Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Material (ESI) for RSC Advances

RSC Advances

Effect of thiophene linker addition to Fluorene-benzotriazole polymers on the purpose of achieving white emission in OLEDs

Cansu Kok^{a,b}, Ceylan Doyranli^b, Betül Canımkurbey^{c,d},

Selin Pıravadılı Mucure*, Sermet Koyuncuf*

^a Department of Energy Resources and Management, Çanakkale Onsekiz Mart University, 17020 Çanakkale, Turkey

^b Department of Chemistry, Faculty of Arts and Sciences, Yıldız Technical University, 34220 Istanbul, Turkey

^c S. Şerefeddin Health Services Vocational School, Amasya University, 05100 Amasya, Turkey

^d Central Research Laboratory, Amasya University, 05100, Amasya, Turkey

^e Materials Institute, The Scientific and Technological Research Council of Turkey (TUBITAK), Marmara Research Center (MAM), 41470, Gebze/Kocaeli, Turkey

^f Department of Chemical Engineering, Faculty of Engineering, Canakkale Onsekiz Mart University, 17100 Canakkale, Turkey

Correspondence to: Selin Piravadili Mucur (e-mail: selin.piravadili@tubitak.gov.tr) and Sermet Koyuncu (e-mail:skoyuncu@comu.edu.tr)

General Information:

Synthetic route to TP2 and SP3 are presented in the Scheme-S1.



Scheme-S1. Synthetic route to SP3 and TP2

In the synthesis of SP3 and TP2, first, 2,2'-(9,9-diallyl-9,9a-dihydro-4H-fluorene-2,7diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was synthesized from the 9,9'-diallyl-2,7dibromofluorene by using clasic borylation reaction procedure in the literature ¹. Besides, 4,7dibromo-2-octyl-2H-1,2,3-benzotriazole and 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2-octyl-2H-1,2,3-benzotriazole were prepared like in the published procedure². Then this two benzotriazole based dibromo derivatives and 2,2'-(9,9-diallyl-9,9a-dihydro-4H-fluorene-2,7diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) were used for the synthesis of SP3 and TP2 by Suzuki polymerization process according to published procedure in our study ³. CHCl₃-d as solvent and TMS as internal standard were used to obtain ¹H-NMR (Bruker Avance DPX-

400) data. Gel permeation chromatography (GPC) was performed in THF relative to polystyrene standards (Scientific Polymer Products) on a system equipped with a threecolumn set (Polymer Laboratories 300 x 7.5 mm; 5 µm; pore sizes, 10⁻⁵, 10⁻⁴, and 10⁻³ Å) and a refractive-index detector (Agillent 1260) at room temperature with a flow rate of 1 mL min⁻¹. Electrochemical characterization was realized by CH Instruments 617D electrochemical workstation to obtain Cyclic voltammetry (CV) technique data. These measurements were carried out under argon atmosphere and the electrochemical cell includes an Ag wire as reference electrode (RE), Pt wire as counter electrode (CE) and glassy carbon (GCE) as working electrode (WE) in supporting electrolyte solution containing 0.1 M TBAPF₆ in acetonitrile. Polymer was drop-casted on the glassy carbon working electrode and then the potential was scanned in the monomer free electrolyte solution. HOMO and LUMO energy levels of SP3 and TP2 were calculated according to the inner reference ferrocene redox couple $E^{\circ}(Fc/Fc^{+})_{on} = +0.41$ V (vs. Ag wire) by using the equation $E_{HOMO/LUMO} =$ $e(E_{ox/red} - E_{Fc}) + (-4.8 \text{ eV})$. Onset values of oxidation/reduction potentials were taken into account while calculating HOMO energy levels. Analytic Jena Speedcord S-600 diode-array spectrophotometer were utilized for UV-Vis absorption spectra. The optical band gap (E_g) of products was calculated from their absorption edges by using this formula $E_g(eV)=1241/\lambda_{on}$.

Synthesis of SP3 and TP2 polymers.

In a 50 mL two neck round bottom flask, 2,2'-(9,9-diallyl-9,9a-dihydro-4H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.498 g, 1 mmol), 4,7-dibromo-2octyl-2H-1,2,3-benzotriazole or 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2-octyl-2H-1,2,3benzotriazole(1 mmol) were dissolved in 20 mL of Toluene-5 mL of 2.0 M K₂CO₃ solution, and the solution was purged with argon for 15 min. Pd(PPh₃)₄ (0.231 g, 0.2 mmol) was added

to the reaction mixture at room temperature under argon atmosphere. The mixture was stirred at 110 °C under argon for 24 hours. After 24h, bromo benzene (0,015 g, 0.10 mmol) was added to the mixture. After that 2 h, benzene boronic acid (0.012 g, 0.10 mmol) was added, and the mixture was further stirred for another 2 h to complete the end-capping reaction. The polymer was precipitated in methanol, and filtered polymer purified by using Soxhlet extraction with methanol, acetone, hexanes, and chloroform, respectively. The chloroform solution was concentrated under reduced pressure, precipitated in methanol (300 mL), filtered, washed with methanol, and dried under vacuum at 60 °C overnight to afford SP3 and TP2 polymers. (SP3: 0.38 g; yield 80%; TP2: 0.62 g; yield 76%)

For SP3: ¹*H*-*NMR* (*CHCl*₃-*d*, *ppm*): δ 8.20, 7.92, 7.77, 7.27 (8*H*, *C*-*H* aromatic); 5.63, 5.05, (6*H*, *C*-*H* allyl); 4.92 (2*H*, *N*-*CH*₂-); 2.89, 2.26, 1.56, 1.40, 1.24 (18*H*, -*CH*₂-); 0.92 (9*H*, *R*-*CH*₃). *GPC*: *Mn*=17200 g/mol, *Mw*= 82132 g/mol; *PDI* 4.78.

<u>For TP2</u>: ¹H-NMR (CHCl₃-d, ppm): δ 7.79, 7.73, 7.58, 7.52, 7.48 (10H, C-H aromatic); 5.41, 4.97, (6H, C-H allyl); 4.85 (2H, N-CH₂-); 2.79, 2.25, 1.42, 1.35 (36H, -CH₂-); 0.93 (9H, R-CH₃). GPC: Mn=17235 g/mol, Mw= 45988 g/mol; PDI 2.67.



Figure S1. ¹H-NMR spectrum of SP3 polymer



Figure S2. ¹H-NMR spectrum of TP2 polymer



Figure S3. GPC curve of SP3 polymer.



Figure S4. GPC curve of TP2 polymer.



Figure S5. Normalized photoluminescence spectra of a) SP3 and b) TP2 powder form (inlet showed the chromacity coordinates of SP3 and TP2)



Figure S6. EL Intensity-voltage Characteristics of a) SP3 and b)TP2 based OLEDs.

References

- 1. Y. W. Li, L. L. Xue, H. Li, Z. F. Li, B. Xu, S. P. Wen and W. J. Tian, *Macromolecules*, 2009, **42**, 4491-4499.
- 2. M. Karakus, A. Balan, D. Baran, L. Toppare and A. Cirpan, *Synthetic metals*, 2012, **162**, 79-84.
- 3. S. P. Mucur, C. Kok, H. Bilgili, B. Canimkurbey and S. Koyuncu, *Polymer*, 2018, **151**, 101-107.