) complexes.[6]

potassium naphthalenide. The main advantage of this approach is that the resulting bipyridine macroligands have hydroxy end units which can be further explored for additional functionalization reactions.[53]

For the preparation of a ruthenium(II) polypyridyl bipyridine–PEG system, a coupling procedure can also be utilized:[38] a monomethyl ether of polyethylene glycol was activated with *N,N′*-carbonyl-di-imidazole (CDI) and the resulting



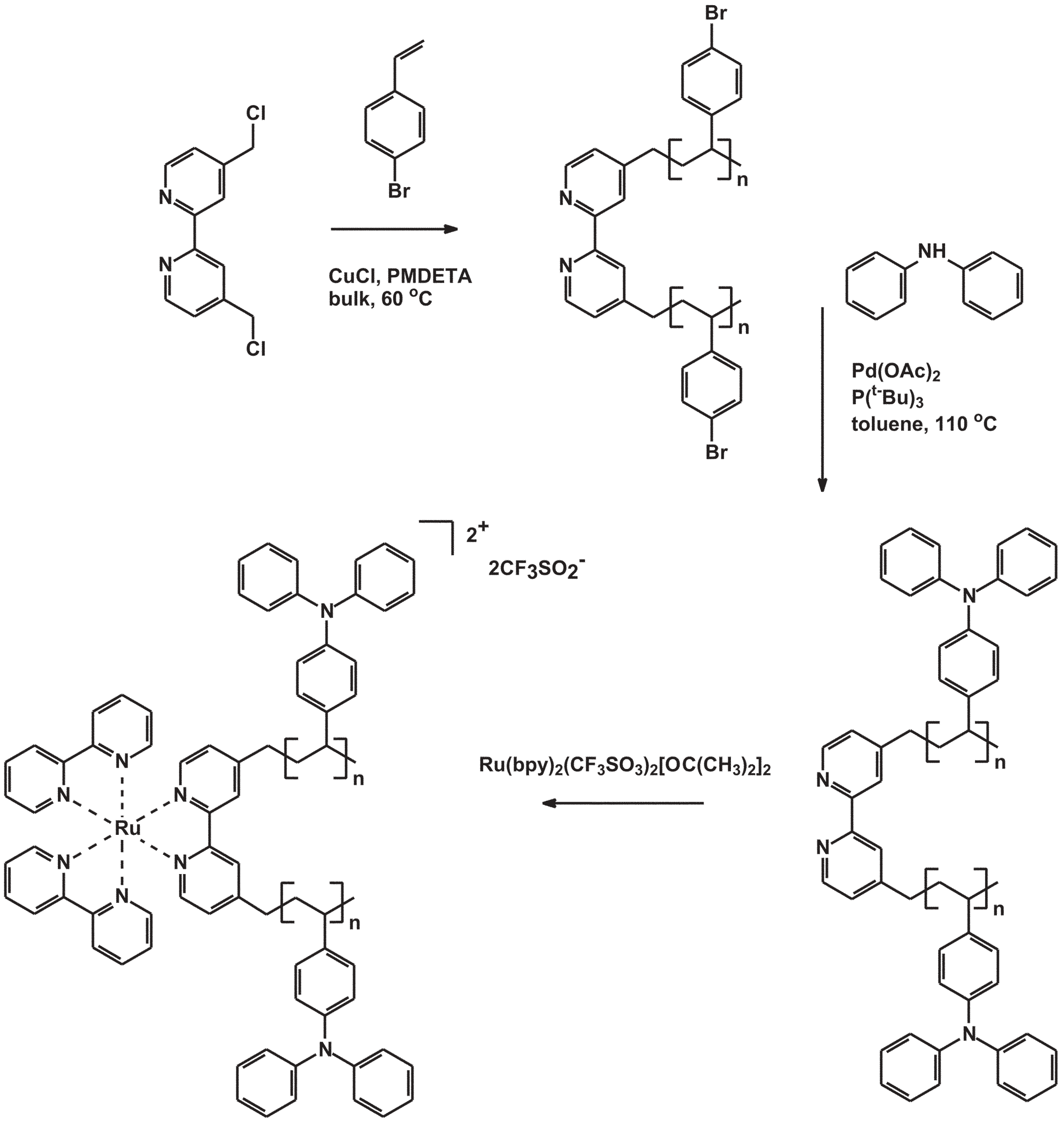
Scheme 7 Synthesis of poly(methyl methacrylate)-containing ruthenium(II) complexes *via* two different routes: (a) copolymerization[45] and (b) grafting approach.[37]



Scheme 8 Synthesis of star-shaped block copolymers functionalized with ruthenium(II) complexes.[10]

imidazolide was subsequently coupled with the amino-bipyridine yielding a bipyridine ligand with one PEG arm in 65% yield. The complexation of the PEG bipyridine macroligand to a phenantroline-based ruthenium(II) precursor followed the complexation route used for small complexes, resulting in the formation of a ruthenium(II) complex with a PEG tail. Characterization by gel permeation chromatography proved the purity and stability of the bipyridine macroligand and of the corresponding complex, with no fragmentation of the metal-to-ligand bonds.

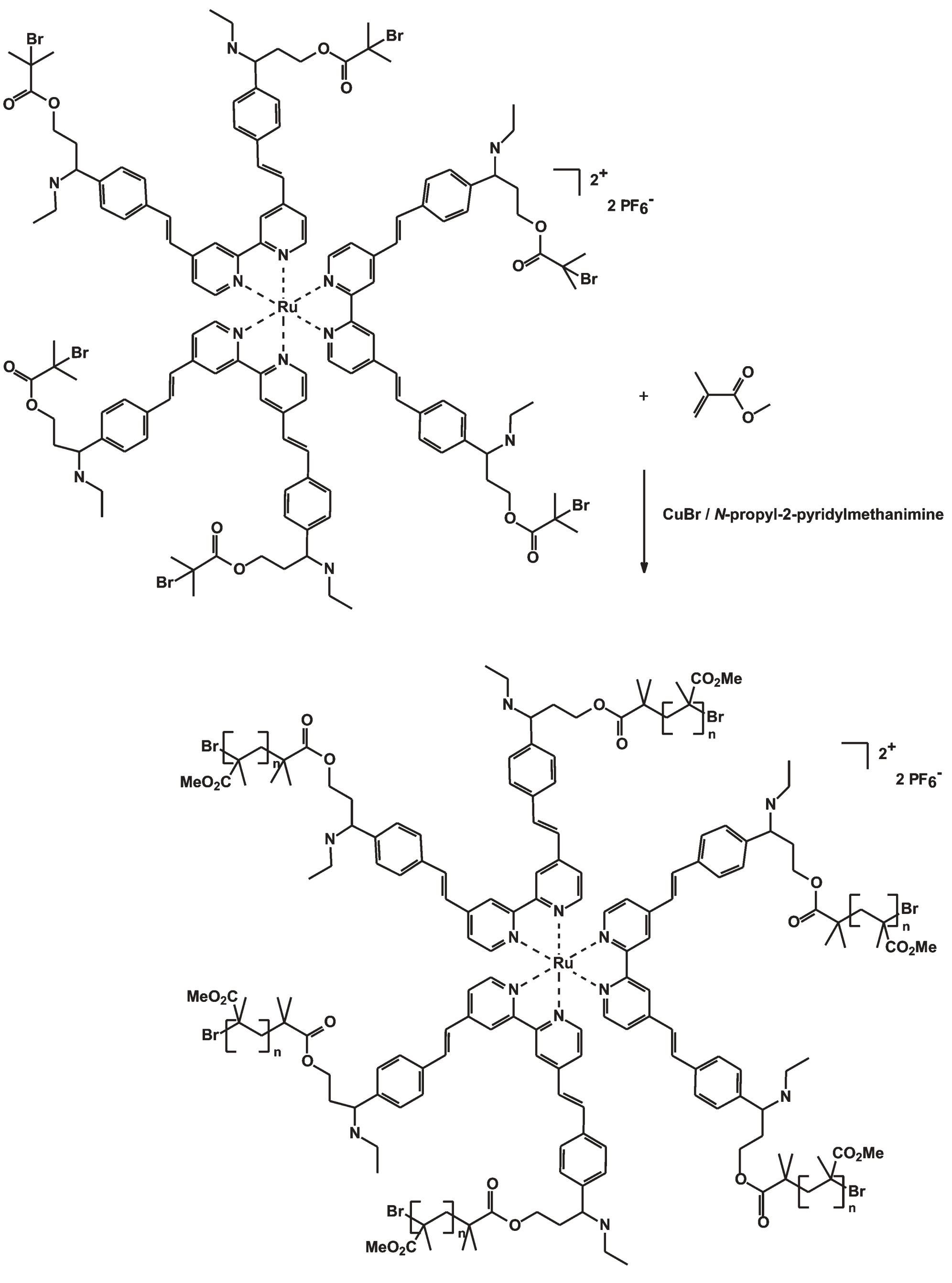
Another example for the end coupling route was described by Thelakkat *et al.*[8] who found a simple synthetic route to design a bifunctional polymer carrying a strongly absorbing polar dye unit attached to well-defined polymer chains carrying charge transport moieties based on triarylamines in view of potential application in dye-sensitized solar cells (Scheme 9). First, a bipyridine with two poly(4-bromostyrene) chains of well-defined molecular weights and low polydispersity indices was synthesized *via* atom-transfer radical polymerization (ATRP), using bis-chloromethyl-bipyridine as



Scheme 9 Synthesis of bifunctional polymers carrying tris-bipyridine ruthenium(II) and triphenylamine units.[8]

initiator, and CuCl/(1,1,4,7,7-pentamethyl-diethylene-triamine) (PMDETA) as catalytic system. Depending on the conditions used, the molecular weights can be tuned in the oligomeric range. At higher conversion, high molecular weights in the range of 30 000 g mol^{-1} were obtained. A high ruthenium(II) content within short polymer chains was needed in order to insure good absorption properties, as well as good filling properties of the polymer into the nanoporous titanium dioxide layer. The bromo-substituents provided an ideal opportunity to attach a charge transport moiety, such as triphenylamine, by amination with diphenylamine on a Pd-catalyzed system. The metallation step with a ruthenium(II) precursor led to a highly soluble bifunctional polymer in which charge transport polymer chains are attached to a tris-bipyridine Ru(II) core (Scheme 9).

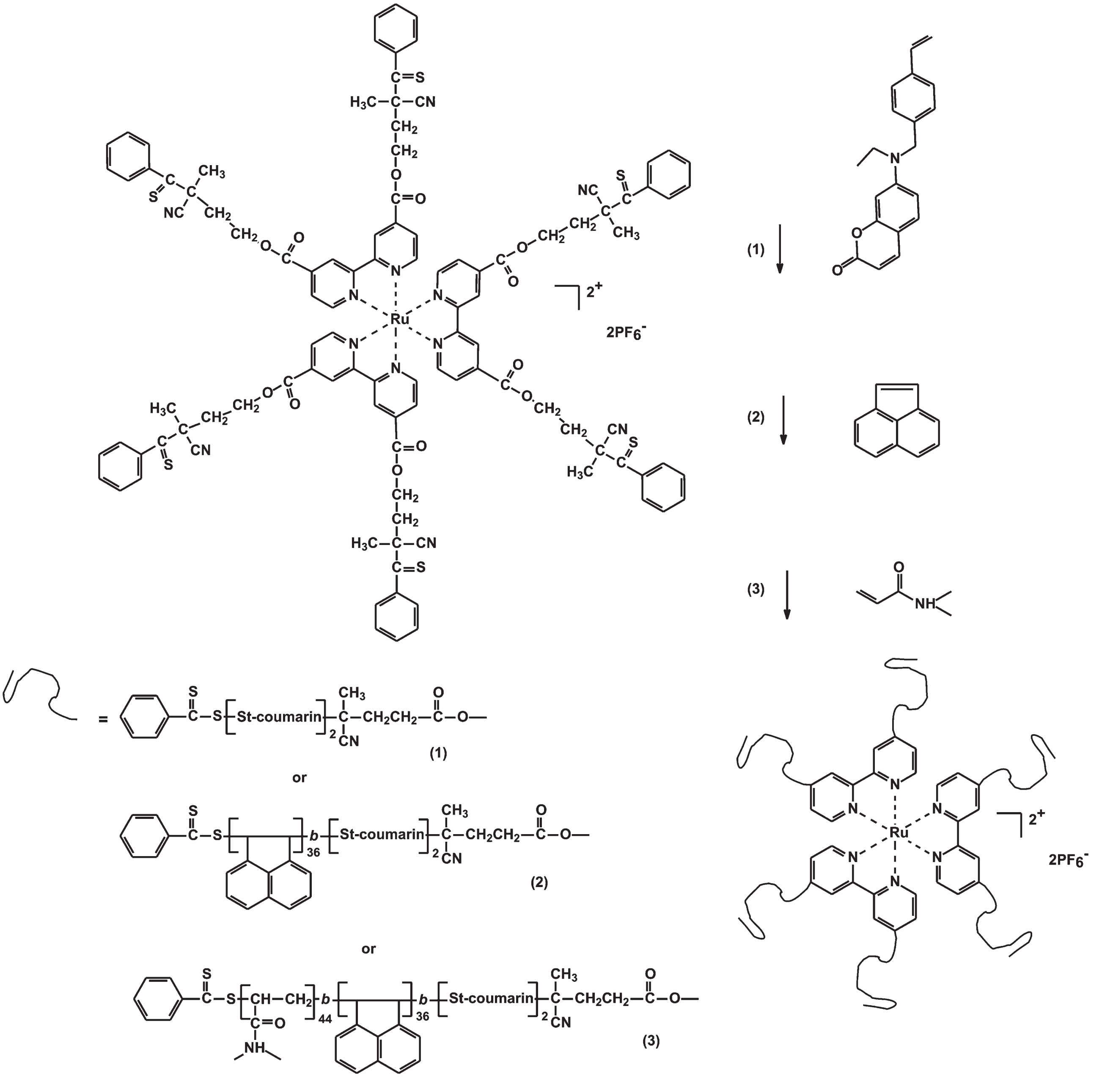
Following the work of Fraser *et al.*[10] who demonstrated the controlled introduction of ruthenium(II) tris-bipyridine complexes functionalized in the 4,4′-positions into polymer architectures, Le Bozec *et al.*[54] also found ATRP to be a suitable method for the design of new polymers containing non-linear optical chromophores featuring photoisomerisable moieties. The ruthenium(II) initiator was prepared in 83% yield by complexation of a three fold excess of 4,4′-bis-alkylaminostyryl-2,2′-bipyridine with $RuCl_2(DMSO)_4$, followed by anionic metathesis. The bromoester groups have been introduced to the 4,4′-dialkylaminostyryl-2,2′-bipyridines under



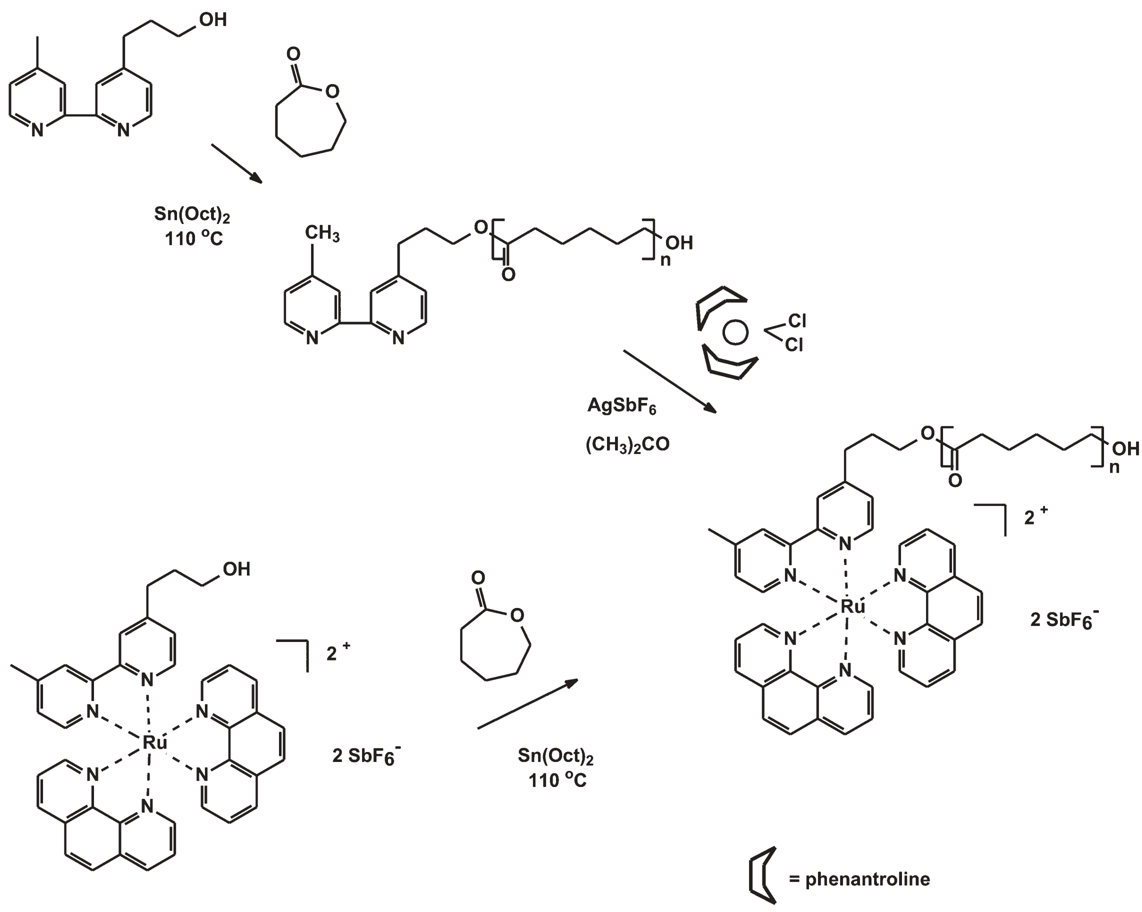
Scheme 10 Star-shaped polymeric chromophores prepared *via* Ru(II) initiators.[54]

basic conditions at room temperature. ATRP of the star-shaped ruthenium initiators was performed in dichlorobenzene at 90 °C using CuBr/*N*-propyl-2-pyridylmethanimine as a catalytic system (Scheme 10). The polymer revealed good processing features from chlorinated solvents. High optical quality thin films were obtained, without chromophore aggregation and thicknesses varying between 1 and 2 μm.

Wilson *et al.*[11] used reversible addition–fragmentation chain transfer polymerization (RAFT) to synthesise star-shaped block copolymers to obtain light-harvesting systems with an energy gradient from the periphery to the core. Ru(II) complexes bearing thiobenzoylsulfanyl functionalized 2,2′-bipyridine ligands were used as chain transfer agents for the RAFT polymerization of styrene functionalized coumarin monomers (st-coumarin) in order to introduce the first block with an average length of two st-coumarin units into each arm.[55] Subsequently, the obtained polymer has been used as a macro-RAFT agent for the polymerization of acenaphthylene to obtain the star-shaped diblock copolymer with a narrow polydispersity index and an average length of 36 acenaphthenyl repeat units in each arm. In order to avoid the competing quenching effect of the dithiobenzoyl groups on the excited chromophores, as observed in a previous study, the authors introduced a third block, synthesizing a triblock copolymer with an average length of 44 *N*-isopropyl acrylamide (NIPAM) repeat units in each arm, by using the di-block copolymer as macro-RAFT agent and NIPAM as monomer. In conclusion, star-shaped block copolymers have been synthesized to obtain light-harvesting systems with an energy gradient from the periphery to the core (Scheme 11). The authors demonstrated



Scheme 11 Step-wise synthesis of star-shaped light-harvesting polymers *via* RAFT.[11,55]



Scheme 12 Schematic representation of the synthesis of poly(ε-caprolactone)-based macroligand complexes.[39,56]

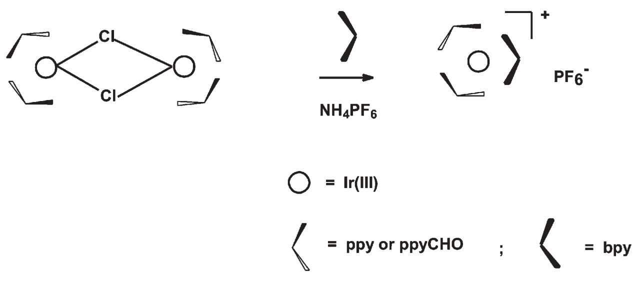
that the energy transfer occurs mainly through a stepwise energy cascade from the initially excited acenaphthyl units to the coumarin chromophores and hence to the Ru(II) complex core.

The ring-opening polymerization of cyclic esters (*e.g.* ε-caprolactone, DL-lactide) has been frequently employed for the controlled synthesis of metal-containing polymers, by using the hydroxy-functionality either on bipyridine ligands or on pre-formed complexes as initiating species.[10,39,56,57] By this procedure, end-functionalized polymers can be obtained using stannous octoate or aluminium alkoxide as catalysts.

The stannous octoate-catalyzed ring opening polymerization of ε-caprolactone was used to prepare ruthenium(II)-containing poly(ε-caprolactone) (PCL) *via* two synthetic routes employing either a pre-formed ruthenium(II) complex as initiator or a hydroxy-functionalized bipyridine ligand, which was subsequently coordinated to a ruthenium(II) precursor.[39] The copolymerization approach[56] proved to be a suitable synthetic route but of less efficiency: 55% yield, compared to 88% yield obtained in the complexation route (Scheme 12). The polymer side-chain did not influence the optical and electrochemical properties of the metal complexes while it improved the solubility and provided film forming properties. In conclusion, by using either end group coupling or different polymerization techniques with (metallo-)supramolecular initiators, ruthenium(II) containing polymers with favorable photophysical and electrochemical properties, as well as good processing features (excluding aggregation phenomena) assured by the film forming properties induced by the polymer, were prepared.

4. Polymers containing polypyridyl iridium(III) complexes

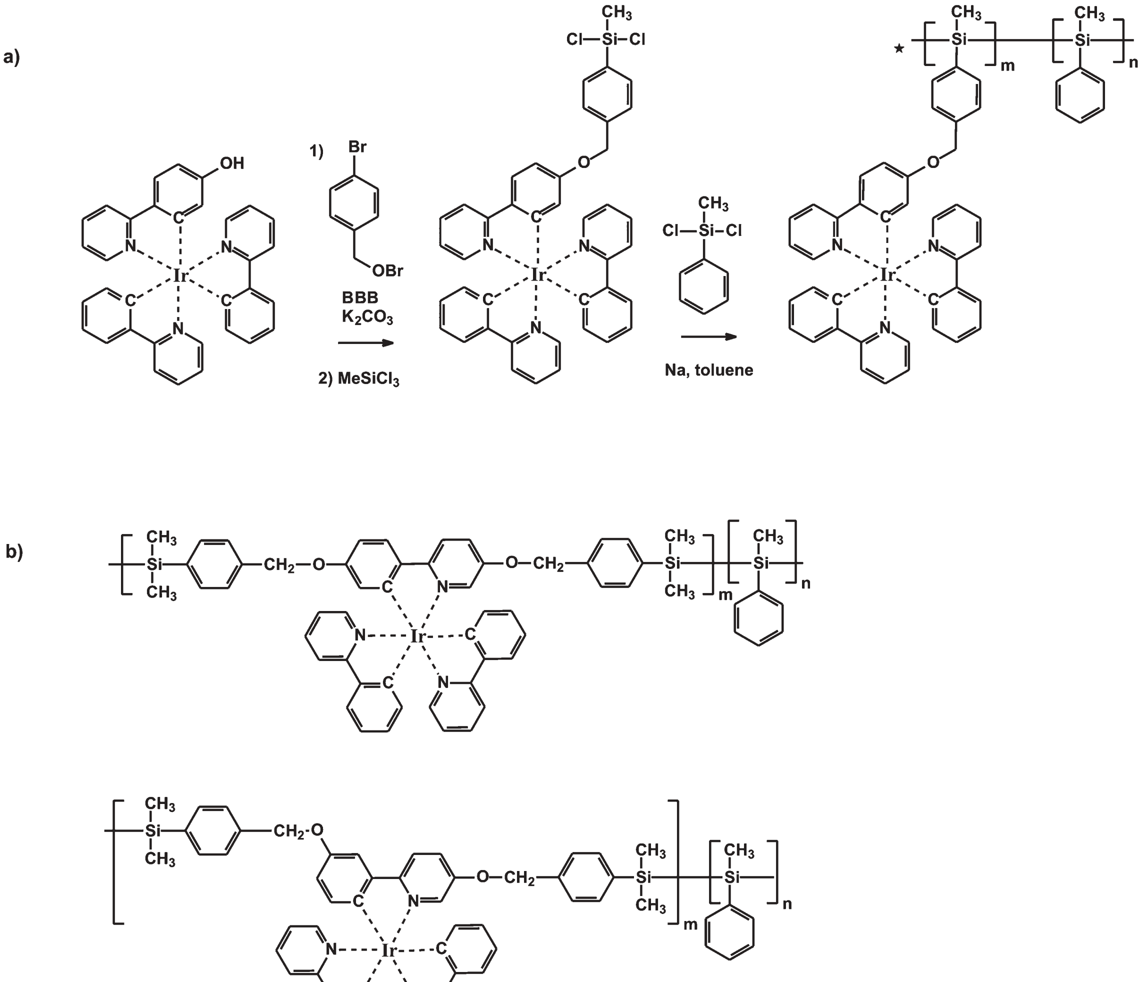
The preparation of iridium(III)-containing polymers makes use of the chelating properties of bipyridine and terpyridine macroligands towards iridium(III) metal ions, resulting in polymeric materials with iridium complexes in the side chains or at the chain ends. The incorporation of Ir(III) species into polymers has been far less investigated than ruthenium(II) species, which is mainly due to synthetic problems in the past. Despite this fact, iridium(III) complexes are highly appealing



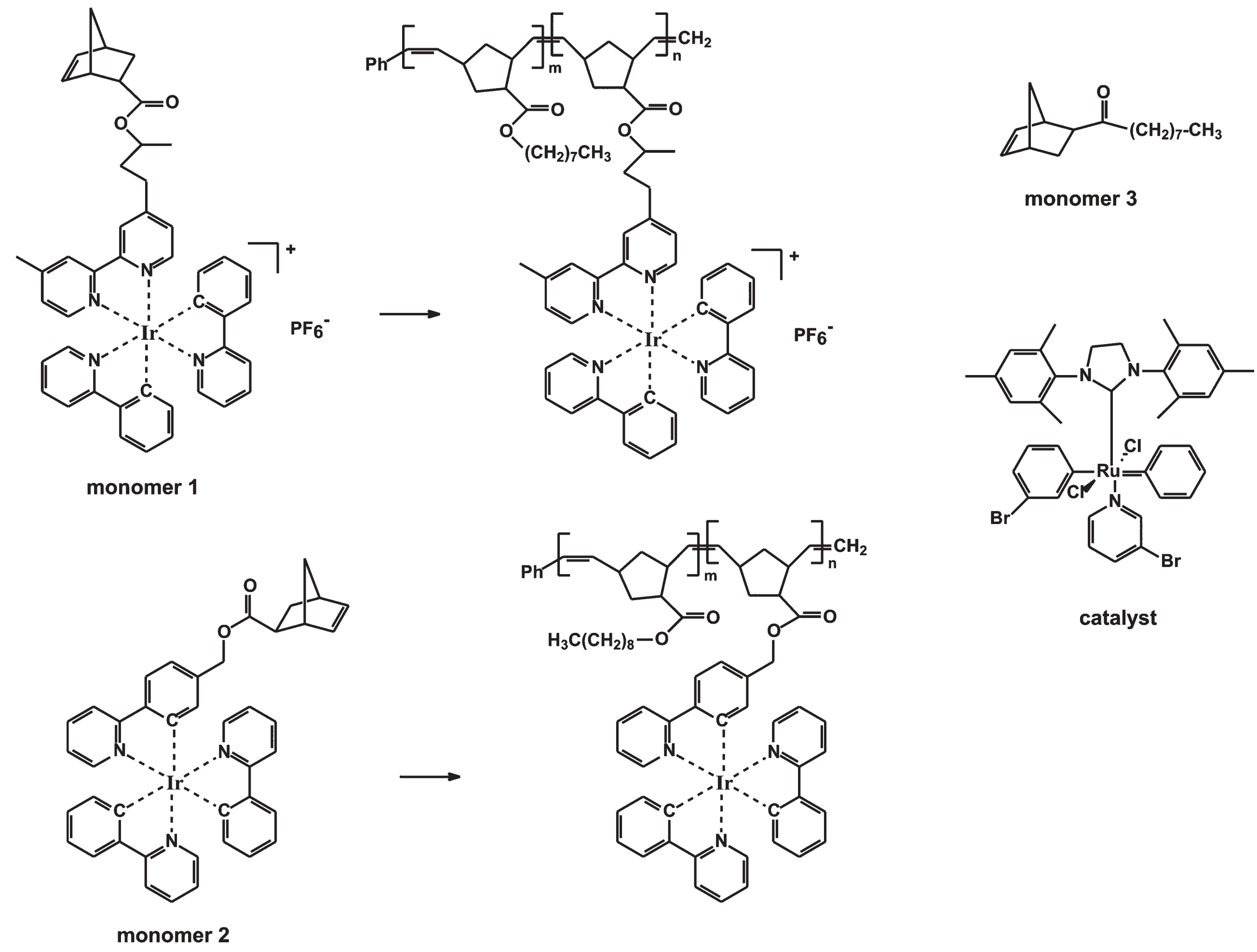
Scheme 13 General bridge-splitting reaction of iridium(III) dimers for the preparation of mixed-ligand iridium(III) complexes.[61]

due to their wide range of emission energies, long lifetimes and high quantum yields.[58–60] However, by improving the reaction conditions, incorporation of various functional substituents became possible. The field has been re-evaluated recently in a review article from the year 2000, which summarizes the family of luminescent iridium(III) polyimine-type complexes,[58] whereas a review from the year 2005 highlights specifically synthetic strategies towards neutral and charged iridium(III) complexes.[1] Scheme 13 depicts briefly general modern approaches towards the synthesis of iridium(III) complexes with two and three cyclometallating species; they could be successfully applied also to ligands with polymeric tails. In 1999, Neve and co-workers[61] introduced a set of substituted 2,2′-bipyridine and terpyridines utilizing the bridge-splitting reaction of the appropriate *ortho*-methallated dimer $[Ir(ppy)_2Cl_2]_2$ (with ppy = 2-phenylpyridine), followed by counter ion exchange reaction. Contrary to the ruthenium(II) complexes, which are rather insensitive to structural adjustments, showing in all cases red emission, the iridium(III) analogues are highly tunable in the emission color by peripheral derivatization of the cyclometallating ligands used for the preparation of the precursors.[60,62]

The preparation of iridium(III)-containing polymers is a rather unexplored field of research. Synthesis of polymers with bipyridine and/or phenyl-pyridine cyclometallating ligands in the side chain or in the backbone includes attachment of iridium(III) complexes to poly(silanes),[63] poly(norbornene),[64] polystyrene and poly(styrene)-copoly(*N*-vinylcarbazole),[65] poly(dimethylsiloxane),[66] and poly(fluorenes).[67] These copolymers show promising results in areas such as sensing, device fabrication and technology. Kamachi *at al.*[63] reported the synthesis of copolymers with iridium(III) complexes either in the side chain or in the main chain. Scheme 14a depicts the synthesis of the phosphorescent polymer with the iridium(III) units in the side chain, whereas the copolymers with iridium(III) complexes in the main chain are displayed in Scheme 14b. A hydroxy-functionalized iridium(III) complex was reacted with 4-bromo-benzyl bromide (BBB) and potassium carbonate. Subsequent reflux with methyltrichlorosilane resulted in a crude product which was purified by column chromatography, followed by recrystallization. Copolymerization with methyltrichlorosilane was performed by reflux in toluene in the presence of sodium. The resulting copolymers are stable, with green luminescence (λ_{em} = 520 nm), showing an



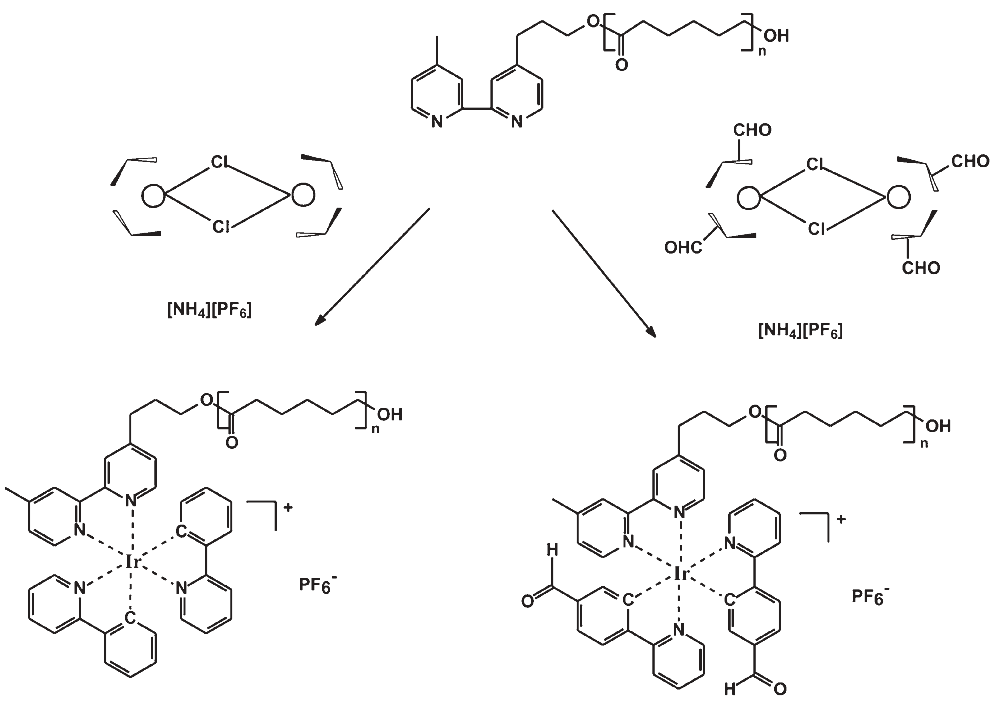
Scheme 14 Phosphorescent poly(methylsilane) copolymers with iridium(III) units in the side chain (a) and in the main chain (b).[63]



Scheme 15 Synthesis of phosphorescent side chain functionalized poly(norbornene)s containing iridium(III) complexes.[64]

external quantum efficiency of 2% in device testing. Weck and coworkers[64] reported the synthesis of phosphorescent side-chain functionalized poly(norbornene)s containing iridium(III) complexes *via* ring-opening metathesis polymerization (ROMP) (Scheme 15). The iridium(III) norbornene-functionalized monomers (bipyridine- and phenyl-pyridine-based) were prepared by esterification of the respective hydroxy-derivatives with exo-5-norbornene-2-carboxylic acid using a dicyclohexylcarbodiimide (DCC) coupling route with 4-(dimethylamino)pyridine (DMAP) as catalyst, followed by subsequent chelation to iridium(III) precursors. Homo- and copolymerization of monomers **1** and **2** with **3** (Scheme 15) in various ratios, were carried out *via* ROMP using Grubbs' third-generation ruthenium(II) catalyst.[64] Further studies on the photophysical properties were carried out in order to confirm the preservation of luminescence activity compared to the known values for small molecules, in solution and in thin films.

Research in our group has been devoted to the synthesis of iridium(III)-containing polymers based on PEG, polystyrene (PS)[68–70] and poly(ε-caprolactone) (PCL)[39,71] backbones, with different cyclometallating ligands as end groups. We have transferred the complexation procedure described for small complexes[72] to bipyridine and terpyridine macroligands.[3,4,73,74] By using a PCL-bipyridine macroligand (for synthesis of the bpy macroligand see Scheme 12), two PCL macroligand complexes have been synthesized by complexation of the *ortho*-metallated dimeric iridium(III) complexes with and without aldehyde functionalities on the cyclometallated ligand (Scheme 16). The aldehyde functionality on the cyclometallating ligand produced a significant change in the emission color in solution, giving rise to yellow–greenish color, whereas the macroligand complex without the aldehyde functionality displayed orange color. In addition, monoterpyridine iridium(III) complexes with PS and PEG tails (Fig. 3) were synthesized using the same bridge-splitting reaction. Beneficial processing features, leading to materials also applicable in inkjet printing, are ensured in this way.[75] Film forming properties and processing performance were investigated by atomic force microscopy with respect to the morphology. In addition, libraries of thin films of iridium(III) copolymers of various thickness were successfully printed on photoresist-patterned substrates, resulting in homogeneous structures. By changing the number of droplets per unit area, the thickness of the films could be varied in a controlled way. Absorption and emission spectra of the copolymers decreased regularly with the film thickness, and were found to be a linear function of the number of droplets per mm^2, as expected. Moreover, inkjet printing allows the



Scheme 16 Schematic presentation of the synthesis of macroligand bipyridines with iridium(III) complexes at the end chain.[71]

preparation of libraries of functional films[76] on one common substrate by using different ''inks'' (*e.g.* orange light-emitting ruthenium(II) copolymers and yellow light-emitting iridium(III) copolymers), which is not possible using conventional methods such as spin coating (Fig. 4).[75]

5. Conclusions

In this contribution we discussed the preparation of metal-containing polymers by introducing functional groups on bipyridine ligands. Incorporation of metal complexes into

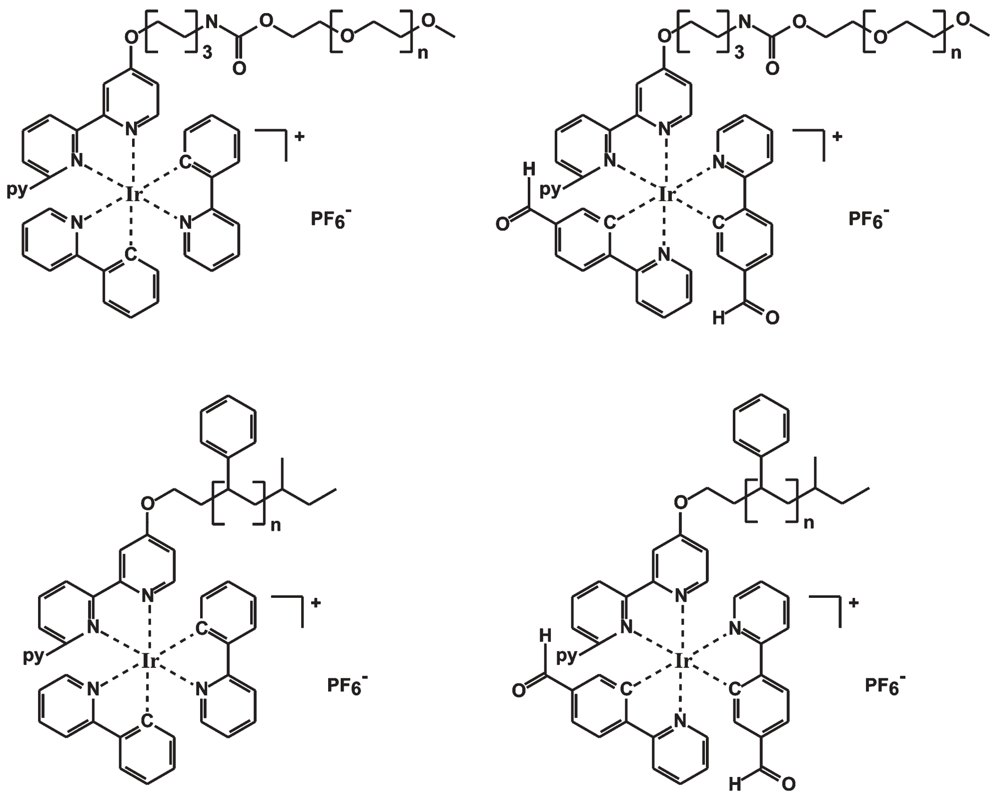


Fig. 3 Schematic representation of light-emitting PEG and PS functionalized mono-terpyridine iridium(III) complexes.[68–70]

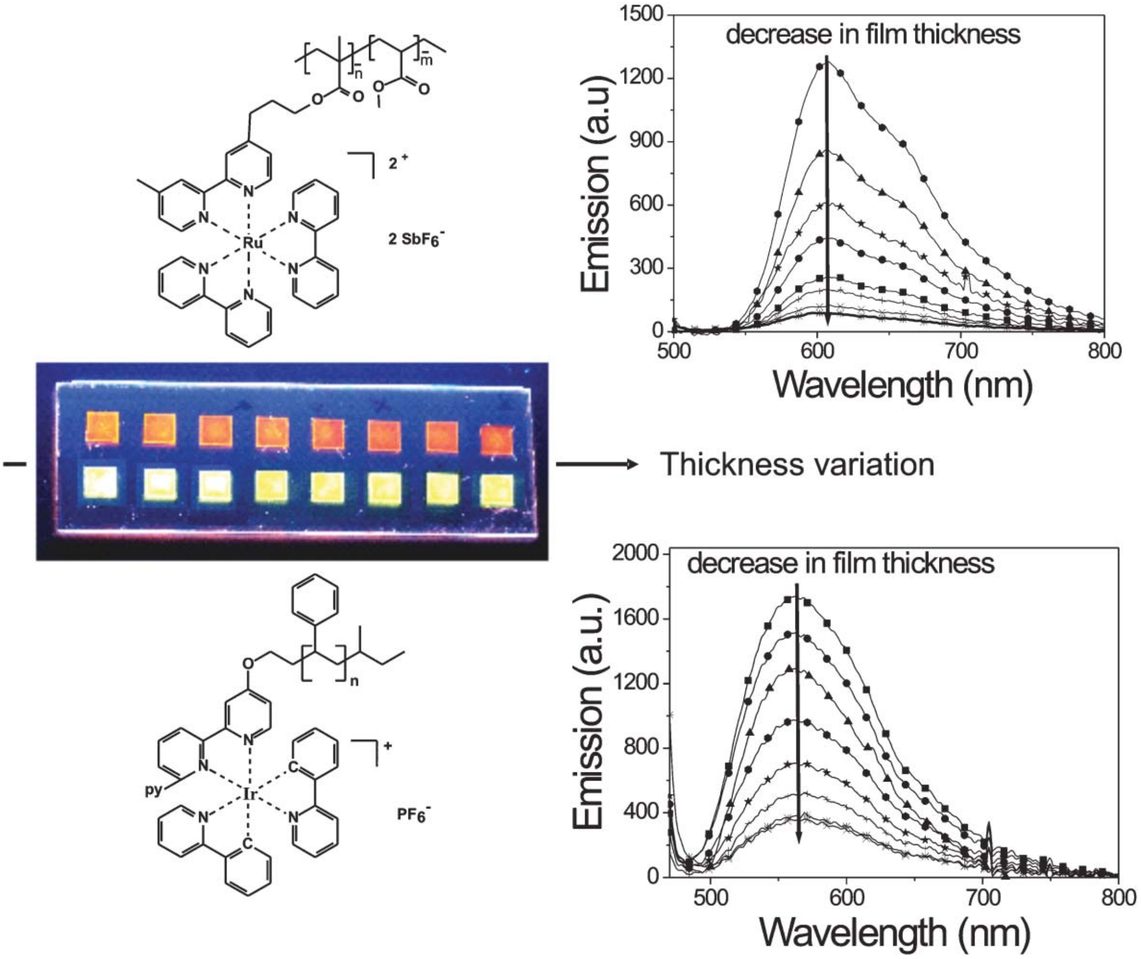


Fig. 4 Orange light-emitting ruthenium(II)-containing PMMA and yellow light-emitting iridium(III)-containing PS. Photo of the inkjet printed films and their corresponding emission spectra of variable thicknesses is also displayed.[75]

polymeric backbone requires a combination of coordination chemistry with different polymerization techniques. We focused on d^6 transition metal ions such ruthenium(II) and iridium(III) due to their interesting photophysical and electrochemical properties.

Pendent end groups, such as carboxy-, methacrylate-, oxazoline or hydroxy-moieties on the 4,4′-functionalized bipyridine ligands, allowed preparation of metal-containing polymers with bipyridines either in the side chains or in the backbone. The hydroxy-functionality could be used as initiating species in the ring opening polymerization of ε-caprolactone or in the anionic polymerization of ethylene oxide, whereas the vinyl and methyl methacrylate functionalized units were exploited as comonomers in free radical polymerization processes. The amino- and carboxylate-moieties allowed covalent attachment to a polymeric backbone *via* coupling procedures, while the oxazoline group offers a great opportunity to introduce bipyridine ligands into polymeric architectures *via* living cationic opening polymerization techniques. The ruthenium(II) ions could be coordinated either in an early stage, by utilizing small complexes as metallo-initiators, or by complexation of metal precursors to the polymers with bipyridine ligands in the side chains or in the backbone.

Iridium(III) complexes could be introduced in the side chain or in the main chain by using appropriate functionalized phenyl-pyridine and/or bipyridine-based comonomers. In addition, the iridium(III)-containing polymers were accessible by bridge-splitting reactions of *ortho*-metallated dimers to polymers with bipyridine and terpyridine ligands at the chain end. Engaging different substituents on the cyclometallating ligands, *e.g.* aldehyde moieties, the color of emission could be tuned from orange to yellow–greenish.

The covalent linkage of these polymers to luminescent metal complexes was shown to result in beneficial processing features, in many of the discussed examples, making these materials suitable for functional thin film applications. Although many synthetic strategies have been developed for the preparation of ruthenium(II) and iridium(III)-containing polymers using 4,4′-bipyridine ligands, the application of these materials in actual devices is still rather unexplored. Future work will therefore certainly focus on the development of new synthetic routes and cover the various possible application fields.

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