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Imidazolium ionic liquids in OLEDs: synthesis and improved electroluminescence of an '*ionophilic*' diphenylanthracene

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ABSTRACT

A 9,10-diarylanthracene having two *ionophilic* imidazolium tags on peripheral positions has been synthesized through a radical chain addition of 1,2-dimethyl-3-(3-mercaptopropyl)imidazolium to 9,10-distyrylanthracene. OLED cells prepared with this derivative exhibits 13.6-fold efficiency enhancement as compared to that prepared with 9,10-diphenylanthracene at the same concentration. Based on electrical conductivity measurements, this efficiency enhancement has been attributed to the blocking of spurious current flow due to ion relocation near the electrodes. The advantage of covalent attachment compared to physical mixtures of 9,10-diphenylanthracene and 1,2-dimethyl-3-(3-mercaptopropyl)imidazolium ionic liquid derives from the experimental difficulty of having an active layer with the target anthracene-to-ionic liquid ratio due to the remarkable differences in viscosity of the two components of the mixture.

1. Introduction

Ionic liquids, particularly those with imidazolium type, have emerged as novel green solvents in catalysis.[1–4] Due to the remarkable physicochemical properties of ionic liquids, particularly the electrical conductivity and electrochemical stability, these compounds have also found application in electrochemistry[5–7] and as components for solar cells and organic electroluminescent diodes (OLEDs).[5,8–14] Specifically, the low volatility of ionic liquids and their ionic conductivity can be used to replace advantageously aqueous electrolytes in fuel cells and dye synthesized solar cells, prolonging the service lifetime of these photovoltaic devices.[11–22]

One general problem in OLEDs is charge transport from the external electrodes through the organic layer in which electron and hole recombination must generate the electronically excited state that eventually will originate light emission.[23–29] In this context, it has been recently reported that the presence of ionic liquids can enhance the efficiency of OLED emission by one or two orders of magnitude.[5,7,8,10,13,16] The positive influence of ionic liquids has been attributed to accumulation of ions near the electrodes that leads to high interfacial fields favoring the tunneling of electrons.[10,16]

One general strategy in catalysis to increase the affinity of a successful catalyst for a particular medium is to modify the active species by introducing in peripheral position a tag that increases the affinity for this solvent.[30] Analogous strategy has been applied to increase the solubility in perfluorinated solvents.[31–35] In the case of ionic liquids, we and others have reported that the affinity of a catalyst for these solvents can be increased by attaching imidazolium units far from the active metal center.[36–39]

Inspired by this work on catalysis and considering the precedents suggesting that the presence of ionic liquids can enhance the performance of OLEDs, in the present work we describe the synthesis and electroluminescent properties of an '*ionophilic*' 9,10-diphenylanthracene (DPA). DPA is an organic compound that exhibits electroluminescence.[40–42] We will show that the covalent attachment of imidazolium tags renders a product that combines the electroluminescent properties imparted by the 9,10-diarylanthracene with the ionic liquid characteristics of the imidazolium moieties. The resulting *ionophilic* derivative exhibits improved electroluminescent properties with respect to cells based on 9,10-diarylanthracene or even a mixtures of the polycyclic aromatic compound and imidazolium ionic liquid.

2. Results and discussion

2.1. Synthesis of *ionophilic* diarylanthracene

In order to implement the properties of ionic liquids on DPA, we designed an *ionophilic* diarylanthracene having two imidazolium rings in peripheral positions. The actual compound 9,10-bis[4-(3-(1,2-dimethyl imidazoliumyl)propylthioethyl)phenyl]anthracene bishexafluorophosphate (compound **7**) was synthesized as indicated in Scheme 1.

The starting compound in the synthesis is 1,10-distyrylanthracene (**3**) that was in turn obtained by the palladium

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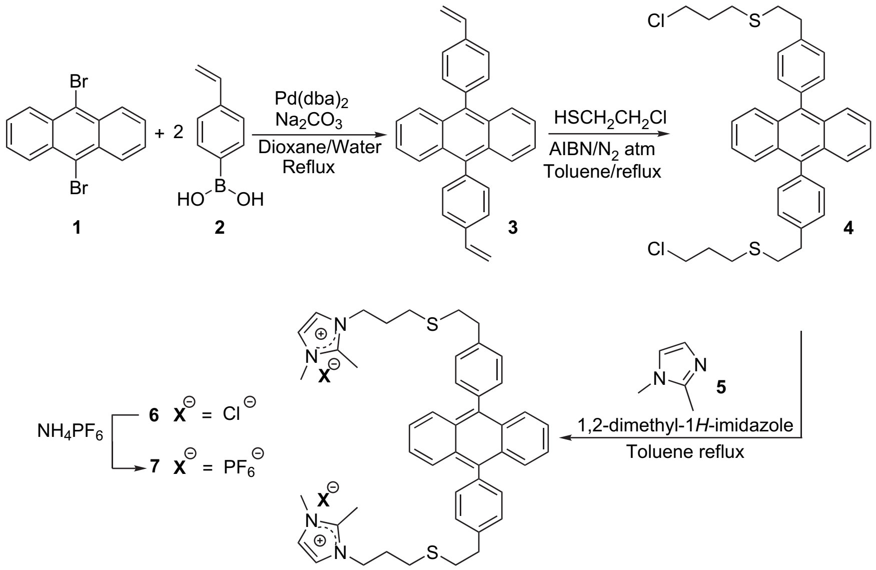

Scheme 1. Synthesis of the *ionophilic* derivative of 9,10-diarylanthracene having two imidazolium units.

catalyzed Suzuki cross-coupling between commercially available 9,10-dibromoanthracene and 4-styrylboronic acid. This styrylanthracene **3** was reacted with 3-chloropropanethiol using AIBN as radical initiator in the absence of oxygen. Radical addition of thiols to electron rich carbon–carbon double bonds is a reaction that occurs in high yields under mild conditions compatible with the presence of a large variety of functional groups.[43] The last step in the synthesis was the nucleophilic substitution of primary chlorine atom by the nucleophilic nitrogen of *N*-methylimidazol. Finally, ion metathesis of Cl^- by PF_6^- renders the hexafluorophosphate salt of bisimidazolium **7**.

The target *ionophilic* diarylanthracene **7** and the synthetic intermediates were characterized by their spectroscopic properties. Compound **3** had been previously reported in the literature[44] and its transformation into **4** is accompanied by the disappearance in ^{1}H NMR of the signals corresponding to vinylic hydrogens and the concurrent appearance of the two triplets at 3.11 and 2.99 ppm due to the methylene groups attached to sulfur.

On the other hand, the introduction of the 1,2-dimethylimidazolium units by substitution of the two terminal chloride atoms in compound **4** is accompanied by the presence of the signals corresponding to the quasi-equivalent four imidazoliumyl hydrogen atoms at low field in the aromatic region. A complete set of spectroscopic data for compound **7** and its synthetic intermediates are given in Section 4.

2.2. Electroluminescence study

9,10-Diphenylanthracene has a fluorescence quantum yield of 0.98. This high photoluminescence efficiency is in part responsible for the use of these compounds in OLEDs. In order to evaluate the influence of the presence of imidazolium tags on the electroluminescence performance of compound **7**, three series of OLED cells were prepared on transparent ITO electrodes previously treated to deposit a nanometric PEDOT–PSS layer. The series of cells contained as active layer DPA, mixtures of DPA and 1,2-dimethyl-3-(3-mercaptopropyl)imidazolium hexafluorophosphate ionic liquid (DMPIM), or compound **7**. The construction of the cells was completed by sublimation of aluminum as back electrode. The configuration of the cells was ITO/PEDOT–PSS/*luminophore*/Al.

Transmission optical spectroscopy of the ITO/PEDOT–PSS/luminophore allowed quantifying the actual amount of diarylanthracene derivative on the electrode. Since the active layer was prepared by spin coating, it was difficult to reproduce exactly the concentration of anthracene luminophore in the film from cells prepared with different anthracene derivatives. Actually, the concentration of the active anthracene units prepared at the same speed varied in each cell depending on the viscosity of the compound. More viscous *ionophilic* anthracene derivative **7** tends to give more concentrated films than less viscous DPA or DPA/imidazolium mixtures. For this reason, the spinning speed was adjusted for each sample to obtain films with matched optical absorbance for anthracene, thus allowing drawing conclusions about the relative light emission efficiency for films with identical anthracene concentrations. To illustrate this point, Figure 1 shows the transmission optical spectra of three representative films of DPA and compound **7**. In this figure, it can be seen that by adjusting the spin coating parameters it was possible to prepare optically matched films for DPA and compound **7**. This figure also shows that it is possible to quantify the relative concentration of anthracenyl chromophore by measuring the optical density at 380 or 410 nm. In

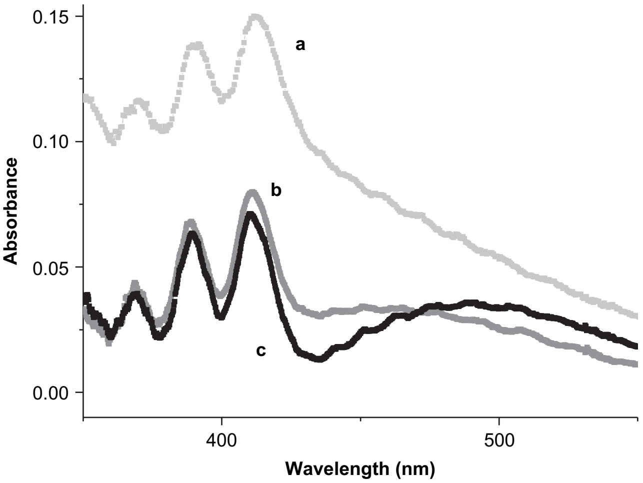

Figure 1. Transmission optical spectrum of ITO/PEDOT–PSS electrode containing a film at two different concentrations: DPA (spectra a and b) or a film of the *ionophilic* anthracene **7** (spectrum c). The broad band spanning from 435 to 600 nm and peaking at 480 nm is due to PEDOT–PSS. The spectra show the vibrational structure characteristic of anthracene chromophore with relative maxima at 345, 380 and 410 nm.

this way, the electroluminescence efficiency of the different cells with optically matched anthracene absorbance could be compared directly.

Using the ITO/PEDOT–PSS/DPA or ITO/PEDOT–PSS/**7** as anodes, two electroluminescent cells were prepared and the corresponding emission measured. No light emission was observed at low DC voltages, but the ITO/PEDOT–PSS/**7** cell started to emit above 6 V. The positive influence of the imidazolium tags favoring the efficiency of the cell was clearly demonstrated by the fact that the cell containing DPA at the same concentration as compound **7** does not emit at all in this voltage range. Actually, working at voltages below 8 V DC we observed emission from the cell containing DPA at the concentration shown in plot ‘a’ of Figure 1 that is higher than that of luminophore in the cell constructed with compound **7**. However, as Figure 2 shows, the intensity of the cell containing higher DPA concentration was still much lower than that of the ITO/PEDOT–PSS/**7** electrode despite that the last cell contains 2.1 times lower chromophore concentration. Thus, the results shown in Figure 2 nicely exemplify the beneficial influence of the imidazolium tags boosting the emission inherent to the DPA electroluminophore.

One point of interest is to disclose whether or not the effect of the imidazolium ionic liquid is also observed for physical mixtures of DPA and DMPIM ionic liquid not covalently bonded. In other words, an interesting issue is to assess the role of the covalent attachment between the electroluminophore unit and the imidazolium tag. This point was addressed by preparing a third cell in which the active layer was a mixture of DPA and DMPIM in a 1:2 M ratio. DMPIM imidazolium ionic liquid has the same structure as the *ionophilic* tag unit present in compound **7**. The cell preparation and, particularly, the spinning rate were again adjusted to obtain films with optically matched absorbance for the anthracene luminophore. However, also for this ITO/PEDOT–PSS/DPA–DMPIM/Al cell, no electroluminescence was observed for voltages below 8 V DC. This control shows again the benefits of the covalent linkage occurring in compound **7** as compared to a physical mixture of two analogous components. Among the reasons for this different behavior, the simplest one is the different relative concentration of DPA versus imidazolium ionic liquid in the initial solution (1:2) and in the film. In this regard we note that, as commented before, due to differences in viscosity, the film becomes more concentrated on the ionic liquid than the initial mixture.

In order to gain understanding on the origin of the beneficial influence of imidazolium substituents on the electroluminescent emission, measurements of the electrical conductivity of the cells were carried out. Figure 3 shows the current density flowing through the cell versus the DC voltage applied for two of the cells shown in Figures 1 and 2 as well as a third cell prepared with the 1:2 physical mixture of DPA and DMPIM.

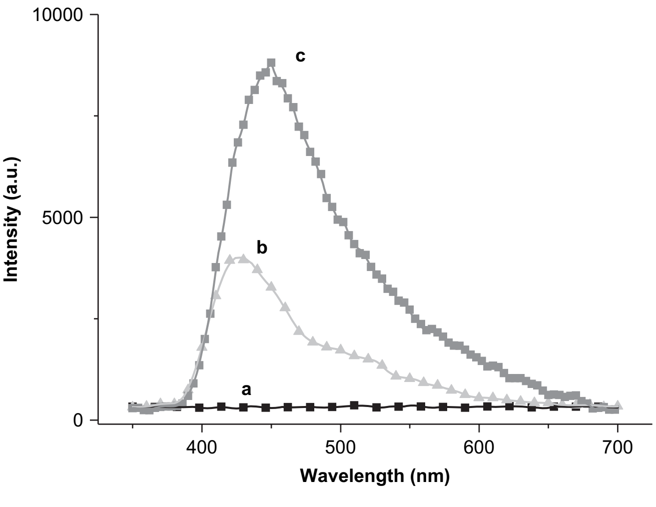

Figure 2. Light emission from OLED cells recorded: (a) ITO/PEDOT–PSS/**7**/Al at 0 V, (b) ITO/PEDOT–PSS/DPA (2.1 times more concentrated)/Al at 8 V DC, and (c) ITO/PEDOT–PSS/**7**/Al at 8 V DC.

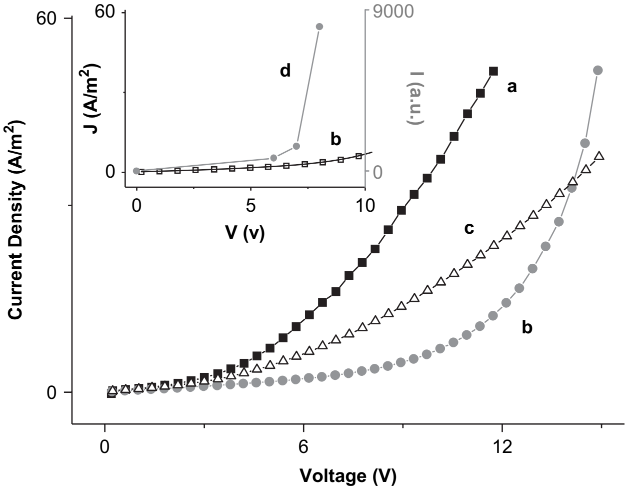

Figure 3. Current density versus the DC voltage applied: (a) ITO/PEDOT–PSS/DPA/Al; (b) ITO/PEDOT–PSS/**7**/Al, and (c) ITO/PEDOT–PSS/DPA–DMPIM/Al. *Inset*: Light emission intensity (*I*, plot d) and current density (*J*, plot b) versus the DC voltage applied (*V*) for the ITO/PEDOT–PSS/**7**/Al cell.

As it can be seen in this figure the cell prepared with compound **7** is the one that exhibits the minimum current flow. Particularly, at the voltage at which the electroluminescence shown in Figure 2 was measured (8 V DC), the current density of the cell prepared with **7** as active layer was 6.1 times smaller than that of the cell prepared with DPA. These values allowed estimating that the efficiency of the cell prepared with compound **7** is 13.7 times higher than that of DPA, again reinforcing the positive influence of attaching the *ionophilic* tags on the electroluminophore unit. Actually, this influence of the ionic liquid on the efficiency of electroluminescence cells had been previously reported although not for compounds having covalent linkage.[10,16] It is interesting to note that also for the sample prepared using a mechanical mixture of DPA and DMPIM the same effect, i.e., a decrease of the current intensity as compared to the cell with DPA lacking ionic liquid, was observed (see Fig. 3, plot ‘c’). According to the precedents in the literature, this effect of the ionic liquid on the conductivity using DC can be explained by the creation of a double layer in contact with the electrodes due to the relocation of the ions.[10] Due to the electrostatic fields, a gradient of ions in the film will occur, the concentration of mobile PF_6^- anions being higher near the cathode and lower near the anode. Thus, a barrier in the electrode–film interface will block the spurious current flow. Also in our case, the explanation proposed in the literature would apply and will be supported by the lower current flow when imidazolium ions are present in the active layer.

Concerning the measurements of the electrical conductivity in the film prepared with a physical mixture of DPA and DMPIM, it is interesting to comment that the reports in the literature used typically a luminophore-to-ionic liquid molar ratio of 1:0.5, i.e., about 4 times less than the initial concentration of our mixture. Moreover, as commented earlier, in the spin coating process a concentration in DMPIM ionic liquid occurs when there is no covalent bonding and, therefore, the film prepared with the DPA–DMPIM mixture contains a DPA/DMPIM ratio lower than 1:2. Thus, it has to be noted that the precedents in the literature focused on the optimization of the OLED cell are using much less concentration in ionic liquid than in our case that deals on the positive influence of the covalent binding of an *ionophilic* tag on an electroluminescent molecules. However, we consider that the initial molar ratio of the mixture employed here is more relevant to the present study in which compound **7** has two imidazolium units per diarylanthracenyl core. Thus, in a simplistic manner, the advantage of the covalent attachment is to ensure a fixed luminophore ionic liquid ratio avoiding viscosity effects and problems associated with the active layer preparation.

3. Conclusion

Analogously to the precedents reporting the beneficial influence of ionic liquids on the efficiency of electroluminescent cells, herein we have observed that a molecule derived from DPA containing two peripheral imidazolium units exhibits over one order of magnitude efficiency enhancement as compared to the parent molecule. This effect seems to arise from the blocking of spurious current flow and a more efficient charge injection into the active layer. Compared to mixtures of luminophore and ionic liquid, the covalent attachment presents the advantage of film preparation, ensuring the fixed luminophore-to-ionic liquid ratio. Overall, our report illustrates the benefits of applying the concept of *ionophilicity* to OLED cells.

4. Experimental section

4.1. Synthesis of organic compounds

*4.1.1. Synthesis of 9,10-bis-(4-vinylphenyl)anthracene (**3**)*

9,10-Distyrylanthracene was prepared according to the method reported in the literature.[44,45] 9,10-Dibromoanthracene (6.04 g, 18 mmol), 4-vinylphenylboronic acid (7.98 g, 54 mmol), ground potassium carbonate (8.292 g, 108 mmol) and $Pd_2(dba)_3/Pd(P^tBu_3)_2$ (108.8:30.6 mg, 0.12:0.06 mmol, 1 mol Pd%) in dry toluene (300 ml) were stirred magnetically in a pre-heated oil bath at 110 °C for 48 h under nitrogen atmosphere. After this time, the suspension was filtered while hot under vacuum and the solvent was evaporated under vacuum, allowing a further evaporation to remove any styrene formed. The crude was submitted to partition in CH_2Cl_2/water, the organic phase was collected, dried and CH_2Cl_2 evaporated under reduced pressure to obtain a bright yellow solid (6.28 g, 16.4 mmol, 91%). IR (KBr) ν (cm^{-1}): 1668, 1627, 1508, 1438, 1392, 1110, 1029, 991, 941, 908, 875, 829; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.75 (4H, dd, J=4 Hz, 7 Hz), 7.65 (4H, d, J=8 Hz), 7.45 (4H, d, J=8 Hz), 7.30 (4H, dd, J=4 Hz, 7 Hz), 6.90 (2H, dd, J=11 Hz, 18 Hz), 5.90 (2H, d, J=18 Hz), 5.40 (2H, d, J=11 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 136.7 (2C), 134.9, 134.8, 129.7, 128.0, 125.1, 124.4, 123.2, 112.3. MS: m/z 382.

*4.1.2. 9,10-Bis(4-(2-(3-chloropropylthio)ethyl)phenyl)anthracene (**4**)*

3-Chloropropanethiol (51 µl, 0.523 mmol) was added to a solution of 9,10-distyrylanthracene (**3**) (100 mg, 0.262 mmol) and AIBN (10 mg) in dry toluene (5 ml). The solution was exhaustively degassed for 30 min before heating at 110 °C for 24 h. The reaction mixture was stirred magnetically while heated. After the required time, the solvent was removed in vacuum and 9,10-bis(4-(2-(3-chloropropylthio)ethyl)phenyl)anthracene (**4**) (98 mg, 95%) was obtained as a yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=7.85–7.30 (m, 16H; arom. H), 3.73 (t, J=6.3 Hz, 2×2H; CH_2–Cl), 3.11 (t, J=8.1 Hz, 2×2H; $ArCH_2CH_2$–S), 2.99 (t, J=8.1 Hz, 2×2H; $ClCH_2CH_2CH_2$–S), 2.81 (t, J=6.9 Hz, 2×2H; Ar–CH_2–CH_2), 2.14 (q, J=6.3 Hz, 2×2H; CH_2–CH_2–CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm)=139.97, 137.36, 137.19, 132.11, 130.18, 128.69, 127.28, 125.86, 43.64, 36.60, 33.87, 32.86, 29.63; IR (KBr): ν (cm^{-1})=3043, 2932, 2850, 2232, 1699, 1603, 1514, 1440, 1392, 1306, 1270, 1207, 1101, 1021, 998, 890, 769, 673, 539. ESI-MS: Calcd for $C_{36}H_{36}Cl_2S_2$ $(MH)^+$ 603, found m/z 610 $(MH-Li)^+$.

*4.1.3. 9,10-Bis[4-(2-(3-(N-1,2-dimethylimidazoliumyl)propylthio)-ethyl)phenyl]anthracene bischloride (**6**)*

A solution of 9,10-bis[4-(2-(3-chloropropylthio)ethyl)phenyl]-anthracene (**4**) (80 mg, 0.133 mmol) and 1,2-dimethylimidazole (**5**) (24 µl, 0.266 mmol) in dry toluene (5 ml) was heated at reflux temperature under Ar atmosphere for 48 h. After removal of the solvent, diethyl ether was added and the evolved solid filtered to obtain 9,10-bis(4-(2-(3-(*N*-1,2-dimethylimidazoliumyl)propylthio)ethyl)phenyl)anthracene bischloride (**6**) (95 mg, 93.1%) as a brown material. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=7.80–7.35 (m, 16H; arom. H), 6.96+6.84 (s+s, 1+1H, $-CH{=}CH-$), 3.68 (t, J=6.3 Hz, 2×2H; N–CH_2), 3.61 (s, 3H, N–CH_3), 3.11 (t, J=7.9 Hz, 2×2H; CH_2–S), 2.97 (t, J=7.2 Hz, 2×2H; S–CH_2), 2.82 (t, J=6.0 Hz, 2×2H; Ar–CH_2–CH_2), 2.45 (s, 3H, C–CH_3), 2.19 (q, J=6.1 Hz, 2×2H; CH_2–CH_2–CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm)=133.92, 131.41, 129.83, 128.55, 126.88, 125.91, 124.89, 120.34, 53.95, 49.23, 43.48, 36.19, 32.17, 29.61, 29.21, 26.71; IR (KBr): ν (cm^{-1})=3045, 2939, 2864, 2232, 1716, 1684, 1606, 1513, 1441, 1399, 1310, 1263, 1098, 1025, 941, 813, 771, 670, 544. ESI-MS: Calcd for $C_{46}H_{56}N_4S_2^{2+}$ $(M+H)^{2+}$ 364.1, found m/z 413 $(MH+AcO^-+HCO_2^-)^{2+}$.

*4.1.4. 9,10-Bis(4-(2-(3-(N-1,2-dimethylimidazolyl)propylthio)-ethyl)phenyl)anthracene bishexafluorophosphate **7***

A saturated aqueous solution of ammonium hexafluorophosphate was mixed with 9,10-bis(4-(2-(3-(*N*-1,2-dimethylimidazoliumyl)propylthio)ethyl)phenyl)anthracene bischloride (**6**) (90 mg, 0.117 mmol) by ultrasonication for 12 h until appearance of an orange solid corresponding to 9,10-bis(4-(2-(3-(*N*-1,2-dimethylimidazolyl)propylthio)ethyl)phenyl)anthracene bishexafluorophosphate (**7**) (110 mg, >95%). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=7.80–7.3 (m, 16H; arom. H), 7.20+6.95 (s+s, 1+1H, $-CH{=}CH-$), 3.74 (s, 3H, N–CH_3), 3.64 (t, J=6.3 Hz, 2×2H; N–CH_2), 3.13 (t, J=7.4 Hz, 2×2H; S–CH_2), 2.93 (t, J=7.2 Hz, 2×2H; CH_2–S), 2.81 (t, J=6.9 Hz, 2×2H; Ar–CH_2–CH_2), 2.74 (s, 3H, C=(N)C–CH_3), 2.13 (q, J=6.3 Hz, 2×2H; CH_2–CH_2–CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm)=132.09, 131.72, 130.17, 128.93, 128.85, 127.25, 125.35, 125.28, 54.32, 49.78, 43.86, 34.03, 31.79, 29.60, 27.10, 26.15; IR (KBr): ν (cm^{-1})=3046, 2944, 2862, 2238, 1689, 1604, 1512, 1446, 1408, 1393, 1313, 1263, 1023, 913, 843, 815, 770, 740, 670, 644, 549. ESI-MS: Calcd for $C_{46}H_{56}N_4S_2^+$, 724.9, found 759 (100) $(MH+Cl^-)$, 761 (33) $(MH+Cl^-)^+$; ESI-MS/MS for the $(MH+Cl)^+$ peak m/z: 759 $(MH+Cl)^+$, 661 $(MH+Cl^- - C_5H_{10}N_2^\bullet)^+$, 563 $(MH+Cl^- - 2\times C_5H_{10}N_2^\bullet)^+$.

4.2. Preparation of light emitting cells

Commercial ITO transparent electrode (OC50 on 175 µm polyester, 40–60 Ω/sqr, 85% transmittance) was rinsed with Alcanox® then with MilliQ water, dried and submitted to deep UV irradiation for 15 min. Recently clean ITOs were spin coated with an aqueous solution of PEDOT–PSS {Aldrich, poly(styrenesulfonate)/poly(2,3-dihydrothieno[3,4-*b*]-1,4-dioxin), 1,3 wt % dispersion in water} at 2000 rpm. After drying the film in a laminar flux hood, the electrode was submitted again to spin coating with a CH_2Cl_2 solution of DPA (2.5 mg/ml), *ionophilic* compound **7** (7.5 mg/ml) or a mixture of DPA and 1,2-dimethyl-3-(3-mercaptopropyl)imidazolium (DMPIM) hexafluorophosphate (2.5:4.8 mg/ml, respectively, in a 1:1 AcN/CH_2Cl_2 solution). The speed of the spin coater was adjusted between 1500 and 2500 rpm. After drying, the concentration of anthracene units was determined by transmission optical spectroscopy of the transparent electrode using a Cary 5 Varian SG spectrophotometer. Finally, the counter electrode was deposited by subliming aluminum in a chemical vapor deposition chamber (Edwards) operating at 10^{-6} mbar.

4.3. Electroluminescent measurements

The OLED cells were electrically connected to a potentiostat (Microbeam) by using colloidal silver and clamps. The cell was placed on a modified spectrofluorimeter (Photon Technology International, LPS-220B) that allows recording the emission spectra of the cell at constant DC voltage. The software controls the data acquisition and has data storage capability.

Electrical conductivity measurements were performed in a homemade system. Basically the measurement system contains an acquisition card from National Instruments, model NI6014, and an electronic system formed by the following components: a voltage-to-current converter from Burr-Brown (XTR110) and a voltage attenuator based on INA146 from Texas Instruments. The virtual acquisition system was developed on LabView 6.1, also from National Instruments. Using this program, a voltage ramp was generated with the acquisition card; this voltage is converted to current with the voltage-to-current converter that was applied to the cell. The voltage developed by the cell is then registered.

Acknowledgements

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