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1. Introduction

Organic light-emitting diodes (OLEDs) have been showing major industrial and salable progress in the field of organic electronics, especially in small and more recently even large area flat panel displays.^{1–3} OLED displays have superior mechanical flexibility, and can be applied in the fabrication of flexible or curved electronics. The main advantage over more established liquid crystal displays (LCDs) is that OLEDs are electrolumines-cent devices and hence do not require backlight illumination, leading to better contrast and higher power efficiency. Polymer semiconductors have been extensively studied as host materials in fluorescent multilayered OLEDs. However, polymers face major drawbacks such as batch-to-batch molecular weight variation,

A new cross-linkable 9,10-diphenylanthracene derivative as a wide bandgap host for solution-processed organic light-emitting diodes†

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Efficient organic light-emitting diodes (OLEDs) can be obtained using multilayered architectures where the processes of charge injection, transport and recombination are separated and optimized in each layer. Processing these structures from solution requires strategies to avoid redissolution or damage of the previously deposited layers. Several reports have demonstrated the development of cross-linkable hole transport materials, while less literature describes the synthesis and applications of such wide bandgap host materials for multilayered OLEDs. In this work we introduce a cross-linkable derivative of 9-(4-(10-phenylanthracene-9-yl)phenyl)-9H-carbazole incorporating styrene moieties (SPhPC) which can be efficiently cross-linked *via* radical polymerization. We present the synthesis and characterization of SPhPC, as well as its application as the host in the light-emitting layer to prove the concept of solution processed blue OLEDs.

> polydispersity, and limited purity. This leads to poor performance reproducibility, and makes industrial scale polymer OLED manufacturing more challenging. In contrast, organic small molecular weight compounds (small molecules) have a precise molecular weight, and can be purified to a high degree via recrystallization or sublimation. In commercial OLEDs, thin films of small molecules are sequentially deposited using thermal vacuum methods leading to high efficiency multi-layer devices.⁴ However, vacuum deposition can alter the morphology of the organic films, as molecules from one layer can diffuse into another one during the process as a result of the high temperatures applied during the use of this technique. In addition, vacuum deposition is a time-consuming and relatively expensive method that at the moment makes OLEDs not compatible with the lighting market. Solution processing can be a valid alternative to vacuum techniques since it meets the requirements of fast, large area and potentially inexpensive manufacturing.5-9 However, the use of solution deposition methods can be very challenging in the fabrication of a multilayered device. The main issue is the similar solubility of many organic semiconductors, implying that a pre-deposited layer can partially be dissolved while processing another layer on top. The use of orthogonal solvents can alleviate this problem;^{10,11} nonetheless, this approach is very challenging as most of the organic semiconductors present very similar polarity, and the library of materials and molecules that are suited for this method are very limited. An alternative

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approach which has been investigated for multilayer solution processing of OLEDs is the introduction of cross-linkable functional groups that helps insolubilizing the organic materials after being deposited using thermal, chemical or light treatments.^{12,13} Several reports have demonstrated the development of cross-linkable hole transport materials (HTMs), such as arylamine-based compounds,14-20 while less literature describes the synthesis and applications of wide bandgap host materials for multilayered OLEDs.²¹⁻²³ In this work we present a crosslinkable derivative of 9-(4-(10-phenylanthracene-9-yl)phenyl)-9Hcarbazole (PhPC). PhPC has been studied previously both as a deep blue emitter (a deep-blue emission maximum at 436 nm)²⁴ and as a host for triplet-triplet annihilation (TTA) OLEDs, in view of its low triplet level (1.74 eV).²⁵ TTA is a mechanism where the otherwise non-radiative triplet states in a fluorescent material can be harvested to generate singlet excitons, substantially contributing to the electroluminescence efficiency.²⁶⁻²⁹ Incorporating styrene moieties into PhPC converts the molecule into an organic semiconductor (SPhPC) which can be efficiently cross-linked via radical polymerization without any major alteration to the molecule energy levels.³⁰ In this paper we report the synthesis and use of SPhPC as a cross-linkable host material for all solution processed fluorescent blue OLEDs.

2. Experimental section

Synthesis of PhPC

The functionalization of PhPC was achieved following the synthetic procedure depicted in Scheme 1. 9-Bromoanthracene was reacted with *n*-phenylcarbazole boronic acid *via* Suzuki coupling to yield 46% of molecule 3, which was brominated using *N*-bromosuccinimide (NBS) to produce 91% of molecule 4. Finally molecule 4 was reacted with 4-vinylphenylboronic acid through Suzuki coupling to generate 51% of the target product, SPhPC.

9-Bromoanthracene (1): in a 500 mL round bottom flask equipped with a stir bar, anthracene (6.00 g, 33.7 mmol, 1 eq.) was dissolved in 300 mL of $CHCl_3$. $CuBr_2$ (15.1 g, 67.4 mmol, 2 eq.) was added to the solution, and the reaction was stirred overnight under reflux conditions. The reaction was filtered over celite and the solution was concentrated under reduced pressure.

The green crude solid was purified *via* chromatography using hexane as an eluent to yield 8.1 g of light green crystalline materials (94%). The structure of compound 2 was characterized by various spectroscopic methods (spectra not showed) including ¹H NMR (400 MHz), UV-vis and mass spectrometry (EIMS *m*/z 257). All spectroscopic results agree with the reported properties.³¹

4-Carbazolyl-1-bromophenylboronic acid (2) was prepared following a literature procedure. 32

9-(4-(Anthracen-9-yl)phenyl)-9H-carbazole (3): in a 100 mL round-bottom flask equipped with a stir bar and a condenser, 1 (1.24 g, 4.76 mmol, 1 eq.) and 2 (1.79 g, 6.21 mmol, 1.3 eq.) were dissolved in 46 mL of dry toluene. K₂CO₃ was dissolved in 4 mL of water (5.14 g, 36.5 mmol, 10 eq.), and was added along with 6 mL of ethanol. The mixture was purged for 30 minutes with nitrogen, and $Pd(PPh_3)_4$ (215 mg, 0.186 mmol, 0.05 eq.) was added before the reaction was brought to reflux and left stirring overnight. The reaction was cooled down to room temperature, and extracted using toluene. The organic phase was dried with MgSO₄ and concentrated under vacuum. The crude solid was purified via chromatography using hexane as an eluent to get rid of starting materials, followed by 4:1 hexane: dichloromethane (DCM) to obtain a white solid powder (46%). ¹H NMR (500 MHz, CDCl₃, δ): 8.57 (s; 1H), 8.21 (d; *J* = 7.72 Hz; 2H), 8.10 (d; 8.46 Hz; 2H), 7.82 (m; 4H), 7.68 (m; 4H), 7.51 (m; 4H), 7.46 (m; 2H), 7.36 (m; 2H). ¹³C NMR (125 MHz, CDCl₃, δ): 140.9, 137.9, 137.05, 135.9, 132.8, 131.4, 130.3, 128.5, 127, 126.9, 126.6, 126, 125.7, 125.2, 123.5, 120.4, 120.1, 109.9. MALDI-TOF MS (m/z): 419.12 [M]⁺.

3,6-Dibromo-9-(4-(10-bromoanthracen-9-yl)phenyl)-9*H*-carbazole (4): in a flame dried 500 mL round bottom flask equipped with a stir bar, 3 (400 mg, 0.957 mmol, 1 eq.) was dissolved in 100 mL of dry dimethylformamide (DMF) and 100 mL of DCM. The flask was covered with aluminum foil and cooled down to 0 °C, then NBS (511 mg, 2.87 mmol, 3 eq.) was added and the reaction was left stirring for 30 minutes at 0 °C and then for 3 hours at room temperature. The reaction mixture was quenched using water and extracted using DCM. The organic phase was washed 5 times with water, dried using MgSO₄, and concentrated under vacuum to yield 572 mg of white-yellow crystalline material (91%). ¹H NMR (500 MHz, CDCl₃, δ): 8.66 (d; 8.85 Hz; 2H), 8.25 (d; 1.84 Hz; 2H), 7.74 (m; 4H), 7.65 (m; 4H), 7.60 (d; 1.92 Hz; 1H),



Scheme 1 Reaction scheme for the synthesis of SPhPC.

7.59 (d; 1.90 Hz; 1H), 7.50 (m; 4H). ¹³C NMR (125 MHz, CDCl₃, δ): 139.8, 138.3, 136.4, 136.2, 132.9, 132.7, 131.0, 130.3, 129.5, 128.1, 127.1, 126.9, 126.7, 126, 124.1, 123.3, 113.3, 111.6. MALDI-TOF MS (*m*/*z*): 655.5 [M]⁺.

3,6-Bis(4-vinylphenyl)-9-(4-(10-(4-vinylphenyl)anthracen-9-yl)phenyl)-9H-carbazole (SPhPC): in a 50 mL RBF equipped with a stir bar and a condenser K₃PO₄ was dissolved slowly in 4 mL of water (3.6 g, 16.98 mmol, 52 eq.). 4 (0.214 g, 0.325 mmol, 1 eq.) was dissolved in 10 mL of dry toluene and added to the solution along with 4-vinylphenylboronic acid (0.241 g, 1.63 mmol, 5 eq.), (o-tolyl)phosphine (45 mg, 0.18 mmol, 0.3 eq.), and 2 drops of aliquat. The reaction mixture was purged for 25 minutes then $Pd_2(dba)_3$ (45 mg, 0.061 mmol, 0.15 eq.) was added and the reaction was brought to 110 °C and left reacting overnight. The reaction was cooled down and extracted with DCM. The organic phase was dried using MgSO₄, concentrated under high vacuum for 15 minutes. The crude solid was purified via chromatography using 3:1 hexane: DCM as an eluent to obtain 118 mg (51%) of a white yellow powder. ¹H NMR (500 MHz, CDCl₃, δ): 8.5 (s; 2H), 7.75 (m; 20H), 7.51 (m; 13H), 6.95 (dd; J = 17.64, 10.95 Hz; 1H), 6.83 (dd; J = 10.81, 6.77 Hz; 2H), 5.97 (d; J = 17.69 Hz; 1H), 5.86 (d; J = 17.7 Hz; 2H), 5.42 (d; J = 11.2 Hz; 1H), 5.32 (d; J = 11.02 Hz; 2H). ¹³C NMR (125 MHz, CDCl₃, δ): 141.3, 140.8, 138.5, 138.4, 136.9, 136.6, 136.5, 136, 135.9, 133.3, 132.9, 131.5, 130, 129.9, 127.4, 127.3, 127.1, 126.7, 126.3, 125.6, 125.4, 125.2, 124.2, 118.8, 114.2, 113.6, 113.5, 110.4: MALDI-TOF MS (m/z): 725.89 $[M]^+$; HRMS: calc. for C₅₆H₃₉N: 725.30825. Found: 725.30695.

Synthesis of F1

The **F1** emitter was synthesized as previously reported in two one-pot steps.³³ Lithium halogen exchange of 2-bromobiphenyl and nucleophilic reactions with 3-bromobenzophenone at low temperature followed by acid-mediated spirocyclization yielded compound 5 in good yield. Submitting this spirocyclic bromide to sequential Pd catalyzed Buchwald–Hartwig C–N coupling reactions afforded the **F1** emitter in a modest yield after several purification steps (Scheme 2).

Spiro compound (5): a flame dried flask was charged with a stirring bar and 2-bromobiphenyl (0.25 g, 1.07 mmol, 1 eq.). After dissolving the white solid in THF (10 mL), the solution

was cooled to -78 °C. Then, *n*-butyl lithium (2.5 M in 2-MeTHF, 0.49 mL, 1.07 mmol, 1 eq.) was added dropwise and the solution was allowed to stir at -78 °C. After 4 h, 3-bromobenzophenone (0.22 g, 0.86 mmol, 0.83 eq.) was added in one solid portion and let stir at -78 °C. After 30 min, the reaction was allowed to warm at rt under stirring and the reaction was monitored via ¹H NMR spectroscopy. After 30 min, the reaction mixture was guenched using MeOH and concentrated on a rotary evaporator. Then, acetic acid (glacial, 20 mL) and HCl (5 mL) were added to the crude product and the mixture warmed to reflux. After 24 h, the reaction mixture was cooled to rt and 10 mL water was added. The precipitate was filtered and dried to yield 0.262 g (88%) of a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 7.3 Hz, 2H), 7.42–7.26 (m, 5H), 7.32-7.26 (m, 4H), 7.25-7.20 (m, 3H), 7.19 (m, 2H), 7.15-7.05 (m, 2H). HRMS: calc. for C₂₅H₁₇Br: 396.0508. Found: 396.0508.

F1: spiro compound 5 (0.262 g, 0.66 mmol, 1 eq.) was dissolved in dry toluene (3 mL). Then, KOtBu (0.22 g, 1.99 mmol, 3 eq.) was added under N₂, followed by Pd₂dba₃ (0.027 g, 0.029 mmol, 0.12 eq.) and PtBu3 (1 M in Tol, 0.016 mL, 0.016 mmol, 0.055 eq.). Finally, m-toluidine (0.072 mL, 0.67 mmol, 1.02 eq.) was added using a syringe and the solution was warmed at 80 °C under stirring and monitored via ¹H NMR spectroscopy. After 2 h, the reaction mixture was cooled to rt and passed through a SiO₂ plug using dichloromethane. It was dried and the solution was added into a flask. Atmospheric air was pump cycled three times, and then dissolved in toluene (3 mL). Then, KOtBu (0.22 g, 1.99 mmol, 3 eq.) was added under an N₂ atmosphere followed by Pd₂dba₃ (0.027 g, 0.029 mmol, 0.12 eq.) and PtBu₃ (1 M in Tol, 0.016 mL, 0.016 mmol, 0.055 eq.). Finally, 1,6-dibromopyrene (0.12 g, 0.33 mmol, 0.5 eq.) was added in one portion, warmed to 80 °C under stirring and monitored via ¹H NMR spectroscopy. After 20 h, it was cooled to rt and passed through a SiO₂ plug using dichloromethane. The solid was dissolved in minimal dichloromethane and hexanes were added to precipitate an orange solid. The solid was washed using boiled hexanes (3 \times 20 mL), then the solid was dissolved in minimal dichloromethane, ~ 1 mL hexane was added, and the solution was concentrated on a rotary evaporator until precipitates just started to form. This suspension was stored in a -15 °C freezer for 72 h, and dried to yield 0.062 g,



Scheme 2 Reaction scheme for the synthesis of F1.

0.006 mmol (a 10% yield over two steps) of an amber colored solid. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.8 Hz, 3H), 7.87 (d, *J* = 9.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 3H), 7.20 (m, 8H), 7.1–6.95 (m, 16H), 6.93 (s, 2H), 6.82 (t, *J* = 7.7 Hz, 4H), 6.74 (d, *J* = 7.6 Hz, 2H), 6.68 (d, *J* = 7.7 Hz, 2H), 2.23 (s, 6H). ¹³C NMR (400 MHz, CDCl₃) δ 151.23, 148.60, 147.07, 146.08, 141.33, 140.31, 139.17, 129.65, 129.12, 128.41, 128.34, 128.15, 127.79, 127.72, 127.57, 126.85, 126.71, 126.30, 123.55, 123.00, 122.89, 122.58, 121.46, 120.59, 120.26, 119.32, 65.64, 21.87. HRMS: calc. for C₈₂H₅₉: 1044.443. Found: 1044.445.

Material characterization and device fabrication

Solutions of all materials were prepared in a nitrogen filled glove box, where the corresponding organic thin-films were spin-coated and annealed. Prior to deposition, all solutions were filtered using a 0.22 µm pore size filter. Optical absorption spectra were collected in transmission mode using an optical fiber system manufactured by Avantes. Photoluminescence spectra and quantum yields in thin films were recorded in an integrating sphere using a Hamamatsu absolute quantum yield C9920 spectrometer. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, CLEVIOS[™] P VP CH 8000) was purchased from Heraeus. The photolithography-patterned indium tin oxide (ITO) glass substrates were purchased from Naranjo Substrates (www.naranjosubstrates.com). The substrates were subsequently cleaned using soap, deionized water, and isopropanol in an ultrasonic bath for 5 minutes each, followed by 20 minutes of UV-ozone treatment. Onto the clean ITO substrates, a 45 nm thick film of PEDOT:PSS was spin-coated at 2500 rpm for 1 minute. The PEDOT:PSS dispersion was filtered using a 0.45 µm pore size filter. The layers were dried at 150 °C for 15 minutes. On top of that, the hole transport layer and the emissive layers were subsequently spin-coated upon cross-linking, as described below. The emissive layer was then coated using an electron transport layer (ETL), 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB). TmPyPB was either solution processed by spin-coating or sublimed in a high vacuum chamber. The devices were finished with a low work function cathode (5 nm thick Ba capped with 100 nm thick Ag). The thicknesses of all films were determined using an Ambios XP1 profilometer. Devices were not encapsulated and were characterized in a glove box. Current density and luminance versus voltage were collected using a Keithley 2400 source meter and a photodiode coupled to a Keithley 6485 pico-amperometer, using a Minolta LS100 instrument to calibrate the photocurrent. An Avantes luminance spectrometer was used to measure the electroluminescence spectra.

3. Results and discussion

Thin-films of SPHPC doped with 5 wt% of the blue fluorescent molecule **F1** (Fig. 1) were deposited *via* spin-casting from toluene solutions onto PEDOT:PSS-coated substrates. **F1** was initially chosen as it can be used in combination with the PhPC type host for efficient TTA OLEDs.^{25,34} At first we attempted to cross-link the film by simple thermal treatment at different



Fig. 1 Chemical structures of the compounds used in the emissive layers for solution-processed OLEDs.

temperatures and for different times, measuring the optical absorption before and after rinsing with toluene. We observed that after annealing at temperatures as high as 180 °C for a prolonged time (1 hour), the absorbance of the layer diminishes after the first rinsing step (Fig. S1, ESI†) and then stabilizes for subsequent toluene rinsing cycles. This implies that the film is only partially cross-linked under the annealing conditions used. Hence, we attempted to quantitatively cross-link the films by means of thiol–ene polymerization, adding pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, 1.5 wt%) and 2,2'-azobis(2-methylpropionitrile) (AIBN, 2 wt%), whose chemical structures are shown in Fig. 2. PETMP allows the formation of a hyper-branched polymer network, in the presence of the radical photoinitiator AIBN.³⁵

SPHPC films containing F1 (5 wt%), PETMP (1.5 wt%) and AIBN (2 wt%) were exposed to UV light for 10 minutes and then annealed at 150 °C for 30 minutes. After this treatment the layer becomes completely resistant to toluene, as the optical absorption of the films is now unvaried (Fig. 3a). We used PETMP (1.5 wt%) and AIBN (2 wt%) at these concentrations as they were found to be the lowest still allowing for quantitative crosslinking. We also measured the photoluminescence (PL) and its quantum yield (PLQY) for the same layers, before and after rinsing twice with toluene (Fig. 3b). Under excitation at 310 nm, we observe a narrow PL signal with a maximum at 470 nm, and an associated PLQY of 47% and 50% for the sample before and after toluene dripping, respectively. The differences in the intensity and quantum yield of the PL spectra are within the sample-to-sample variation and can therefore be neglected. These results confirm a quantitative cross-linking of the active materials in the presence of PETMP and AIBN, without compromising its optical properties.

The cross-linked SPhPC films were tested as the active material in solution-processed multi-layered OLEDs (Fig. 3a). PEDOT:PSS was used as the hole injection layer (HIL) to smooth

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Fig. 3 (a) Device structure with the corresponding (b) current density and (c) luminance *versus* applied voltage of OLEDs with a solution-processed or sublimed ETL. (d) Efficacy as a function of luminance for the same devices. The inset in (c) is the electroluminescence spectrum of a blue OLED with a solution-processed ETL. The corresponding color coordinates are reported in the CIE 1931 color space, see the inset of (d).

the indium tin oxide (ITO) electrode and enlarge its work function. The hole transport (electron blocking) layer used was KR386 (Fig. 2), as it can be solution processed and quantitatively cross-linked by a simple thermal treatment.³⁶ The emissive layer, consisting of SPhPC:**F1** (5 wt%):PETMP (1.5 wt%):AIBN (2 wt%), was spin-coated from toluene and cross-linked as described above. The emissive layer was then coated with TmPyPB and with a low work function cathode (5 nm thick Ba capped with 100 nm thick Ag). We compared the performance of hybrid devices where TmPyPB is thermally deposited in a vacuum chamber using fully solution processed OLEDs with a spin-coated TmPyPB film from toluene.

The current density *vs.* voltage curves (Fig. 3b) for the devices with sublimed or solution-processed ETLs show similar characteristics. We noticed a slightly lower current leakage for the solution-processed device, which might originate from the device planarization during spin-coating of the ETL. Current injection takes place at about 3 V reaching about 400 and 600 A m⁻² at 10 V, for the fully-solution processed and for the hybrid device, respectively. With our setup, the turn-on

voltage for electroluminescence was detected at 2.7 V for both types of devices (Fig. 3b). The light intensity was found to increase rapidly reaching a maximum of 623 cd m⁻² for the fully solution-processed OLED and 849 cd m⁻² for the one with the sublimed ETL. The electroluminescence spectrum of the devices results in CIE coordinates x = 0.19 and y = 0.30, corresponding to the sky blue zone of the CIE 1931 color space (Fig. 3d). We obtained a current efficiency (efficacy) of 2.18 cd A^{-1} and 2.15 cd A⁻¹, for the OLED with the sublimed ETL and for the fully solution-processed one, respectively (Fig. 3d). The essentially equal maximum efficacies validate SPHPC as a promising material for solution-processed multilayer organic devices. We do observe, however, a slightly lower efficiency at high luminance for the fully-solution processed devices, which can be attributed to unavoidable impurities introduced during solution preparation and film casting.

In order to further validate SPhPC as a suitable host for fluorescence blue emitters, we prepared fully solution-processed devices with the same structure and materials depicted in Fig. 3a, but using either 4,4'-bis(2,2-diphenylethenyl)-1,1'-biphenyl (DPVBI)³⁷ or 4-(di-*p*-tolylamino)-4'-[(di-*p*-tolylamino)-styryl]stilbene (DPAVB) (Fig. 1) as dopants. SPhPC films containing the blue emitter (5 wt%), PETMP (1.5 wt%) and AIBN (2 wt%) were spin-coated and cross-linked as described



Fig. 4 (a) Efficacy as a function of luminance for fully solution-processed devices using different blue emitters. (b) Electroluminescence spectrum of the same devices with (inset) corresponding color coordinates in the CIE 1931 color space.

above (UV light exposure for 10 minutes and annealing at 150 °C for 30 minutes). The PLQY was measured under excitation at 310 nm, and was found to be 85% for DPAVB and 61% for DPVBI (Fig. S2, ESI†). The corresponding OLEDs showed low leakage and current injection at about 3 V (Fig. S3a, ESI†). We noted that the current density at high bias (10 V) was rather low for these devices, about 22 A m⁻² and 100 A m⁻² for the OLEDs employing DPAVB and DPVBI, implying a very good charge selectivity at the hole and electron blocking interfaces, respectively (about 400 A m⁻² was obtained for devices with **F1**).

As a consequence of the very efficient charge selectivity a promising maximum current efficiency of $3.73 \text{ cd } \text{A}^{-1}$ was obtained for a blue emitting solution processed LED. The corresponding luminance (104 cd m⁻²) was modest as a consequence of the somewhat low current density. A slightly blue shifted electroluminescence was obtained using DPVBI (color coordinates 0.23, 0.32, Fig. 4b), even though the maximum efficacy was limited to 1.24 cd A⁻¹.

4. Conclusions

We present a cross-linkable wide bandgap host organic semiconductor (SPhPC), suitable for the preparation of solution processed multilayer OLEDs. The molecule is obtained by introducing styrene moieties at the periphery of the wide bandgap material 9-(4-(10-phenylanthracene-9-yl)phenyl)-9*H*-carbazole. Upon functionalization, SPhPC can be efficiently cross-linked *via* radicals or polymerization, in the presence of suitable activators. The optical properties of the film do not change upon this chemical reaction which demonstrates its usefulness for use in multilayered opto-electronic devices. As a proof of concept, a multilayered blue light emitting OLED was prepared showing excellent rectification and promising current efficiency.

Conflicts of interest

There are no conflicts to declare.

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