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Copolymers of Ionic Liquids with Polymeric or Metallocomplex Chromophores for Quasi-Solid State DSSC Applications

Panagiotis Giannopoulos,^a Aikaterini K. Andreopoulou,^{a,b}* Charalampos Anastasopoulos,^a Dimitrios Raptis^{b,c}, Georgia Sfyri^{b,d}, Joannis K. Kallitsis,^{a,b} Panagiotis Lianos^{b,c}

^a Department of Chemistry, University of Patras, University Campus, Rio-Patras, GR26504, Greece

^b Foundation for Research and Technology Hellas / Institute of Chemical Engineering Sciences (FORTH/ICE-

HT), Platani Str., Patras, GR26504, Greece

^c Department of Chemical Engineering, University of Patras, 26504 Patras, Greece.

^d Department of Physics, University of Patras, 26504 Patras, Greece

Abstract: The development of copolymers based on ionic liquid vinyl-monomers of the imidazole family, which are combined with polymerizable chormophoric units, is presented herein. Thus, ruthenium complexes bearing polymerizable vinyl groups or ω -end vinyl *rr*-poly(3-alkyl thiophene) were prepared and copolymerized with the ionic liquid monomers under free radical polymerization conditions affording chromophore/polyelectrolyte combinations. Homopolymer ionic liquids were also synthesized in order to select the optimum conditions for the copolymers thereafter. All monomers and polymers were characterized for their optical properties and were also structurally characterized using various complementary techniques. Selected copolymers and homopolymers were tested in quasi-solid-state sensitized solar cells based on titania and regioregular poly(3-hexyl thiophene) acting as hole-transporting semiconducting polymer. The ionic liquid, which is miscible with the hole-conductor and can be deposited with the latter, provides a functionality

that, in some cases, supports the increase of open-circuit voltage thus increasing cell efficiency.

Introduction

cells $(DSSCs)^2$.

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Research is focusing over the last years in the replacement of silicon- based photovoltaic devices. This is mainly due to their high cost of production and the limited range of applicable materials, something that turned the interest to organic photovoltaic devices (OPVs), where the active layers of the device mainly consist of organic materials¹. OPVs show some advantages regarding the cost and environmental issues despite their lower efficiency in comparison to inorganic light converters that are currently commercially available. One technology that has shown increased conversion efficiency among OPVs is dve-sensitized solar

- In a typical DSSC, an inorganic semiconductor, usually TiO₂^{3,4,5,6} or ZnO^{7,8}, acts as an electron acceptor and transporter. The semiconductor also supports the sensitizer, i.e. a material that absorbs visible light and injects the photogenerated electron into the conduction band of the supporting (acceptor) semiconductor. In DSSCs, a dye plays the role of sensitizer. The dye must have anchoring groups to form stable bonds with the semiconductor's surface. Such anchoring groups are mainly carboxylic, although other anchors have been suggested, such as the perfluorophenyl group, which was recently reported by our group^{9,10}. The remaining functional components of a DSSC are a counter electrode, carrying usually Pt nanoparticles as catalyst, although various attempts have been reported aiming to the replacement of Pt mainly with carbon hybrids¹¹, and an electrolyte^{12,13,14}.
- The electrolyte in DSSCs is very important, because it provides the required ionic conductivity and helps dye regeneration with charge transfer reactions with the dye molecules. Liquid electrolytes present a major drawback in the use of DSSCs due to solvent evaporation and the reduction of device lifetime and performance, especially when the device is not perfectly sealed¹⁵. Thus, the replacement of typical solvents (or solvent mixtures) with solid or quasi solid electrolytes is a very interesting and active field of research¹⁶. Commonly ionic liquids, p-type hole-transport organic semiconductors, plastic crystals and polymer gel electrolytes have been used instead of the typical liquid ones. This kind of electrolytes show long term stability, although in many cases the efficiency remained lower when compared with typical DSSCs^{17,18,19,20,21,22,23,2425}
- ILs are widely studied organic salts, that have gained much attention for a wide range of applications in various chemical and industrial fields. This is attributed to their unique properties, such as high ionic conductivity, good thermal, chemical and electrochemical stability and low vapor pressure^{26,27}. Due to these properties, ILs are commonly used as solvents for organic synthesis or catalysis (green solvents) and polymerization processes, such as free radical polymerization^{28,29} and atom transfer radical polymerization (ATRP)^{30,31}. Their use is also extended into other applications, such as lithium batteries^{32,33,34}, light emitting devices³⁵ and electrochemical capacitors³⁶. Various IL chemical structures have been reported employing for example imidazolium or pyrrolidinium moieties as cations and hexafluorophosphate or tetrafluoroborate as
- 35 example imidazolium or pyrrolidinium moieties as cations and hexafluorophosphate or tetrafluoroborate as anions. In the field of DSSCs, imidazolium-based ionic liquids^{37,38,39}, or more recently electrolytes based on these ionic liquids^{40,41} have been studied.

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Polymerizable ionic liquid monomers and their respective polymers (PILs) are recently considered as a specific field in polymer science. These polymeric ionic liquids show increased thermal stability combined with interesting electrochemical properties. One of the most studied imidazolium based PIL is poly[1-(4-vinylbenzyl)-3-butyl imidazolium tetrafluoroborate] (PVBT) which remains stable up to 300 °C⁴², is highly polar, is soluble in solvents such as N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO) or acetonitrile because of its ionic nature, and at the same time is hydrophobic. Polymeric ionic liquids (PILs) are identified as exotic polyelectrolytes for various applications, like in dye-sensitized solar cells (DSSCs) in which they could effectively replace liquid electrolytes used up to now^{43,44,45,46}. Although a lot of progress has been reported in this field, with recent works aiming to the formation of IL-based hybrids^{47,48}, the use of IL-based polymer gels has only resulted to a few successful works^{28,49} and even less with the employment of copolymers⁵⁰. Despite that, research is focusing on this topic, since ILs can overcome solvent electrolyte leakage, whereas the combination of an IL based electrolyte with a dye could improve cell stability without sacrificing the overall efficiency of the cell⁵¹.

An optimum concept for such organic solvent-free quasi-solid-state DSSCs, could be the simultaneous 15 incorporation of chromophores and ILs that should broaden absorption and ion transfer in the final device. These facts urged us to investigate the use of PILs as electrolytes in DSSC applications and compare them with copolymers based on ILs and suitable dyes. Both organic dyes and metallocomplexes have been employed, in order to compare the applicability of organic versus organometallic dyes, even though the drawbacks of ruthenium (or other metal) containing dyes, such as toxicity and availability, should be also taken into consideration. Therefore, in the present study, we employed two polymerizable vinyl-ILs, namely 20 1-(4-vinvlbenzvl)-3-methyl imidazolium tetrafluoroborate (VBMImT)⁵² and 1-vinvl-3-hexyl-imidazolium bromide (VHImBr)⁵³ and polymerizable dve (macro)molecules, a low molecular weight ω -end vinyl terminated regioregular poly (3-alkylthiophene)⁵⁴ and a vinylphenyl-bipyridine ruthenium complex with two bipyridines as co-ligands⁵⁵, in order to prepare homopolymer and copolymer PILs. Polymerizations were 25 carried out in various conditions in order to achieve the best yields for the homopolymers, but also as a first test regarding the forthcoming copolymerizations. Through this route, the homopolymers PVBMImT and

PVHImBr were synthesized, followed by the synthesis of copolymers based in the ionic liquids combined with the ω -end vinyl-poly(3-octyl-thiophene) or the (vinylphenyl-bipyridine)-Ru(II)-di(bipyridine) complex. Both homopolymer and copolymer PILs were structurally characterized and also their optical properties were

evaluated. Such materials were then employed in the fabrication of solar cells and the testing of their

performance.

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Experimental Section

Materials

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 ω -end vinyl-poly(3-octylthiophene) (vinyl-P3OT)⁵⁴ and Ru(bpy)₂(styrylbpy)⁵⁵ were prepared according to literature. The synthetic procedures of the ionic liquid monomers VBMImT⁵² and VHImBr⁵³ are given in the Supporting Information.

All solvents and reagents were purchased from Sigma Aldrich, Alfa Aesar or Acros Organics and were used without further purification unless otherwise stated. All reactions were carried out under argon atmosphere.

Tetrahydrofuran (THF) was dried and distilled just before use over sodium wire in the presence of
 benzophenone. Acetonitrile (MeCN) was dried and distilled over calcium hydride (CaH₂). 2,2'-Azobis(2-methylpropionitrile) (AIBN) was recrystallized using methanol (MeOH).

Dye sensitizer N719 was obtained from Solaronix, conductive polymer PEDOT:PSS (Baytron P) from H.C.Starck, regioregular poly(3-hexyl thiophene) from Rieke Metals and silver ink (5007E) from DuPont.

15 Characterization methods

¹H NMR spectra were recorded on a Bruker Advance DPX 400.13 MHz spectrometer, using MeOH- d_1 , DMSO- d_6 or CDCl₃ as solvents containing TMS as internal standard.

Thermogravimetric analysis (TGA) was carried out on about 8 mg samples contained in alumina crucibles in a Labsys TM TG apparatus of Setaram under nitrogen and at a heating rate of 10 °C min⁻¹.

- 20 IR spectra were recorded on an ALPHA-P diamond ATR spectrometer of Bruker Optics GmbH. Mass spectra were recorded on a Waters Acquity ESI-MS system with a Waters 2966 Photodiode Array detector coupled to a Waters Micromass ZQ mass spectrometer. A single-quadrupole Quattro micro mass spectrometer (ACQUITY SQ Detector) equipped with an electrospray ionization (ESI) interface was used for analytical detection. ESI-MS was operated in positive mode under the following operating parameters:
- 25 capillary voltage, 3.5 kV; cone voltage, 30 V; source temperature, 80 °C; desolvation temperature, 300 °C; desolvation gas (nitrogen), 5500 L/h; cone gas (nitrogen), 50 L/h. All data were acquired and processed using Masslynx 4.1 software (Waters Corp., MA, Milford, USA).

Size exclusion chromatography (SEC) measurements were carried out at 25 °C with a flow rate of 1 mL/min, using a polymer lab chromatographer equipped with two Ultra Styragel linear columns (104 Å, 500 Å) and a UV detector. Polystyrene standards were used for the calibration and the eluent was CHCl₃.

UV-Vis spectra were recorded using a Hitachi U-1800 spectrophotometer. Photoluminescence (PL) spectra were recorded using a Perkin–Elmer LS45 luminescence spectrometer, after excitation at the UV-Vis absorption maxima.

For solar cell characterization, illumination of the samples was made with a PECCELL PEC-L01 Solar Simulator set at 100 mW/cm². J-V characteristic curves were recorded under ambient conditions with a Keithley 2601 source meter that was controlled by Keithley computer software (LabTracer).

Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM2100 operating at 200 kV. Sample preparation for TEM examination involved the preparation of dilute solutions of the samples

5 in CHCl₃. A drop of the solution was placed on 3 mm carbon coated copper grids (Electron Microscopy Sciences) and the samples were dried in air for 2 days.

Synthetic Procedures

10 Synthesis of homopolymers PVBMImT and PVHImBr

Polymerizations of the above monomers were carried out in dry MeCN, under inert atmosphere. MeCN was used as solvent, using different solvents and monomer/initiator ratios, as shown in Table 1. Specifically, using the optimum procedure's conditions, 1.155 mmol (1.5 eq) of using monomer (either VBMImT or VHImBr) and 0.077 mmol AIBN (0.1 eq), were dissolved in 2 mL MeCN, under inert atmosphere and heated at reflux for 24 h. The formed polymer was precipitated with diethyl ether at 0 °C and dried in a vacuum oven at 60 °C

overnight.

Synthesis of copolymer poly(P3OT-co-VBMImT)

Vinyl-P3OT n-hexane fraction (40 mg) and VBMImT (320 mg) were dissolved in a dry MeCN/Chloroform mixture (10 mL, 1/1:v/v) (with the addition of 0.2 mL oDCB in order to fully dissolve vP3OT) in a round bottom flask, equipped with a stirring bar and a reflux condenser under inert atmosphere. AIBN (10.8 mg) was then added, the system was degassed again and heated at reflux for 48 h. The solvents were removed after heating at 60 °C. The forming copolymer was washed consecutively with ethyl acetate (EtOAc) and MeCN in order to remove unreacted species. The reddish solid, was filtrated and dried under vacuum overnight.

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Synthesis of copolymer poly(P3OT-co-VHImBr)

The copolymerization of vinyl-P3OT (40 mg) with VHImBr (320 mg) was carried out using analogous conditions to the as described before poly(P3OT-co-VBMT) (Polymer 1) with a slight modification. Instead of the MeCN/chloroform mixture, only chloroform was used (again with the addition of 0.2 mL oDCB) since the VHImBr monomer is also soluble in chloroform.

30 VHImBr monomer is also soluble in chloroform.

Synthesis of copolymer poly(Ru-co-VBMImT)

Ru(bpy)₂(styrylbpy)⁵⁵ (61 mg, 0.06 mmol) and VBMImT (100 mg, 0.35 mmol) were dissolved in 3 mL of dry MeCN, under inert atmosphere. Afterwards, 5.2 mg (0.03 mmol) AIBN were added and the system was
heated at reflux for 48 h. The solution was cooled to RT, filtered and thoroughly washed with MeCN. The remaining solid was dried under vacuum overnight and used without further purification.

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The cells studied in the present work were quasi-solid-state DSSCs with a layer structure obeying the following configuration: (1) a layer of mesoscopic titania sensitized with a standard dye sensitizer; (2) a mixed layer composed of a blend of the hole transporting polymer P3HT (Poly(3-hexylthiophene-2.5-diyl) with 5 polymeric ionic liquid at various proportions; and (3) a top layer of conductive PEDOT:PSS plus silver conduct electrodes making the counter electrode. Such cells were fabricated as follows. FTO-coated glass substrates were cut in pieces of dimensions 1 cm \times 3 cm. One third of the conductive layer was removed using zinc powder and hydrochloric acid. Then they were washed with detergent, rinsed with distilled water and subsequently with ethanol in an ultrasonic bath, finally dried under air stream. A thin layer of compact titania 10 was first sprayed over the patterned FTO electrode using 0.2 mol L⁻¹ diisopropoxytitanium bis(acetylacetonate) solution in ethanol and then it was heated at 500 °C for 1 h. On this thin bottom laver, a titania paste made of P25 nanoparticles was applied by screen printing, 90 mesh screen was used. The film was heated again up to 500 °C for 20 min. Then, the film was treated with a 0.04 mol L^{-1} aqueous solution of TiCl₄ for 30 min at 70 °C, followed by heating up to 500 °C for 20 min. This final titania film was about 10 15 um thick, as determined by its profile using SEM. As soon as the final film was taken out of the oven, it was dipped in a 0.5 mmol L^{-1} N719 solution in ethanol containing 5 mmol L^{-1} chenodeoxycholic acid and was left overnight. The film was then heavily coloured with attached dye. It was rinsed with ethanol and dried in a N₂ stream. The presence of chenodeoxycholic acid is a recent common practice^{56,57} and it was beneficial also in 20 the present case. Next step of cell fabrication was the deposition of the mixture of the hole transporting P3HT with polymeric ionic liquid. The mixture was prepared by making 20 mg/mL solutions in chloroform using various proportions of the two materials. Optimal results were obtained by mixing 18 mg of P3HT with 2 mg of polymeric ionic liquid. Both homopolymer and copolymer ionic liquids were tried. This layer was deposited by spin-coating at 3000 rpm for 1 min and it was dried in an oven for 15 min at 100 °C. Then a layer of PEDOT: PSS was deposited by spin coating the commercial solution at 1500 rpm, which was annealed 25 in an oven for 15 min at 150 °C. Finally, silver electrodes were painted on the top with a brush using a mask. The electrodes were rapidly annealed (30 s) at 130 °C. Their size was 1 mm x 10 mm.

Results and Discussion

Synthesis of the vinyl monomer ILs

The first step of this work was the synthesis of IL polymerizable monomers. We used two different starting materials, 1-vinyl imidazole and 1-methyl imidazole, in order to synthesize two, different type of ionic liquid monomers. As a result we obtained two monomers, 1-(4-vinylbenzyl)-3-methyl imidazolium tetrafluoroborate (VBMImT)⁵² (after ion exchange between chloride and tetrafluoroborate) and 1-vinyl-3-hexyl-imidazolium bromide (VHImBr)⁵³.



10 Scheme 1: Synthetic procedures for the monomer VBMImT and for the homopolymer PVBMImT.



Scheme 2: Synthetic procedures for the monomer VHImBr and for the homopolymer PVHImBr.

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The first part of **Schemes 1** and **2** show the synthetic procedures for the preparation of the ionic liquid monomers VBMImT and VHImBr respectively.

- The successful formation of the desired monomers was confirmed by ¹H NMR (**Figures S1a, S2a**) and ESI-MS (**Figure S3**). The assignment of the NMR peaks, to the monomers' protons show the absence of any byproducts. This is also proven by the mass spectra, which show the M⁺ ion mass as the ESI-MS instrument has been tuned in positive ion mode. In the case of VBMImT, an intense m/z of 117.38 [M⁺] and 118.39 [M+H⁺] can be observed, besides the one at 199.32 [M⁺] and 200.33 [M+H⁺] attributed to the product. This
- 25 peak is due to the fragment that occurs when the methylimidazolium unit has been cleaved from VBMImT. IR spectroscopy of the monomers was also carried out as shown in Figures S4a and S4b for the two monomers,

respectively, and in comparison to the starting materials in each case. In both ionic liquid monomers, characteristic bands from the presence of the imidazolium unit can be observed. More specifically, the symmetric C=C stretching vibration around 1565-1570 cm⁻¹, the aromatic C-H stretch (3050-3100 cm⁻¹), the C=N stretch (1630-1650 cm⁻¹), the C-N stretch (1160-1170 cm⁻¹) and the in-plane C-C vibrations of the imidazolium ring (around 1580 cm⁻¹) exist in both products. On the other hand, the VBMImT monomer presents two peaks at 760 cm⁻¹ and 1150 cm⁻¹, respectively, due to the BF₄⁻ anion. The VHImBr monomer shows an aliphatic C-H peak around 2850 cm⁻¹ because of the hexyl chain and a broad peak at 3300 – 3500 cm⁻¹, due to the hydration of the ionic liquid^{58,59,60,61}.

10 Preparation of homopolymers and copolymers

For the synthesis of the homopolymers PVBMImT and PVHImBr (as shown in Scheme 1 and 2, respectively), a number of different conditions were tested (Table 1) by varying the monomer to initiator ratio and the solvent used. Successful polymerizations were obtained using the conditions of entries 3, 5 and 6 of Table 1. As it can be seen from the data of Table 1, best results were obtained when MeCN and/or CHCl₃ were used as solvents. After purification, the formed homopolymers were characterized via ¹H NMR spectroscopy (Figure S1b and S2b) and via ATR spectroscopy (the respective ATR spectra are given in Figures 2a and 2b in comparison to the respective copolymers (Figure S1b for PVBMImT and Figure S2b for PVHImBr) compared to their respective monomers (Figures S1a and S2a, respectively), no monomer residues can be observed since the vinyl protons (located at 5.2, 5.6 and 6.8 ppm) have disappeared completely and broad peaks are formed proving the polymeric nature of the final purified products.

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Table 1: Polymerization conditions used for the preparation of homopolymers PVBMImT and PVHImBr, and
for the copolymers poly(P3OT-co-VBMImT), poly(P3OT-co-VHImBr) and poly(Ru-co-VBMImT).

a/a	Monomer	Solvent	Monomer/AIBN ratio					
Homopolymers								
1	VBMImT	DMF	20/1					
2	VBMImT	DMSO	15/1					
3	VBMImT	MeCN (dry)	15/1					
4	VHImBr	DMF	20/1					
5	VHImBr	CHCl ₃	15/1					
6	VHImBr	MeCN (dry)	15/1					
Copolymers								
1	VBMImT/v-P3OT	MeCN (dry)/ CHCl ₃	15/1					
2	VHImBr/v-P3OT	CHCl ₃	15/1					
3	VBMImT/Ru(bpy) ₂ (styrylbpy)	MeCN (dry)	11/1					

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After the successful formation of the homopolymers, respective copolymers based on the ionic liquid vinyl monomers and vinyl functionalized dye molecules, either a ω -end vinyl-polythiophene macromonomer (Schemes 3) or a ruthenium complex (Scheme 4) were formed.



poly(P3OT-co-VHImBr)

Scheme 3: Synthesis of polythiophene – ionic liquid random copolymers poly(P3OT-co-VBMImT) and poly(P3OT-co-VHImBr).



Figure 1: ¹H NMR of poly(P3OT-co-VBMImT) (a) and poly(P3OT-co-VHImBr) (b) in CDCl₃.

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vinyl monomers with vinyl-P3OT, the specific peak is more intense, because of the thiophene's octyl chain. Vibrations from the imidazolium group can be observed at 1040 and 1140 cm⁻¹ due to the C-N bond and near 1550 cm⁻¹ due to C=N^{59,62}. Furthermore, bands appearing in the area 700 – 900 cm⁻¹ can also be ascribed to contributions from ring bending modes of the imidazolium cation⁶³.



Figure 2: ATR spectra of poly(P3OT-co-VBMImT) (a) and poly(P3OT-co-VHImBr) (b) in comparison to the starting materials and the respective homopolymers.

Efforts were also done for the characterization of the copolymers via GPC. However, due to the ionic nature and the nitrogen containing heterocycles of the polymeric ionic liquid blocks the molecular weights were substantially underestimated leading to even lower molecular weights than the initial vinyl polythiopene macromonomer. In particular, for the poly(P3OT-co-VBMImT) copolymer an Mn=6.500 was found while for the copolymer poly(P3OT-co-VHImBr)] its Mn was in the range of 4.800 which are significantly lower than the initial vinyl-P3OT macromonomer's Mn of 21.000.

The polythiophene-ionic liquid copolymers were also characterized by thermogravimetric analysis (TGA). Specifically, as seen in **Figure S5**, both copolymers show increased thermal stability when compared to the ionic liquid monomers and homopolymers, that are almost completely degraded around 450 °C (VBMImT and PVBMImT) and 350 °C (VHImBr and PVHImBr). On the other hand, vinyl-P3OT is thermally stable until 500 °C leading to copolymers of higher degradation temperatures.

- 20 500 °C leading to copolymers of higher degradation temperatures. Regarding the optical properties of the synthesized compounds, UV-Vis absorption and PL emission spectra were carried out in solution. Vinyl-P3OT and the corresponding copolymers poly(P3OT-co-VBMImT) and poly(P3OT-co-VHImBr) were dissolved in CHCl₃. VHImBr is also soluble in chloroform, in contrast with the other monomeric ionic liquid, VBMImT, for which acetonitrile was used instead. Finally, both homopolymers
- 25 were dissolved in MeOH. The two copolymers have similar behaviors in their absorption spectra presenting a broad peak around 450 nm. As can be seen in **Figure 3**, this peak is slightly shifted to lower wavelength in the

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copolymers' cases in comparison to the pure vinyl-P3OT. The intense peak at 280 nm in poly(P3OT-co-VBMImT) is attributed to VBMImT and is shifted around 25 nm in comparison to the monomeric VBMImT. **Figure 4** shows the PL spectra of the copolymers versus the vinyl-P3OT macromonomer in chloroform solutions, after excitation at the P3OT absorption maximum. The PL spectra of the respective ionic liquid homopolymers are given in the inset of **Figure 4**. For both the copolymers emissions due to the P3OT blocks are detected at 564 nm, slightly blue shifted compared to the net vinyl-P3OT which emits at 570 nm.



Figure 3: UV-Vis spectra of poly(P3OT-co-VBMImT) (a) and poly(P3OT-co-VHImBr) (b) in comparison tothe starting materials and the respective homopolymers.



Figure 4: PL spectra of poly(P3OT-co-VBMImT and poly(P3OT-co-VHImBr) in comparison to vinyl-P3OT after excitation at 450 nm. The inset shows the initial monomers' PL spectra, VBMImT in MeOH and VHImBr in MeCN, after excitation at 220 and 250 nm, respectively.

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Scheme 4 presents the copolymerization reaction of the Ru(bpy)₂(styrylbpy) monomer⁵⁵ with the monomeric VBMImT. Since, both the ruthenium complex and the monomeric ionic liquid are soluble in acetonitrile, MeCN was used as the polymerization solvent while the IL/initiator ratio was 11/1 (Table 1).



5 Scheme 4: Synthesis of the copolymer poly(Ru-co-VBMImT).



Figure 5: ¹H NMR of poly(Ru-co-VBMImT) in DMSO-d₆.

The structural characterization of the copolymer was carried out using ¹H NMR and ATR spectroscopies 10 (Figures 5 and S6a). Thermogravimetric analysis of poly(Ru-co-VBMImT) showed increased thermal stability in comparison to the ionic liquid monomer and homopolymer (Figure S6b), which is attributed to the increased thermal stability of the ruthenium complex monomer.

UV-Vis and PL spectroscopies of acetonitrile solutions of the Ru(bpy)₂(styrylbpy) and of the copolymer 15 poly(Ru-co-VBMImT) were employed for their optical properties evaluation as shown in Figure 6, respectively. In the absorption spectra of the poly(Ru-co-VBMImT), no significant alternation was observed in comparison to the monomer complex $Ru(bpy)_2(styrylbpy)$ in the region above 260 nm (Figure 6a). On the other hand, the copolymer showed an intense peak around 210 nm, which does not exist in the monomeric ruthenium complex, and is attributed to VBMImT. At 320 nm both the monomeric complex and the

copolymer show an absorption due to the π - π * LC (ligand-centered) transitions of 2,2'-bipyridine, and also an absorption at around 450 nm, which is characteristic of the d- π * MLCT (metal to ligand charge transfer) of the Ru(bpy)₂(styrylbpy) complexes.⁵⁵ The photoluminescence examination in solution of both the copolymer poly(Ru-co-VBMImT) and of the monomer complex Ru(bpy)₂(styrylbpy) showed a broad peak around 600 nm, after excitation at 450 nm, due to the ruthenium complex's d- π * MLCT absorption band (**Figure 6b**).



Figure 6: UV-Vis spectra (a) and PL spectra (b) after excitation at 450 nm of VBMImT, PVBMImT, Ru(bpy)₂(styrylbpy) and poly(Ru-co-VBMImT), in MeCN solutions.

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Quasi-solid-state DSSC fabrication and testing

Quasi-solid-state DSSCs were constructed in a layer structure using a standard mesoporous titania film sensitized by the most frequently employed Ru-based dye N719. We used P3HT as hole collecting and transfer layer and a combination of PEDOT:PSS with silver electrodes as counter electrode. The novelty of the present work was the introduction of a small quantity of polymeric ionic liquid into the hole transporting layer. It has been previously reported that ionic content in the hole transporting layer may modify its electronic properties and subsequently affect the efficiency of solid state sensitized solar cells^{64,65,66}. This was also verified by the presently studied cells. The term quasi-solid-state DSSC has been used in the present work to underline the fact that the P3HT/polymeric ionic liquid blend can no more be considered as a purely solid material

20 material.

A few different polymeric ionic liquids have been employed and tested in quasi-solid-state DSSC configuration. **Figure 7** and **Table 2** show current-voltage data for the studied cells. It must first be underlined that cells showed an acceptable performance when the polymeric ionic liquid content was relatively low. Thus optimized data were obtained when the P3HT/polymeric ionic liquid ratio was 9:1 w/w. On the other hand, most polymeric ionic liquids did not show any substantial influence to the cell performance compared to pure

P3HT. However, one of the prepared samples did demonstrate a marked improvement of cell efficiency.

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Indeed, as seen in **Figure 7** and **Table 2**, introduction of PVHImBr resulted in about 30% improvement of efficiency. This increase was due to the large increase of the open-circuit voltage of the cell and the improvement of the fill factor despite the fact that a substantial decrease of the current density was caused by the introduction of the ionic liquid. The decrease of the current is most probably due to the fact that the above cells function by hole collection and transfer through the hole-conducting P3HT. The interference of the ionic agent most probably disrupts some of the hole-transporting channels. On the contrary, the presence of the ionic agent establishes a potential gradient that results in open-circuit voltage increase. Such a voltage increase was also observed in a previous publication treating a solid state quantum dot sensitized solar cell where a tiny quantity of Na₂S was added as an ionic agent⁶⁶. Even though, current dropped in the present case, voltage increase had a marked beneficial effect on cell performance. The advantage of the presently introduced materials is that they can be mixed with P3HT eliminating solubility problems.



Figure 7: J–V curves for solar cells made of photoanodes bearing a nanocrystalline titania film on FTO electrode sensitized by N719 dye and on the top P3HT mixed with 10% w/w of a polymeric poly ionic liquid: (1) no ionic liquid, 2) P3HT and poly(P3OT-co-VHImBr), (3) P3HT and PVBImT, (4) P3HT and PVHImBr.

Composition of the hole transporting/ionic liquid layer		V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
1	P3HT alone	0.42	17.0	35	2.5
2	P3HT/ poly(P3OT-co-VHImBr)	0.42	7.0	30	0.9
3	P3HT/ PVBImT	0.29	11.2	33	1.1
4	P3HT/ PVHImBr	0.55	14.1	42	3.2

Table 2: Current voltage	characteristics of	of the cells.	Data extracted	from Figure 13
U				

Morphology characterization of the polymeric materials employed in DSSC testing

Having the results from the DSSC measurements in mind, and in an effort to clarify the unexpected better performance of the net PIL homopolymer versus its copolymer with P3HT, we proceed with the morphology evaluation of blends as those that were prepared and tested in the DSSC devices. The transmission electron microscopy (TEM) images of the net P3HT, the 9:1 blend of P3HT/poly(P3OT-co-VHImBr) and the 9:1 blend of P3HT/PVHImBr, all casted from dilute CHCl₃ solutions, are presented in the below **Figure 8**.

As can be seen in **Figure 8a**, the net P3HT formed uniform films that presented some degree of organization into fibrillary structures due to the close packing and crystallization of the high molecular weight P3HT.1 The casting procedure for the preparation of the TEM samples of course does not allow ordering to a great extend but the method for preparing the P3HT film on the DSSC device which is accompanied by thermal treatment

should have a more prominent effect on the crystallization of the P3HT macromolecular chains. On the contrary, the 9:1 blend of P3HT/poly(P3OT-co-VHImBr) shown in **Figure 8b** did not present any fibrillar morphological features. The insertion of even a small percentage of the poly(P3OT-co-VHImBr) copolymer to the P3HT matrix obviously led to the compatibilization of the P3HT and the PIL fractions and

moreover suppressed the crystallization ability of the net P3HT.

Surprisingly, the P3HT/PVHImBr 9:1 blend, Figure 8c, presented the same crystallization tendency of the net P3HT (see Figure 8a) while some darker regions were observed. When looking deeper into those darker regions we noticed that they consisted of dark spots of about 2 nm and up to 6 nm diameter (inset of Figure 8c). These higher contrast spots are attributed to the charged imidazolium cation and Br anion of the PVHImBr ionic liquid hompolymer and more specifically to the high contrast of the Br atoms under the electron beam.⁶⁷ Therefore it can be concluded that the presence of the homopolymer PVHImBr did not disturb the crystallization and ordering of the P3HT and that it was quite uniformly dispersed in selective regions along the polythiophene matrix.

The above findings constitute an explanation of the better DSSC device performance of the P3HT/PVHImBr blend over the P3HT/poly(P3OT-co-VHImBr) one, since for P3HT it is known that charge transport is promoted along its crystalline domains which are interconnected with amorphous regions.1⁶⁸ Thus, the net P3HT and the P3HT/PVHImBr blend, did work nicely in the DSSC devices whereas the P3HT/poly(P3OTco-VHImBr) blend with no ordering into crystalline species did not show the analogous DSSC performance.

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Figure 8: TEM images of **(a)** P3HT scale bar 200 nm (inset scale bar 50 nm) **(b)** P3HT/poly(P3OT-co-VHImBr) 9:1 scale bar 100 nm (inset scale bar 50 nm) and **(c)** P3HT/PVHImBr 9:1 scale bar 200 nm (inset scale bar 20 nm).

Conclusions

Polymeric ionic liquids based on the imidazole moiety and their respective copolymeric ionic liquids using ω end vinyl *rr*-poly(3-octyl thiophene) or (vinylphenyl-bipyridine)-Ru(II)-di(bipyridine) were prepared in this present study. Aiming at materials that could eventually be employed in quasi solid state DSSC we prepared these ionic liquid polymers and copolymers in order to aid the ionic character of the hole transporting layer of the cell.

The homopolymer PILs and copolymer PILs with the thiophene or ruthenium based dyes were prepared via radical polymerizations. Their adequate solubility in common organic solvents allows their processability and introduction as an additive of the net organic hole transporting layer of the cell. Although further improvements are of course necessary in order to increase the efficiency of the solid state DSSCs, the methodology reported herein shows a promising route for the enhancement of the cells performance. Perhaps the most important finding of this present work is that the presence of the PIL fraction into the hole transporting P3HT layer does improve the device performance as long as it does not disturb the development of crystalline domains that promote the necessary charge carrier transport.

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Copolymers of Ionic Liquids with Polymeric or Metallocomplex Chromophores for Quasi-Solid State DSSC Applications

Panagiotis Giannopoulos, Aikaterini K. Andreopoulou,* Charalampos Anastasopoulos, Dimitrios Raptis, Georgia Sfyri, Joannis K. Kallitsis, Panagiotis Lianos

Table of Contents entry

Polymeric and copolymeric ionic liquids were prepared and tested in quasi solid DSSCs as additives of a P3HT hole transporting layer. The blend's morphology played a decisive role on the cell performance. The PIL/P3HT blend retained the organization of P3HT increasing the cell's performance due to the increased ionic nature of the blend. Contrary, the P3HT/ poly(P3OT-co-VHImBr) blend showed reduced efficiency due to the disruption of P3HT's ordering.

