Synthesis and characterization of nanostructured functional polymer-metal complexes via ATRP and polycondesation and their applications

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The recent research in polymeric materials bearing metal complexes, has arise scientific interest, while at the same time has create a novel extensive field of macromolecular chemistry. The combination of inorganic metal groups with macromolecules has led to supramolecular structures with interesting physical and chemical properties. Thus the main objective is to create materials that combine the desired properties that arise from both the polymers and the inorganic metal groups, as well as examining their scale and dimensions which are a main factor for their applications.

Among the various transition metal ions, the Ru(II) ion is the most promising for use in the area of polymer complexes, since it allows the direct synthesis of both symmetric or non-symetric systems. This advantage creates a route towards nanostructured materials and nanocomposites.

In recent literature polymer and copolymer metal complexes are extensively investigated in respect to their optoelectronic behavior and their possible application in LEDs or PVs and Lasers. Moreover the nanostructured nature of such supramolecular materials is widely studied via SEM and AFM technique.

Most commonly, for the incorporation of metal binding sites into polymers, bidentate and tridentate ligands like 2,2'-bipyridine (bpy) and 2,2':6',2''-terpyridine (tpy) are used. In this work we present the polymerization of such ligands bearing the Ru(II) ion via ATRP using proper functional initiator (dicarboxy) resulting in end functionalized macromonomers is expected to give complex polymer architectures which combine moieties with complementary functionalities. The resulting graft copolymers were characterized through H-NMR, GPC, UV-Vis, PL, SEM and AFM in respect to their self organization ability and their nanostructured nature and their possible application in Hybrid Photovoltaic Cells (PVs).

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Synthesis and characterization of polymeric [Ru(bpy)$_3^{2+}$] complex via ATRP and their application in Solar Cells

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The recent research in polymeric materials bearing metal complexes has arisen scientific interest, while at the same time has created a novel extensive field of macromolecular chemistry. The combination of inorganic metal groups with macromolecules has led to supramolecular structures with interesting physical and chemical properties. Thus the main objective is to create materials that combine the desired properties that arise from both the polymers and the inorganic metal groups.

In recent literature the use of such polymeric materials in optoelectronics is extensively reported i.e. LEDs or PVs and Lasers. Among the various transition metals (Ru, Os, Co, Zn, Cu, and Fe), the Ru(II) ion looks the most promising for use in the area of polymer complexes, since it allows the direct synthesis of both symmetric or non-symmetric systems. In an attempt to mimic traditional inorganic systems, Ru(II)$^{2+}$ complexes bearing the 2,2'-bipyridyl ligand seem to be excellent candidates.

In this work we present the synthesis of a novel vinylic monomer of (2, 2'-bipyridyl)$_3$Ru(II)$^{2+}$ complex. Polymerization of this monomer using ATRP, combined with functional initiators has led to the synthesis of homopolymers that can be used in applications such as Hybrid Photovoltaic Cells (PVs) and Polymeric Light Emitting Diodes (PLEDs). The resulting polymer structures were confirmed via NMR and their optical properties were investigated using UV-Vis and Photoluminescence.

A homopolymer having a functional initiator with two carboxylic groups was able to be attached onto TiO_2 and the resulting photoelectrodes were tested in dye sensitized solar cells. The evaluation of their photovoltaic performance gave short circuit photocurrent density J_{sc}= 39 μA/cm^2, open circuit potential V_{oc}= 350 mV, fill factor ff=0.39 and power conversion efficiency n=0.005%. Besides this relatively poor efficiency, the obtained results look promising and justify further investigations in the field.

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Synthesis and Characterization of Polymeric [Ru^{2+}] Complexes and their Application as Dyes in Solar Cells

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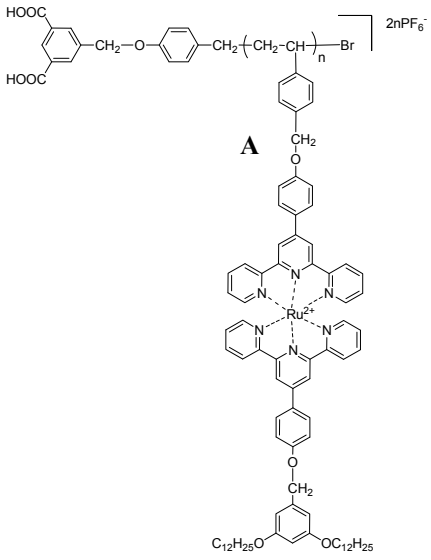
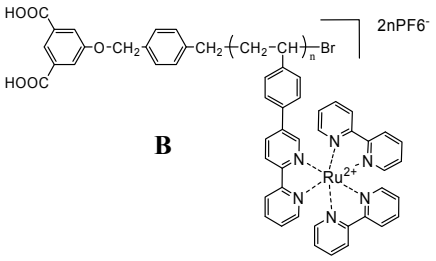
The technology of renewable energies, aims in the long run, to efficiently contribute to the solution of the energy problem both economically and environmentally friendly. In respect to the materials science, the development of energy related materials is of great interest and one of the main achievements focused into Organic Solar Cells. These are categorized to Cells of Organic Molecules, Polymeric/Plastic Cells (OPVs) and Dye Sensitized Cells (DSSCs). Our group is mainly focused in the development of the two latter systems, the Plastic and the Dye Sensitized Solar Cells.

Our main objective in DSSCs is to replace the commonly used dyes (complexes of transition metal ions with organic molecules) with polymeric dyes, thus utilizing the advantages of the polymers' character in a sensitized Solar Cell. Such materials, consist of polymeric complexes of the Ruthenium (II) ion, with tridentate or bidentate ligands like 2,2':6',2''-terpyridine and 2,2'-bipyridine, respectively.

More specifically in this work we prepared terpyridine and bipyridine vinyl monomers and in consequence we performed Atom Transfer Radical Polymerization, using functional initiators (carrying carboxylic groups aiming at the attachment of the dye onto the TiO_2) leading to homopolymers of controlled architecture (e.g. homopolymer **A** and **B**). After complexation with Ruthenium (II) ions, these materials can be applied as dyes in Hybrid Photovoltaic Cells (PVs).

In close cooperation with the laboratory of prof. Falaras in NCSR Demokritos, we managed to evaluate the photovoltaic performance of these materials. As an example, homopolymer **B** gave a short circuit photocurrent density J_{sc}= 39 μA/cm^2, open circuit potential V_{oc}= 350 mV, fill factor ff=0.39 and power conversion efficiency n=0.005%. Besides this relatively poor efficiency, the obtained results look promising and justify further investigations in the field. In an attempt to improve the efficiency of these systems we have managed to combine the polymeric dyes with the electrolyte most commonly used; poly(ethylene oxide). This new random copolymers of various ratios are now under investigation for their photovoltaic performance.





Dye	JSC (μA/cm2)	VOC (mV)	ff	n (%)
A	*54*	*248*	*0.44*	*0.006*
B	*39*	*350*	*0.39*	*0.005*
N719	*9290*	*583*	*0.53*	*2.87*

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Synthesis and Characterization of Polymeric [Ru2+] Complexes and their Application as Dyes in Solar Cells

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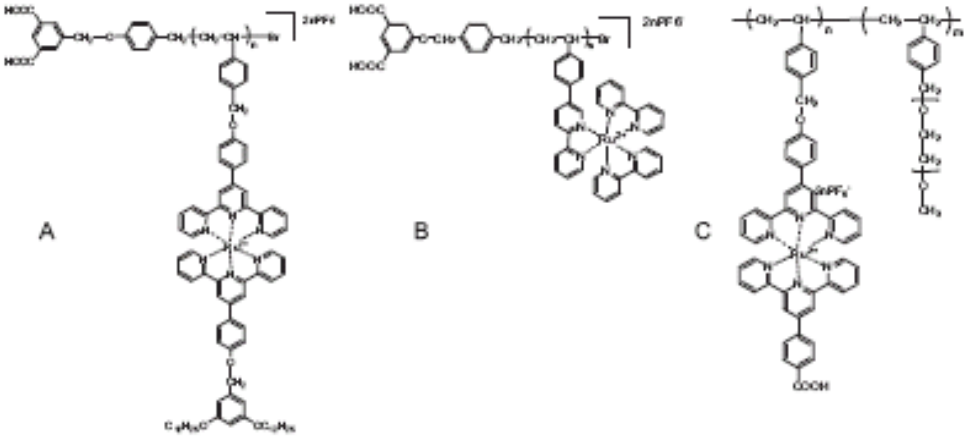
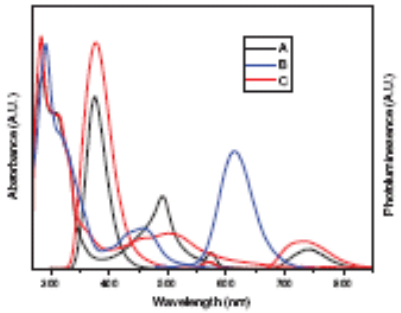
More specifically in this work we prepared terpyridine and bipyridine vinyl monomers and in consequence we performed Atom Transfer Radical Polymerization, using functional initiators (carrying carboxylic groups aiming at the attachment of the dye onto the TiO2) leading to homopolymers of controlled architecture (e.g. homopolymer A and B). After complexation with Ruthenium (II) ions, these materials can be applied as dyes in Hybrid Photovoltaic Cells (PVs). The resulting polymer structures were confirmed via NMR and their optical properties were investigated using UV-Vis and Photoluminescence.





Taking this effort one step further we combined the polymeric dye of Ru(II) complexes with the most commonly used polyelectrolyte in hybrid PVs, like PEO. The random copolymers produced (copolymer C) were examined equally as before with NMR, UV-Vis and Photoluminescence.

The performance of these materials in solar cells was also tested. As an example, homopolymer B gave a short circuit photocurrent density Jsc= 39 μA/cm2, open circuit potential Voc= 350 mV, fill factor ff=0.39 and power conversion efficiency n=0.005%.

Dye	JSC (μA/cm2)	VOC (mV)	ff	n (%)
A	54	248	0.44	0.006
B	39	350	0.39	0.005
N719	9290	583	0.53	2.87

Besides this relatively poor efficiency, the obtained results look promising and justify further investigations in the field. In an attempt to improve the efficiency of these systems we combined the polymeric dyes with poly(ethylene oxide) in copolymers with different architectures. These new copolymers of various structural compositions are now under investigation for their photovoltaic performance.

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