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Supporting Information

Poly(para-phenyleneethynylene)s as Emitters in Polymer LEDs.

Emanuel Smarsly[a], Dominik Daume[b,c], Felix Braig[b,c], Silke Koser[a], Edgar Dörsam[b,c] and Uwe H.F. Bunz[a,c] *

a) Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 FRG.

b) Institute of Printing Science and Technology, Technische Universität Darmstadt, Magdalenenstraße 2, 64289 FRG.

c) InnovationLab GmbH (iL), Speyerer Straße 4, 69115 FRG.

Corresponding Author

* Uwe H. F. Bunz, Email: uwe.bunz@oci.uni-heidelberg.de

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General Experimental Details

All reactions requiring exclusion of oxygen and moisture were carried out in dry glassware under a dry and oxygen free nitrogen atmosphere. The addition of solvents or reagents was carried out using nitrogen flushed stainless steel cannulas and plastic syringes.

Flash column chromatography was carried out using silica gel S (32 µm-62 µm), purchased from Sigma Aldrich, according to G. Nill, unless otherwise stated.[1] As noted, Celite® 545, coarse, (Fluka) was used for filtration.

Gel Permeation Chromatography (GPC): Number- (M_n) and weight-average (M_w) molecular weights and polydispersities (PDI, M_w/M_n) were determined by GPC versus polystyrene standards. Measurements were carried out at room temperature in chloroform or THF with PSS-SDV columns (8.0 mm x 30.0 mm, 5 µm particles, 102-, 103- and 105- Å pore size) on a Jasco PU-2050 GPC unit equipped with a Jasco UV-2075 UV- and a Jasco RI-2031 RI-detector. Data processing was done using PSS WinGPC Unity software.

^{1}H NMR NMR spectra were recorded in $CDCl_3$ at room temperature on a Bruker DRX 300 (300 MHz), Bruker Avance III 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) or Bruker Avance III 600 (600 MHz) spectrometer. The data were interpreted in first order spectra. All spectra were recorded in $CDCl_3$. Chemical shifts are reported in δ units relative to the solvent residual peak ($CHCl_3$ in $CDCl_3$ at δ_H = 7.27 ppm) or TMS (δ_H = 0.00 ppm) due to Goldberg *et al.*.[2] The following abbreviations are used to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), quin (quintet), dd (doublet of doublet), br. s (broad signal) and m (multiplet). Coupling constants (*J*) are given in Hz and refer to H,H-couplings. All NMR spectra were integrated and processed using ACD/Spectrus Processor.

^{13}C NMR spectra were recorded at room temperature on the following spectrometers: Bruker DRX 300 (75 MHz), Bruker Avance III 300 (75 MHz), Bruker Avance III 400 (100 MHz), Bruker Avance III 500 (125 MHz) or Bruker Avance III 600 (150 MHz). The spectra were recorded in $CDCl_3$. Chemical shifts are reported in δ units relative to the solvent signal: $CDCl_3$ [δ_C = 77.00 ppm (central line of the triplet)] or TMS (δ_c = 0.00 ppm) due to Goldberg *et al.*.[**Error! Bookmark not defined.**] The following abbreviations are used to indicate the signal multiplicity: s = singlet (quaternary C atom), d = doublet (CH group), t = triplet (CH2 group), q = quartet (CH3 group), m = multiplet. The abbreviations s, d, t and q are theoretical multiplicities as they would occur in a 1H-coupled spectrum. However, the measurement was always 1H-decoupled, so that no coupling constants can be specified.

To identify the primary, secondary and tertiary carbon atoms, DEPT-135, HSQC and HMBC spectra were recorded. In addition, H, H-COSY spectra were recorded for new compounds.

High resolution mass spectra (HR-MS) were either recorded on the JEOL JMS-700 (EI^+, FAB^+), Bruker ApexQehybrid 9.4 T FT-ICR-MS (ESI^+, $DART^+$) or a Finnigan LCQ (ESI^+) mass spectrometer at the Organisch-Chemisches Institut der Universität Heidelberg.

Elemental Analyses were carried out at the Organisch-Chemisches Institut der Universität Heidelberg.

IR spectra were recorded on a JASCO FT/IR-4100. Substances were applied as a film, solid or in solution. Processing of data was done using the software JASCO Spectra Manager™ II.

UV/Vis spectra were recorded on a JASCO UV-VIS V-660 or JASCO UV-VIS V-670 and processed with the software JASCO Spectra Manager™ II. ASCII-files were exported and visualized by OriginPro 2018b (64 bit) b9.5.5.409 (Lehre)

Fluorescence spectra were recorded on a JASCO FP-6500. Rawa data was obtained with the software JASCO Spectra Manager™ 1.5 and processed using JASCO Spectra Manager™ II. ASCII-files were exported and visualized OriginPro 2018b (64 bit) b9.5.5.409 (Lehre).

Profilometry (thicknesses and rough profiles) of organic as well as inorganic layers were measured by a Bruker DekTak XT profilometer. A diamond tipped stylus with 2 µm tip was used for all measurements. To acquire the layer thickness a small incision with a sharp tip was made.

Chemical formulas were drawn with CamebridgeSoft ChemBioDraw® Ultra (Version 16.0.1.4 (77)) for Windows®.

Nomenclature of chemical compounds in the experimental part was determined with CamebridgeSoft ChemBioDraw® Ultra (Version 16.0.1.4 (77)) for Windows®.

Graphs were visualized with OriginPro 2018b (64 bit) b9.5.5.409 (Lehre) and processed using Adobe® Illustrator CS5 Version 15.0.2 for Windows® or PowerPoint® 2010 SP2.

General procedure for PPE polymerisations

All polymerisations were carried out in a nitrogen atmosphere. The diine and diiodide were presented in a 1:0.9 ratio in a flicker tube in a mixture of degassed toluene (3.33 mL/mmol) and degassed piperidine (2.92 mL/mmol minus 0.5 mL due to added volume of stock solution). Then the palladium pre-catalyst bis(triphenylphosphine)¬dichloro¬palladium(II) (1) (0.2 mol%) and the cocatalyst copper(I)iodide (0.4 mol%) were added. In order to achieve the highest possible accuracy, a catalyst stock solution was used. The palladium catalyst (2.0 mol%) and the copper (I) iodide (4.0 mol%) were dissolved in degassed piperidine (5 mL) in a separate Schlenk tube under a nitrogen atmosphere. Then 0.5 mL of this measurement solution was added to the dissolved monomers with a syringe. Polymerizations were stirred at 80 °C for 5 days, unless otherwise stated.

For processing, the reaction mixture was transferred to a single neck flask with toluene and stirred with hydrochloric acid (1M, approx. 100 mL/mmol) and toluene (approx. 100 mL/mmol) at 70-80 °C for at least 2 hours. After phase separation, this was repeated twice with water. The organic phase was constricted under reduced pressure at about 60 °C and the raw polymer was precipitated by dropping the most concentrated solution possible into methanol (min. 500 mL). This was followed by purification by means of Soxhlet extraction. Unless otherwise stated, this was carried out with each of the following solvents for 24 hours in the order indicated: 1. methanol, 2. acetone, 3. diethyl ether, 4. DCM, 5. chloroform and 6. toluene. The DCM, chloroform and toluene fractions were each constricted under reduced pressure. The concentrated fractions were each dripped in methanol to precipitate the corresponding polymer fractions. The polymers were filtered and dried under vacuum.

Syntheses of Compounds

Synthesis of Hexyloxy-PPE (1hex): 1,4-Bis(hexyloxy)-2,5-diiodobenzene (795.3 mg, 1.5 mmol) and 1,4-Bis(hexyloxy)-2,5-diethynylbenzene (489.7 mg, 1.5 mmol) were dissolved in toluene (V = 5.0 mL) and piperidine (V = 3.9 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (21.1 mg, 30.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$ and 11.4 mg, 60.0 µmol, 4.0 mol%, CuI in 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs a yellow-orange solid was obtained (990.3 mg, quant., 3.0 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.03 (s, 2H, H_{aryl}), 4.20-3.95 (m, 4H, -CH_2-O-), 1.92-1.78 (m, 4H, -CH_2-CH_2-O-), 1.61-1.48 (m, 4H, -CH_2-), 1.43-1.28 (m, 8H, -CH_2-), 0.95-0.83 (m, 6H, -CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.58 (s, 2C, -C_{aryl}-O), 117.41 (d, 2C, -C_{aryl}-H), 114.44 (s, 2C, C_{aryl}-C≡C-), 91.67 (s, 1C, -*C*≡*C*-), 91.52 (s, 1C, -*C*≡*C*-), 69.78 (t, 2C, -*C*H_2-O-), 31.63 (t, 2C, -*C*H_2-CH_2O-), 29.33 (t, 2C, -*C*H_2-), 25.69 (t, 2C, -*C*H_2-), 22.63 (t, 2C, -*C*H_2-), 14.00 (q, 2C, -*C*H_3) ppm. IR (neat): $\tilde{\nu}$ = 2925.48, 2857.02, 1535.06, 1510.95, 1465.63, 1426.10, 1384.64, 1273.75, 1209.15, 1125.26, 1026.91, 947.84, 899.63, 858.16, 763.67, 726.07, 464.76 cm^{-1}. GPC: M_n = 44351 gmol^{-1}, M_w = 110210 gmol^{-1}, PDI = 2.47, degree of polymerization P_n = 148. TGA-DSC: melting point with decomposition T = 275.0 °C.

Synthesis of Dodecyloxy-PPE (1dodec): 1,4-Bis(dodecyloxy)-2,5-diiodobenzene (1.4 g, 2.0 mmol) and 1,4-Bis(dodecyloxy)-2,5-diethynylbenzene (989.6 mg, 2.0 mmol) were dissolved in toluene (V = 6.6 mL) and piperidine (V = 5.3 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (28.1 mg, 40.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 15.2 mg, 80.0 µmol, 4.0 mol%, CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs an orange solid was obtained (1.86 g, 99%, 7.92 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.02 (s, 2H, H_{aryl}), 4.15-3.95 (m, 4H, -CH_2-O-), 1.95-1.85 (m, 4H, -CH_2-CH_2-O-), 1.60-1.17 (m, 40H, -CH_2-), 0.93-0.83 (m, 6H, -CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.54 (s, 2C, -C_{aryl}-O), 117.37 (d, 2C, -C_{aryl}-H), 114.40 (s, 2C, C_{aryl}-C≡C-), 91.64 (s, 2C, -*C*≡*C*-), 69.73 (t, 2C, -*C*H_2-O-), 31.93 (t, 2C, -*C*H_2-CH_2O-), 29.73-29.69 (t, 10C, -*C*H_2-), 29.50 (t, 2C, -*C*H_2-), 29.38 (t, 2C, -*C*H_2-), 26.04 (t, 2C, -*C*H_2-), 22.69 (t, 2C, -*C*H_2-), 14.09 (q, 2C, -*C*H_3) ppm. IR (neat): $\tilde{\nu}$ = 2953.21, 2919.22, 2849.79, 1737.07, 1533.85, 1514.57, 1467.80, 1455.75, 1428.99, 1388.26, 1377.89, 1278.33, 1214.21, 1073.43, 1045.23, 1031.25, 1015.34, 1003.04, 856.96, 720.28 cm^{-1}. GPC: M_n = 48000 gmol^{-1}, M_w = 81540 gmol^{-1}, PDI = 1.70, degree of polymerization P_n = 102. TGA-DSC: phase transition T = 97.7 °C, melting point T = 193.5 °C and decomposition T = 302.0 °C.

Synthesis of 1,4-Bis(octadecyloxy)-2,5-diiodobenzene: 1,4-Bis(octadecyloxy)-benzene (30.7 g, 50.0 mmol), iodine (22.8 g, 1.8 eq., 90.0 mmol) and potassium periodate (11.5 g, 1.0 eq., 50.0 mmol) were dissolved in glacial acetic acid (V = 300.0 mL). After adding sulfuric acid (1.5 mL) the reaction was stirred at 75 °C for 5 days. The reaction mixture was quenched on ice, washed with sodium sulfite, extracted with chloroform and dried over $MgSO_4$. The organic solvent was concentrated under reduced pressure. After recrystallization in toluene colorless needles were obtained (39.4 g, 45.5 mmol, 91%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.17 (s, 2H, H_{aryl}), 3.93 (t, 4H, J = 6.4 Hz, -CH_2-O), 1.84-1.75 (m, 4H, -CH_2-CH_2-O-), 1.54-1.44 (m, 4H, -CH_2-), 1.41-1.21 (m, 50H, -CH_2-), 0.88 (t, 6H, J = 6.8 Hz, -CH_3) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 153.09 (s, 2C, C_{aryl}-OR), 123.05 (d, 2C, C_{aryl}-H), 86.50 (s, 2C, C_{aryl}-I), 70.59 (t, 2C, -CH$_2$-O-), 32.09 (t, 2C, -CH$_2$-), 29.98-29.68 (m, 20C, -CH$_2$-), 29.52 (t, 2C, -CH$_2$-), 29.45 (t, 2C, -CH$_2$-), 29.33 (t, 2C, -CH$_2$-), 26.20 (t, 2C, -CH$_2$-), 22.85 (t, 2C, -CH$_2$-), 14.26 (q, 2C, -CH$_3$) ppm. IR (neat): $\tilde{\nu}$ = 2913.91, 2847.38, 1483.96, 1469.49, 1459.85, 1445.39, 1385.60, 1352.82, 1305.57, 1263.15, 1246.75, 1214.93, 1146.47, 1066.44, 1051.01, 1031.73, 1018.23, 997.02, 968.09, 938.20, 910.24, 871.67, 846.60, 811.88, 787.78, 766.57, 751.14, 735.71, 716.43, 619.04, 542.86, 510.08, 436.80 cm^{-1}. HRMS (FAB (+)): $C_{42}H_{76}I_2O_2$ (866.86 g/mol), $[C_{42}H_{76}I_2O_2]^+$ calcd: 866.3934 g/mol, found: 866.3921 g/mol, error - 0.3 mmu; $[C_{42}H_{76}IO_2+H]^{+\cdot}$ calcd: 740.4968 g/mol, found: 740.4940 g/mol, error - 2.8 mmu. Melting point: 81.5 °C.

Synthesis of Octadecyloxy-PPE (1odec): 1,4-Bis(octadecyloxy)-2,5-diiodobenzene (1.1 mg g, 1.2 mmol) and 1,4-Bis(octadecyloxy)-2,5-diethynylbenzene (795.7 g, 1.2 mmol) were dissolved in toluene (V = 4.0 mL) and piperidine (V = 3.0 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (16.8 mg, 24.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$ and 9.1 mg, 48.0 µmol, 4.0 mol%, CuI in 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for

5 days. Followed by the general work up for PPEs an orange solid was obtained (1.2 g, 77%, 1.9 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.01 (br s, 2H, *H*$_{\text{aryl}}$), 4.03 (br s, 4H, -C*H*$_2$-O), 1.85 (br s, 4H, -C*H*$_2$-CH$_2$-O-), 1.58-0.98 (m, 60H, -(C*H*$_2$)$_{16}$-), 0.88 (br s, 6H, -C*H*$_3$) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 153.75 (s, 2C, *C*$_{\text{aryl}}$-O), 117.56 (d, 2C, *C*$_{\text{aryl}}$-H), 114.63 (s, 2C, *C*$_{\text{aryl}}$-C≡C-), 91.79 (s, 2C, -*C*≡*C*-), 69.93 (t, 2C, -*C*H$_2$-O), 32.10 (t, 2C, -*C*H$_2$-CH$_2$-O), 30.10-29.46 (m, 24C, -(*C*H$_2$)$_{12}$-), 26.30-26.12 (m, 4C, -(*C*H$_2$)$_2$-), 22.85 (t, 2C, -*C*H$_2$-), 14.25 (q, 2C, -*C*H$_3$) ppm. IR (neat): $\tilde{\nu}$ = 2916.81, 2849.31, 1509.03, 1467.56, 1428.03, 1387.53, 1275.68, 1213.97, 1071.26, 1035.59, 856.24, 719.32 cm^{-1}.GPC: M_n = 51343, M_w = 166300, PDI = 3.23, degree of polymerization P_n = 81. TGA-DSC: melting point T = 100.7 °C and decomposition T = 298.6 °C.

Synthesis of Hexyl-PPE (2hex): 1,4-Dihexyl-2,5-diiodobenzene (1.7 g, 3.5 mmol) and 1,4-Dihexyl-2,5-diethynylbenzene (1.0 mg, 3.5 mmol) were dissolved in toluene (V = 11.7 mL) and piperidine (V = 9.7 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (49.1 mg, 70.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 26.7 mg, 140.0 µmol, 4.0 mol%, CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs a yellow solid was obtained (1.86 g, 99%, 7.92 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 2H, *H*$_{\text{aryl}}$), 2.86 (br s, 4H, -C*H*$_2$-C$_{\text{aryl}}$-), 1.74 (br s, 4H, -CH$_2$-C*H$_2$*-), 1.60-1.21 (m, 12H, -C*H*$_2$-), 0.93-0.86 (m, 6H, -C*H*$_3$) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 141.96 (s, 2C, -*C*$_{\text{aryl}}$-CH$_2$-), 132.45 (d, 2C, -*C*$_{\text{aryl}}$-H), 122.84 (s, 2C, *C*$_{\text{aryl}}$-C≡C-), 93.12 (s, 2C, -*C*≡*C*-), 34.22 (t, 2C, -*C*H$_2$-C$_{\text{aryl}}$-), 31.84 (t, 2C, -*C*H$_2$-CH$_2$-C$_{\text{aryl}}$-), 30.71 (t, 2C, -*C*H$_2$-), 29.31 (t, 2C, -*C*H$_2$-), 22.67 (t, 2C, -*C*H$_2$-), 14.08 (q, 2C, -*C*H$_3$) ppm. IR (neat): $\tilde{\boldsymbol{\nu}}$ = 2954.41, 2921.63, 2853.17, 1502.28, 1455.99, 1376.93, 1351.86, 1305.57, 1259.29, 1216.86, 1186.01, 1113.69, 893.84, 840.81, 789.71, 761.74, 723.18, 666.29, 550.58 cm^{-1}. GPC: M_n = 78280 gmol^{-1}, M_w = 238320 gmol^{-1}, PDI = 3.05, degree of polymerization P_n = 292. TGA-DSC: melting point T = 284.5 °C and decomposition T = 320.0 °C.

Synthesis of Dodecyl-PPE (2dodec): 1,4-Didodecyl-2,5-diiodobenzene (799.8 mg, 1.2 mmol) and 1,4-Didodecyl-2,5-diethynylbenzene (555.3 mg, 1.2 mmol) were dissolved in toluene (V = 4.0 mL) and piperidine (V = 3.0 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (16.8 mg, 24.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 9.1 mg, 48.0 µmol, 4.0 mol%, CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs a yellow solid was obtained (988.5 mg, 94%, 2.3 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38 (s, 2H, H_{aryl}), 3.10-2.60 (m, 4H, -CH_2-C_{aryl}-), 1.84-1.16 (m, 40H, -CH_2-), 0.88 (t, 6H, J = 6.8 Hz, -CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 142.11 (s, 2C, -C_{aryl}-CH_2-), 132.61 (d, 2C, -C_{aryl}-H), 123.09 (s, 2C, C_{aryl}-C≡C-), 93.35 (s, 2C, -*C*≡*C*-), 34.39 (t, 2C, -CH_2-C_{aryl}-), 32.11 (t, 2C, -CH_2-CH_2-C_{aryl}-), 30.93 (t, 2C, -CH_2-), 29.73-29.69 (t, 12C, -CH_2-), 29.55 (t, 2C, -CH_2-), 22.68 (t, 2C, -CH_2-), 14.08 (q, 2C, -CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2954.41, 2918.73, 2870.31, 1771.30, 1748.16, 1732.73, 1716.34, 1698.02, 1683.55, 1558.20, 1540.85, 1520.60, 1504.20, 1465.63, 1456.96, 1436.71, 1396.21, 1375.96, 1363.43, 1339.32, 1259.29, 891.92, 720.28, 506.22, 484.05, 473.44, 465.73, 457.05, 442.58, 430.05, 418.48, 405.94 cm^{-1}. GPC: M_n = 149920 $gmol^{-1}$, M_w = 456850 $gmol^{-1}$, PDI = 3.05, degree of polymerization P_n = 343. TGA-DSC: phase transition at 167.0 °C and decomposition T = 318.0 °C.

Synthesis of (*rac*)-Citronellyloxy-PPE (1racCtr): 1,4-Bis((3,7-dimethyloctyl)oxy)-2,5-diiodobenzene (777.0 mg, 1.2 mmol) and 1,4-Diethynyl-2,5-bis((3,7-dimethyloctyl)oxy)benzene (526.5 mg, 1.2 mmol) were dissolved in toluene (V = 4.0 mL) and piperidine (V = 3.0 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (16.8 mg, 24.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 9.1 mg, 48.0 µmol, 4.0 mol%, CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs an orange solid was obtained (909.3 mg, 91%, 2.2 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.02 (s, 2H, H_{aryl}), 4.07 (t, 4H, -O-CH_2-), 1.91-1.87 (m, 2H, -CH-), 1.76-1.68 (m, 4H, -O-CH_2-CH_2-), 1.53-1.45 (m, 4H, -CH-), 1.37-1.13 (m, 12H, -CH_2-), 0.99 (d, 6H, -CH_3), 0.85 (d, 12H, -CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.54 (s, 2C, -C_{aryl}-O), 117.22 (d, 2C, -C_{aryl}-H), 114.32 (s, 2C, C_{aryl}-C≡C-), 91.82 (s, 2C, -*C*≡*C*-), 68.21 (t, 2C, -CH_2-O-), 39.27 (t, 2C, -CH_2-), 37.36 (t, 2C, -CH_2-), 36.35 (t, 2C, -CH_2-CH_2-O), 30.12 (d, 2C, -*C*H-), 24.71 (t, 2C, -CH_2-), 24.55 (t, 2C, -*C*H-), 22.69 (q, 2C, -CH_3), 22.58 (q, 2C, -CH_3), 19.90 (q, 2C, -CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2951.52, 2924.52, 2867.63, 1509.99, 1465.63, 1423.21, 1381.75, 1273.75, 1209.15, 1046.19, 1017.27, 915.06, 862.03, 717.39 cm^{-1}. GPC: M_n = 38921 $gmol^{-1}$, M_w = 72782 $gmol^{-1}$, PDI = 1.87, degree of polymerization P_n = 94. TGA-DSC: melting point T = 150.9 °C and decomposition at T = 235.0 °C.

Synthesis of (*S*)-(*rac*)-Citronellyloxy-PPE (1SracCtr): 1,4-Bis(((*S*)-3,7-dimethyl-octyl)oxy)-2,5-diiodobenzene (777.0 mg, 1.2 mmol) and 1,4-Diethynyl-2,5-bis((3,7-dimethyloctyl)oxy)benzene (526.5 mg, 1.2 mmol) were dissolved in toluene (V = 4.0 mL) and piperidine (V = 3.0 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (16.8 mg, 24.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 9.1 mg, 48.0 µmol, 4.0 mol%, CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs an orange solid was obtained (475.3 mg, 48%, 1.15 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.02 (s, 4H, H_{aryl}), 4.07 (t, 8H, $-O-CH_2-$), 1.91-1.87 (m, 4H, -CH-), 1.76-1.68 (m, 8H, $-O-CH_2-CH_2-$), 1.53-1.45 (m, 4H, -CH-), 1.37-1.13 (m, 24H, H), 0.99 (d, 12H, $-CH_3$), 0.85 (d, 24H, $-CH_3$) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.54 (s, 4C, $-C_{aryl}-O$), 117.22 (d, 4C, $-C_{aryl}-H$), 114.53 (s, 4C, $C_{aryl}-C{\equiv}C-$), 91.82 (s, 4C, $-C{\equiv}C-$), 68.20 (t, 4C, $-CH_2-O-$), 39.27 (t, 4C, $-CH_2-$), 37.36 (t, 4C, $-CH_2-$), 36.35 (t, 4C, $-CH_2-CH_2-O$), 30.14 (d, 4C, -*C*H-), 24.73 (t, 4C, $-CH_2-$), 24.55 (t, 4C, -*C*H-), 22.68 (q, 4C, $-CH_3$), 22.61 (q, 4C, $-CH_3$), 19.90 (q, 4C, $-CH_3$) ppm. IR (neat): $\tilde{\nu}$ = 2951.52, 2923.56, 2867.63, 1509.99, 1465.63, 1422.24, 1381.75, 1272.79, 1208.18, 1045.23, 1016.30, 915.06, 862.03, 802.24, 716.43 cm^{-1}. GPC: M_n = 18022 $gmol^{-1}$, M_w = 32594 $gmol^{-1}$, PDI = 1.81, degree of polymerization P_n = 22. TGA-DSC: melting point T = 169.7 °C and decomposition at T = 289.1°C.

Synthesis of (*S*)-Citronellyloxy-PPE (1SCtr): 1,4-Bis(((*S*)-3,7-dimethyloctyl)oxy)-2,5-diiodobenzene (777.0 mg, 1.2 mmol) and 1,4-Diethynyl-2,5-bis(((*S*)-3,7-dimethyloctyl)oxy)benzene (526.5 mg, 1.2 mmol) were dissolved in toluene (V = 4.0 mL) and piperidine (V = 3.0 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (16.8 mg, 24.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 9.1 mg, 48.0 µmol, 4.0 mol%, CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs an orange solid was obtained (909.3 mg, 91%, 2.2 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.02 (s, 2H, H_{aryl}), 4.07 (t, 4H, $-O-CH_2-$), 1.91-1.87 (m, 2H, -CH-), 1.76-

1.68 (m, 4H, -O-CH_2-CH_2-), 1.53-1.45 (m, 2H, -CH-), 1.37-1.13 (m, 12H, H), 0.99 (d, 6H, -CH_3), 0.85 (d, 12H, -CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.54 (s, 2C, -C_{aryl}-O), 117.22 (d, 2C, -C_{aryl}-H), 114.32 (s, 2C, C_{aryl}-C≡C-), 91.82 (s, 2C, -*C*≡*C*-), 68.21 (t, 2C, -*C*H_2-O-), 39.27 (t, 2C, -*C*H_2-), 37.36 (t, 2C, -*C*H_2-), 36.35 (t, 2C, -*C*H_2-CH_2-O), 30.12 (d, 2C, -*C*H-), 24.71 (t, 2C, -*C*H_2-), 24.55 (t, 2C, -*C*H-), 22.69 (q, 2C, -*C*H_3), 22.58 (q, 2C, -*C*H_3), 19.90 (q, 2C, -*C*H_3) ppm. IR (neat): $\tilde{\nu}$ = 2951.52, 2924.52, 2867.63, 1510.95, 1466.60, 1423.21, 1381.75, 1263.15, 1209.15, 1095.37, 1044.26, 1017.27, 915.06, 862.03, 800.31, 717.39, 466.69 cm^{-1}. GPC: M_n = 41350 gmol^{-1}, M_w = 84150 gmol^{-1}, PDI = 2.04, degree of polymerization P_n = 100. TGA-DSC: Recrystallization T = 106.9 °C, melting point T = 172.0°C and decomposition at T = 282.0 °C.

Synthesis of 3,7,11-Trimethyldodecan-1-ol: 3,7,11-Trimethyldodec-2,6,10-trien-1-ol (50.0 g, 225 mmol), cesium carbonate (3.66 g, 11.25 mmol), palladium on carbon (10w%) (3.6 g, 3.38 mmol) were dissolved in abs. ethanol (V = 500 mL). Hydrogen (16.5 L, 3.0 eq., 775 mmol) was added via a hydration aperture overnight into the stirred reaction mixture. After purification through filtration over silica gel (eluent diethyl ether), drying over $MgSO_4$ and evaporation under reduced pressure a colorless oil (77%, 39.5 g, 173 mmol) was obtained. ^{1}H-NMR (250 MHz, $CDCl_3$), δ (ppm): = 3.74-3.58 (m, 2H, -C*H_2*-OH), 2.03 (s, 1H, -O*H*), 1.67-0.79 (m, 29H) ppm.

3,7,11-Trimethyldodecan-1-ol was synthesized according to literature.[3]

Synthesis of 1-Bromo-3,7,11-Trimethyldodecane: 3,7,11-Trimethyldodecan-1-ol (26.8 g, 117.2 mmol), triphenylphosphane (36.9 g, 1.2 eq., 141 mmol.) were dissolved in DCM (V = 164.0 mL). After cooling with an ice bath, N-Bromosuccinimide was added portion wise (25.0 g, 1.2 eq., 141 mmol). The reaction mixture was stirred for 2h at room temperature. After constraining under reduced pressure impurities were precipitated in hexane. After filtration over silica gel and removing solvents under reduced pressure a colorless oil (96%, 32.9 g, 112.9 mmol) were obtained. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.52-3.35 (m, 2H, -C*H_2*-Br), 1.95-0.81 (m, 29H) ppm.

1-Bromo-3,7,11-trimethyldodecane was synthesized according to literature.[4]

Synthesis of 1,4-Bis((3,7,11-trimethyldodecyl)oxy)-2,5-diiodobenzene: 1-Bromo-3,7,11-Trimethyldodecane (16.0 g, 2.2 eq., 52.5 mmol) was dissolved in butanone (V

=125 mL) and degassed with nitrogen for 45 min. After adding 2,5-diiodobenzen-1,4-diol (7) (9.1g, 25.0 mmol), potassium iodide (415.0 mg, 2.5 mmol) and potassium carbonate (34.6g, 10 eq., 250 mmol) the reaction mixture was stirred at 70 °C for 5 days. The crude product was washed with DCM and water. The organic phase was dried over $MgSO_4$ and the organic solvents were removed under reduced pressure. After column chromatography (SiO_2, PE, PE:EA (30:1)) a colorless oil (91 %, 17.8 g, 22.8 mmol) was obtained. ^1H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (s, 2H, H_{aryl}), 4.02-3.91 (m, 4H, -CH_2O-), 1.91-1.00 (m, 34H), 0.95 (d, 6H, J = 6.6 Hz, -CH_3), 0.86 (m, 18H, -CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.11 (s, 2C, C_{aryl}-O), 122.99 (d, 2C, C_{aryl}-H), 86.45 (s, 2C, C_{aryl}-I), 68.92 (t, 2C, -CH_2-O), 39.55 (t, 2C, -CH_2-), 37.75-37.25 (m, 6C, -CH_2-), 36.-36.27 (t, 2C, -CH_2-CH_2-O), 32.96 (d, 2C, -CH-), 29.96 (d, 2C, -CH-), 28.15 (d, 2C, -CH-), 25.04-24.92 (m, 2C, -CH_2-), 24.56 (t, 2C, -CH_2-), 22.89 (q, 2C, -CH_3), 22.79 (q, 2C, -CH_3), 19.97-19.81 (m, 4C, -CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2951.52, 2922.59, 2866.67, 1485.88, 1458.89, 1379.82, 1348.96, 1262.18, 1208.18, 1053.91, 1013.41, 979.66, 878.42, 850.45, 760.78, 734.75, 433.91 cm^{-1}. HRMS [DART$^+$] m/z: [M$^+$] calcd for $[C_{36}H_{64}I_2O_2]^+$,· 782.29957; found,782.29902.

Synthesis of ((2,5-bis((3,7,11-trimethyldodecyl)oxy)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane): 1,4-Bis((3,7,11-trimethyldodecyl)oxy)-2,5-diiodobenzene (5.48g, 6.5 mmol) was dissolved in a mixture of toluene (V = 35.0 mL) and piperidine (V = 17.5mL). After degassing with nitrogen for 45 min the catalysators $Pd(PPh_3)_2Cl_2$ (49.1 mg, 65.0 µmol), CuI (26.7 mg, 130.0 µmol) and TMSA (1.72 g, 2.5 eq., 16.25 mmol) were added. The reaction was stirred over night at room temperature. The crude product was washed with diethyl ether, saturated ammonium chloride solution and brine. Drying over $MgSO_4$, column chromatography (SiO_2, PE: EA, 100:1) led to the isolation of a honey yellow oil (4.31 g, 92%, 5.98 mmol). ^1H-NMR (400 MHz, $CDCl_3$), δ (ppm): 6.90 (s, 2H, H_{aryl}), 4.03-3.93 (m, 4H, -CH_2-O), 1.89-1.00 (m, 34H, -CH_2-), 0.95 (d, 6H, J = 6.6 Hz, -CH_3), 0.91-0.82 (m, 18H, -CH_3), 0.27-0.24 (m, 18H, Si-CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 154.21 (s, 2C, C_{aryl}-O), 117.43 (d, 2C, C_{aryl}-H), 114.16 (s, 2C, C_{aryl}-C≡C-Si), 101.30 (s, 2C,-C≡C-Si), 100.18 (s, 2C, -C≡C-Si), 68.00 (t, 2C, -CH_2-O), 39.55 (t, 2C, -CH_2-), 37.75-37.50 (m, 5C, -CH_2-), 37.44 (t, 1C, -CH_2-), 36.53-36.46 (t, 2C, -CH_2-CH_2-O), 32.98 (d, 2C, -CH-), 30.00 (d, 2C, -CH-), 28.14 (d, 2C, -CH-), 24.98-24.96 (t, 2C, -CH_2-), 24.61 (t, 2C, -CH_2-), 22.88 (q, 2C, -CH_3), 22.78 (q, 2C, -CH_3), 19.95-19.83 (m, 4C, -CH_3), 0.14 (q, 6C, Si-$(CH_3)_3$). IR (neat):

$\tilde{\nu}=$ 2953.45, 2924.52, 2868.59, 2154.10, 1496.49, 1466.60, 1405.85, 1378.85, 1272.79, 1247.72, 1221.68, 1199.51, 1176.36, 1050.05, 1018.23, 983.52, 899.63, 858.17, 837.92, 756.92, 734.75, 698.11, 625.79, 478.26, 439.69, 431.01 cm^{-1}. HRMS [$DART^+$] m/z: [M^+] calcd for [$C_{46}H_{82}O_2Si_2$ + H]$^+$, 723.59316; found,723.59261.

Synthesis of 1,4-Diethynyl-2,5-bis((3,7,11-trimethyldodecyl)oxy)benzene: ((2,5-bis((3,7,11-trimethyldodecyl)oxy)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethyl-silane) (2.89 g, 4.0 mmol) was dissolved in methanol (V = 12.0 mL) and DCM (V = 36.0 mL). After degassing with nitrogen for 30 min, potassium carbonate (5.5 g, 10.0 eq., 40.0 mmol) was added. The reaction was stirred over night at room temperature. The crude product was filtrated with DCM over SiO_2 and dried under reduced pressure to obtain a honey yellow oil (2.31 g, quant., 4 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm*)*: 6.96 (s, 2H, H_{aryl}), 4.06-3.95 (m, 4H, -CH_2-O), 3.31 (s, 2H, -C≡C-*H*), 1.91-1.00 (m, 34H), 0.95 (d, 6H, *J* = 6.6 Hz, -CH_3), 0.90-0.82 (m, 18H, -CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 154.20 (s, 2C, C_{aryl}-O), 117.90 (d, 2C, C_{aryl}-H), 113.46 (s, 2C, C_{aryl}-C≡CH), 82.53 (s, 2C, -C≡C-H), 79.99 (d, 2C, -C≡C-H), 68.27 (t, 2C, -CH_2-O), 39.55 (t, 2C, -CH_2-), 37.65-37.35 (m, 6C, -CH_2-), 36.31-36.22 (t, 1C, -CH_2-CH_2-O), 32.98 (d, 2C, -*C*H-), 30.06 (d, 2C, -*C*H-), 28.14 (d, 2C, -*C*H-), 24.98-24.96 (t, 2C, -CH_2-), 24.55 (t, 2C, -CH_2-), 22.88 (q, 2C, -CH_3), 22.78 (q, 2C, -CH_3), 20.05-19.75 (m, 4C, -CH_3) ppm. IR (neat): $\tilde{\nu}=$ 3314.07, 2951.52, 2923.56, 2867.63, 1496.49, 1466.60, 1402.96, 1378.85, 1273.75, 1218.79, 1198.54, 1160.94, 1046.19, 1015.34, 984.48, 889.02, 862.99, 734.75, 642.18, 602.65 cm^{-1}. HRMS [$DART^+$] m/z: [M^+] calcd for [$C_{40}H_{66}O_2$ + H]$^+$, 579.51356; found, 579.51287.

Synthesis of Farnesanyloxy-PPE (1Fs): 1,4-Bis((3,7,11-trimethyldodecyl)oxy)-2,5-diiodobenzene (1.2 g, 1.5 mmol) and 1,4-Diethynyl-2,5-bis((3,7,11-trimethyl-dodecyl)oxy)benzene (868.4 mg, 1.5 mmol) were dissolved in toluene (V = 5.0 mL) and piperidine (V = 3.9 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (21.1 mg, 30.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 11.4 mg, 60 µmol, 4.0 mol% CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs an orange solid was obtained (1.1 g, 65%, 2.0 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.02 (s, 2H, H_{aryl}), 4.22-3.93 (m, 4H, -CH_2-O-), 1.97-0.79 (m, 58H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.72 (s, 2C, -C_{aryl}-O), 117.41 (d, 2C, -C_{aryl}-H), 114.53 (s, 2C, C_{aryl}-C≡C-

), 91.82 (s, 2C, -$C{\equiv}C$-), 68.40 (t, 2C, -CH_2-O-), 39.55 (t, 2C, -CH_2-), 37.85-37.55 (t, 6C, -CH_2-), 36.43-36.34 (t, 1C, -CH_2-CH_2-O), 32.81 (d, 2C, -CH-), 30.16 (d, 2C, -CH-), 27.96 (d, 2C, -CH-), 24.80 (t, 2C, -CH_2-), 24.44 (t, 2C, -CH_2-), 22.70 (q, 2C, -CH_3), 22.61 (q, 2C, -CH_3), 19.94 (q, 1C, -CH_3), 19.89 (q, 1C, -CH_3), 19.68 (q, 1C, -CH_3), 19.61 (q, 1C, -CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2952.48, 2923.56, 2867.63, 1558.20, 1540.85, 1513.85, 1490.70, 1458.89, 1427.07, 1376.93, 1366.32, 1339.32, 1274.72, 1212.04, 1046.19, 1018.23, 986.41, 917.95, 886.13, 860.10, 733.78, 717.39, 474.40, 463.80 cm^{-1}. GPC: M_n = 43862 $gmol^{-1}$, M_w = 72889 $gmol^{-1}$, PDI = 1.66, degree of polymerization P_n = 80. TGA-DSC: melting point T = 91.5 °C and decomposition T = 320.5 °C.

Synthesis of 3,7,11,15-tetramethylhexadecan-1-ol: 3,7,11,15-Tetramethylhexadec-2-en-1-ol (30.00 g, 101.20 mmol), caesium carbonate (1.63 g, 5.05 mmol), palladium on carbon (10w%) (1.62 g, 1.52 mmol) were dissolved in abs. ethanol (V = 150 mL). Hydrogen (1.13 L, 1.00 eq., 101.20 mmol) was added via a hydrogenation aperture overnight into the stirred reaction mixture. After purification through filtration over silica gel (eluent diethyl ether), drying over magnesium sulfate and evaporation under reduced pressure a colorless oil (65%, 19.77 g, 66.22 mmol) was obtained. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm*)*: 3.74-3.63 (m, 2H, -O-CH_2-), 1.70-0.99 (m, 24H, -CH_2-CH_2-), 0.95-0.77 (m, 15H, -CH_3).

3,7,11,15-tetramethylhexadecan-1-ol was synthesized according to literature.[3,5]

Synthesis of 3,7,11,15-tetramethylhexadecyl 4-methylbenzenesulfonate: 3,7,11,15-tetramethylhexadecan-1-ol (14.93 g, 50.00 mmol) was dissolved in pyridine (V = 50 mL), ice bath cooled and degassed for 45 min with nitrogen. After adding 4-methylbenzenesulfonyl chloride (9.55 g, 1.00 eq., 50.0 mmol) the mixture was stirred for 1 hour at 0 °C and another 2 hours at room temperature. The reaction mixture was quenched with 1M hydrochloride acid, extracted with ethyl acetate, dried over $MgSO_4$ and organic solvents were removed under reduced pressure. After column chromatography (SiO_2, PE: EA, 10:1) a colorless oil could be obtained (15.0 g, 66%, 33.0 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm*)*: 7.80 (d, 2H, J = 8.2 Hz, H_{aryl}), 7.35 (d, 2H, J = 8.2 Hz, H_{aryl}), 4.14-4.02 (m, 2H, O-CH_2-), 2.46 (s, 3H, -CH_3), 1.72-1.63 (m, 1H, -(CH$_2$)$_2$-C*H*-CH$_3$), 1.58-1.47 (m, 3H, -(CH$_2$)$_2$-C*H*-CH$_3$), 1.46-0.99 (m, 21H, -C*H$_2$*-), 0.90-0.80 (m, 15H, -C*H$_3$*).

3,7,11,15-tetramethylhexadecyl 4-methylbenzenesulfonate was synthesized according to literature.[6]

Synthesis of 1,4-diiodo-2,5-bis((3,7,11,15-tetramethylhexadecyl)oxy)benzene: 3,7,11,15-tetramethylhexadecyl 4-methylbenzenesulfonate (7.2 g, 2.0 eq., 15.9 mmol) was dissolved in butanone (V = 40 mL) and degassed with nitrogen for 45 min. After adding 2,5-diiodobenzen-1,4-diol (2.9 g, 8.0 mmol) and potassium carbonate (11.0 g, 10.0 eq., 80 mmol) the reaction mixture was stirred at 70 °C for 5 days. The crude product was washed with ethyl acetate and water. The organic phase was dried over MgSO$_4$ and the organic solvents were removed under reduced pressure. After column chromatography (SiO$_2$, PE, PE:EA (100:1)) a honey yellow oil (84 %, 6.1 g, 6.7 mmol) was obtained. ^{1}H-NMR (500 MHz, CDCl$_3$), δ = 7.19 (s, 2H, *H*$_{\text{aryl}}$), 1.90-1.84 (m, 2H, -CH$_2$-C*H*-CH$_2$-), 1.80-1.71 (m, 2H, -CH$_2$-C*H*-CH$_2$-), 1.63-1.59 (m, 2H, -CH$_2$-C*H*-CH$_2$-), 1.58-1.50 (m, 2H, -CH$_2$-C*H*-CH$_2$-), 1.44-1.01 (m, 40H), 0.96 (d, 6H, *J* = 6.6 Hz, -C*H*$_3$), 0.88-0.84 (m, 24H, -C*H*$_3$) ppm. ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 152.85 (s, 2C, *C*$_{\text{aryl}}$-O), 122.67 (d, 2C, *C*$_{\text{aryl}}$-H), 86.23 (s, 2C, *C*$_{\text{aryl}}$-I), 68.64 (t, 2C, -*C*H$_2$-O), 39.36 (t, 2C, -*C*H$_2$-), 37.50-37.24 (m, 10C, -*C*H$_2$-), 36.13-36.04 (t, 2C, -*C*H$_2$-CH$_2$-O), 32.81-32.77 (m, 4C, -*C*H-), 29.74 (d, 2C, -*C*H-), 27.97 (d, 2C, -*C*H-), 24.83-24.78 (m, 2C, -*C*H$_2$-), 24.53-24.48 (t, 2C, -*C*H$_2$-), 24.40-24.36 (t, 2C, -*C*H$_2$-), 22.73-22.63 (q, 4C, -*C*H$_3$), 19.77-19.66 (q, 6C, -*C*H$_3$) ppm. IR (neat): $\tilde{\nu}$ = 2951.52, 2922.59, 2866.67, 1485.88, 1459.85, 1376.93, 1365.35, 1348.96, 1262.18, 1209.15, 1168.65, 1151.29, 1053.91, 1014.37, 979.66, 878.41, 851.41, 760.78, 735.71, 433.90 cm^{-1}. HRMS [FAB$^+$] m/z: [M$^+$] calcd for $[C_{46}H_{84}I_2O_2]^{+}$,$^{\cdot}$ 922.4561; found,922.4550.

Synthesis of ((2,5-bis((3,7,11,15-tetramethylhexadecyl)oxy)-1,4-phenylene)bis-(ethyne-2,1-diyl))bis(trimethylsilane): 1,4-diiodo-2,5-bis((3,7,11,15-tetramethylhexadecyl)oxy)benzene (2.8 g, 3.0 mmol) was dissolved in a mixture of toluene (V = 15.0 mL) and piperidine (V = 7.5 mL). After degassing with nitrogen for 45 min the catalysators Pd(PPh$_3$)$_2$Cl$_2$ (21.1 mg, 30.0 µmol), CuI (11.4 mg, 60.0 µmol) and TMSA (736.6 mg, 2.5 eq., 7.5 mmol) were added. The reaction was stirred overnight at room temperature. The crude product was washed with DCM, saturated ammonium chloride solution and brine. Drying over $MgSO_4$, column chromatography (SiO_2, PE: EA, 100:1) led to the isolation of a honey yellow oil (2.4 g, 92%, 2.8 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm*)*: 6.90 (s, 2H, H_{aryl}), 4.02-3.95 (m, 4H, -CH_2-O), 1.90-1.81 (m, 2H, -CH_2-C*H*-CH_2-), 1.80-1.70 (m, 2H, -CH_2-C*H*-CH_2-), 1.64-1.48 (m, 4H, -CH_2-C*H*-CH_2-), 1.43-1.01 (m, 40H), 0.96 (d, 6H, *J* = 6.6 Hz, -CH_3), 0.88-0.84 (m, 24H, -CH_3), 0.26 (s, 18H, Si-CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 153.96 (s, 2C, C_{aryl}-O), 136.60 (d, 2C, C_{aryl}-H), 123.16 (s, 2C, C_{aryl}-C≡CH), 101.70 (s, 2C,-C≡C-Si), 100.03 (s, 2C, -C≡C-Si), 67.69 (t, 2C, -CH_2-O), 39.35 (t, 2C, -CH_2-), 37.50-37.38 (m, 10C, -CH_2-), 36.10-36.30 (t, 2C, -CH_2-CH_2-O), 32.81-32.76 (m, 4C, -*C*H-), 29.80 (d, 2C, -*C*H-), 27.97 (d, 2C, -*C*H-), 24.83-24.78 (m, 2C, -CH_2-), 24.84-24.80 (t, 2C, -CH_2-), 24.49-24.44 (t, 2C, -CH_2-), 22.72-22.62 (q, 4C, -CH_3), 19.75-19.62 (q, 6C, -CH_3), 0.14 (q, 6C, Si-(CH_3)$_3$) ppm. IR (neat): $\tilde{\nu}$ = 2953.45, 2924.52, 2867.63, 2153.13, 1496.49, 1463.71, 1406.82, 1376.93, 1247.72, 1222.65, 1200.47, 1176.36, 1050.05, 896.73, 860.09, 840.81, 758.85, 698.10, 626.75, 476.33, 432.94, 419.44 cm^{-1}. HRMS [FAB$^+$] m/z: [M$^+$] calcd for [$C_{56}H_{102}O_2Si_2$]$^+$, 862.7418; found, 862.7451.

Synthesis of 1,4-diethynyl-2,5-bis((3,7,11,15-tetramethylhexadecyl)oxy)benzene: ((2,5-bis((3,7,11,15-tetramethylhexadecyl)oxy)-1,4-phenylene)bis(ethyne-2,1-diyl))-bis(trimethylsilane) (1.7 g, 2.0 mmol) was dissolved in methanol (V = 6.0 mL) and DCM (V = 12.0 mL). After degassing with nitrogen for 30 min, potassium carbonate (2.8 g, 10.0 eq., 20.0 mmol) was added. The reaction was stirred over night at room temperature. The crude product was filtrated with DCM over SiO_2 and dried under reduced pressure to obtain a honey yellow oil (98%, 1.4 g, 2.0 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm*)*: 6.97 (s, 2H, H_{aryl}), 4.06-3.96 (m, 4H, -CH_2-O), 3.33 (s, 2H, -C≡C-*H*), 1.92-1.82 (m, 2H, -CH_2-C*H*-CH_2-), 1.74-1.67 (m, 2H, -CH_2-C*H*-CH_2-), 1.66-1.58 (m, 2H, -CH_2-C*H*-CH_2-), 1.57-1.48 (m, 2H, -CH_2-C*H*-CH_2-), 1.43-1.02 (m, 40H), 0.96 (d, 6H, *J* = 6.6 Hz, -CH_3), 0.86 (dd, 24H, *J* = 10.5 Hz, *J* = 6.6 Hz, -CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 153.98 (s, 2C, C_{aryl}-O), 117.57 (d, 2C, C_{aryl}-H), 113.16 (s, 2C, C_{aryl}-C≡CH), 82.44 (s, 2C, -C≡C-H), 79.81 (d, 2C, -C≡C-H), 68.02 (t, 2C, -CH_2-O), 39.38 (t, 2C, -CH_2-), 37.51-37.28 (m, 10C, -CH_2-), 36.10-36.01 (t, 2C, -CH_2-CH_2-O), 32.83-32.79 (m, 4C, -*C*H-), 29.88 (d, 2C, -*C*H-), 28.00 (d, 2C, -*C*H-), 24.83-24.78 (m, 2C, -CH_2-), 24.83-24.82 (t, 2C, -CH_2-), 24.51-24.40 (t, 2C, -CH_2-), 22.75-22.65 (q, 4C, -CH_3), 19.80-19.66 (m, 6C, -CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2951.52, 2923.56, 2867.63, 1731.76, 1497.45, 1462.74, 1404.89, 1377.89, 1273.75, 1219.76, 1199.51, 1047.16, 1016.30, 889.98, 863.95, 735.71, 643.14, 603.61 cm^{-1}. HRMS [DART$^+$] m/z: [M$^+$] calcd for [$C_{50}H_{86}O_2$ + H]$^+$, 719.67006; found 719.67006.

Synthesis of Phytanyloxy-PPE (1Pt): 1,4-diiodo-2,5-bis((3,7,11,15-tetramethylhexadecyl)oxy)benzene (1.1076 g, 1.2 mmol) and 1,4-diethynyl-2,5-bis((3,7,11,15-tetramethylhexadecyl)oxy)benzene (863.1 mg, 1.2 mmol) were dissolved in toluene (V = 4.0 mL) and piperidine (V = 3.0 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of catalysator stock solution (16.8 mg, 24.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 9.1 mg, 48.0 µmol, 4.0 mol%, CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 70 °C and stirred for 5 days. Followed by the general work up for PPEs a yellow-orange solid was obtained (94%, 1.56 g). ^{1}H-NMR (500 MHz, $CDCl_3$), δ = 7.02 (s, 2H, H_{aryl}), 4.23-3.95 (m, 4H, -CH_2-O), 1.97-1.84 (m, 2H, -CH_2-CH-CH_2-), 1.81-1.65 (m, 4H, -CH_2-CH-CH_2-), 1.55-1.47 (m, 2H, -CH_2-CH-CH_2-), 1.43-0.93 (m, 40H), 0.91-0.79 (m, 30H, -CH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$), δ = 153.46 (s, 2C, C_{aryl}-O), 117.04 (d, 2C, C_{aryl}-H), 114.22 (s, 2C, C_{aryl}-C≡C-), 91.60 (s, 2C, -C≡C-), 68.12 (t, 2C, -CH$_2$-O), 39.36 (t, 2C, -CH$_2$-), 37.56-37.30 (m, 10C, -CH$_2$-), 36.38-36.28 (t, 2C, -CH$_2$-CH$_2$-O), 32.83 (m, 2C, -CH-), 30.16 (m, 2C, -CH-), 29.70 (d, 2C, -CH-), 27.97 (d, 2C, -CH-), 24.82-24.81 (m, 2C, -CH$_2$-), 24.54 (t, 2C, -CH$_2$-), 24.41 (t, 2C, -CH$_2$-), 22.73 (q, 2C, -CH$_3$), 22.63 (q, 2C, -CH$_3$), 19.76 (m, 6C, -CH$_3$) ppm. IR (neat): $\tilde{v}$ = 2951.52, 2922.59, 2866.67, 1513.85, 1460.81, 1427.07, 1376.93, 1275.68, 1212.04, 1019.19, 918.91, 886.13, 860.10, 803.21, 733.78, 718.35 cm^{-1}. GPC: M_n = 51584 gmol^{-1}, M_w = 1000670 gmol^{-1}, PDI = 1.95, degree of polymerization P_n = 74. TGA-DSC: melting point 75.0 °C and decomposition 294.0 °C.

Synthesis of 2-Ethylhexyloxy-PPE (1Ethex): 1,4-Bis((2-ethylhexyl)oxy)-2,5-diiodobenzene (879.5 mg, 1.5 mmol) and 1,4-Bis((2-ethylhexyl)oxy)-2,5-diethynylbenzene (573.8 mg, 1.5 mmol) were dissolved in toluene (V = 5.0 mL) and piperidine (V = 3.9 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (21.1 mg, 30.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 11.4 mg, 60 µmol, 4.0 mol% CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 70 °C and stirred for 5 days. Followed by the general work up for PPEs an orange solid was obtained (72%, 768.2 mg). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm): 7.01 (s, 2H, H_{aryl}), 4.05-3.75 (m, 4H, -CH_2-O-), 1.90-1.73 (m, 2H, -CH-), 1.72-1.20 (m, 18H, -CH_2-), 1.07-0.94 (t, 6H, -CH_3), 0.94-0.80 (t, 6H, -CH_3). ^{13}C-NMR (10.0 MHz, $CDCl_3$), δ (ppm): 153.75 (s, 2C, -C_{aryl}-O), 116.74 (d, 2C, -C_{aryl}-H), 114.29 (s, 2C, C_{aryl}-C≡C-), 91.60 (s, 2C, -*C*≡*C*-), 71.98 (t, 2C, -CH_2-O-), 39.64 (d, 2C, -CH-CH_2O-), 30.64 (t, 2C, -CH_2-), 29.13 (t, 2C, -CH_2-), 24.09 (t, 2C, -CH_2-), 23.09 (t, 2C, -CH_2-), 14.06 (q, 2C, -CH_3), 11.31 (q, 2C, -CH_3). IR (neat): $\tilde{v}$ = 2956.82, 2923.80, 2870.76, 2363.82, 2342.36, 2332.00, 1513.12, 1460.81, 1442.97, 1378.85, 1274.96, 1207.22, 1117.79, 1032.69, 905.90, 859.61, 770.91, 737.64, 728.24 cm^{-1}. GPC (MDa): M_n = 34512, M_w = 53926, PDI = 1.56, degree of polymerization, n = 97. TGA-DSC: melting point 115.1 °C, phase transition 232.5 °C and decomposition 300.2°C.

Synthesis of Heptan-4-yl-4-methylbenzenesulfonate: Heptan-4-ol (11.3 g, 97.5 mmol) was dissolved in pyridine (V = 97.5 mL), ice bath cooled and degassed for 45 min with nitrogen. After adding 4-methylbenzenesulfonyl chloride (18.6 g, 1.0 eq., 97.5 mmol) the mixture was stirred for 1 hour at 0 °C and another 2 hours at room temperature. The reaction mixture was quenched with 1M hydrochloride acid, extracted with ethyl acetate, dryed over $MgSO_4$ and organic solvents were removed under reduced pressure. After column chromatography (SiO_2, PE: EA, 10:1) a colorless oil could be obtained (21.6 g, 82%, 80.0 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm*)*: 7.80 (d, 2H, *J* = 16 Hz, H_{aryl}), 7.33 (d, 2H, *J* = 7.9 Hz, H_{aryl}), 4.61 (quin, 1H, *J* = 6.1 Hz , O-C*H*-), 2.45 (s, 3H, -CH_3), 1.64-1.49 (m, 4H, -CH-CH_2-), 1.38-1.19 (m, 4H, -CH_2-CH_2-), 0.84 (t, 6H, *J* = 7.3 Hz, -CH_2-CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 144.25 (s, 1C, -C_{Aryl}-SO_3-), 134.91 (s, 1C, C_{Aryl}-CH_3), 129.60 (d, 2C, -C_{Aryl}H-), 127.67 (d, 2C, -C_{Aryl}H-), 84.04 (d, 1C, -SO_3-*C*H-), 36.28 (t, 2C, -CH-*C*H_2-), 21.58 (s, 1C, C_{Aryl}-*C*H_3), 18.00 (t, 2C, -CH_2-*C*H_2-), 13.76 (q, 2C, -*C*H_3). IR (neat): $\tilde{\nu} =$ 3335.28, 2959.23, 2935.13, 2874.38, 1649.80, 1597.73, 1561.09, 1495.53, 1458.89, 1354.75, 1305.57, 1291.11, 1186.97, 1173.47, 1095.37, 1044.26, 1020.16, 961.34, 893.84, 814.77, 783.92, 727.99, 685.57, 665.32, 575.64, 553.47, 506.22, 496.58, 478.26, 461.86, 415.58, 404.01 cm^{-1}. HRMS [EI$^+$] m/z: [M$^+$] calcd for $[C_{14}H_{22}O_3S]^+$, 270.1274; found, 270.1284. Elemental Analysis: calcd for $C_{14}H_{22}O_3S$ 62.19 % C, 8.20 % H, found 62.30 % C, 8.13 % H.

Synthesis of 1,4-Bis(heptan-4-yloxy)-2,5-diiodobenzene: Heptan-4-yl-4-methylbenzenesulfonate was dissolved in butanone (V = 125 mL) and degassed for 1 hour with nitrogen. After adding 2,5-diiodohydroquinon (7) (27.6 mmol, 10.0 g) and potassium carbonate (276 mmol, 10 eq., 38.2 g) the suspension was stirred at 75 °C for 5 days. The reaction mixture was quenched with water, extracted with ethylacetate and dried over $MgSO_4$. The organic solvent was removed under reduced pressure. Purification via column chromatography (SiO_2, PE:EA 50:1) led to a colorless solid (10.1 g, 65 %, 17.9 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm*)*: 7.15 (s, 2H, H_{aryl}), 4.16 (quin, 2H, *J* = 5.8 Hz, -O-C*H*-), 1.73-1.56 (m, 8H, -CH-CH_2-), 1.52-1.35 (m, 8H, -CH_2-CH_2-), 0.94 (t, 6H, *J* = 7.3 Hz, -CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$), δ (ppm): 152.1 (s, 2C, C_{aryl}-O), 124.0 (d, 2C, C_{aryl}-H), 87.7 (s, 2C, C_{aryl}-I), 80.4 (t, 2C, -*C*H-O), 35.8 (t, 4C, O-CH-CH_2-), 18.6 (t, 4C, -CH_2-CH_2-), 14.2 (q, 2C, -CH_3). IR (neat): $\tilde{\nu}$ = 2954.41, 2931.27, 2869.56, 2363.34, 2355.62, 2341.16, 1598.70, 1462.74, 1454.06, 1432.85, 1375.96, 1347.03, 1304.61, 1257.36, 1238.08, 1201.43, 1164.79, 1126.22, 1070.30, 1047.16, 1009.55, 985.44, 939.16, 903.48, 882.27, 857.20, 776.20, 744.38, 729.92, 617.10, 517.79, 429.08 cm^{-1}. HRMS [FAB$^+$] m/z: [M$^+$] calcd for $[C_{20}H_{32}I_2O_2]^+$, 558.0492; found, 558.0488. Elemental Analysis: calcd for $C_{20}H_{32}I_2O_2$ 43.03 % C, 5.78 % H, found 43.22 % C, 5.84 % H.

Synthesis of ((2,5-Bis(heptan-4-yloxy)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(tri-methyl-silane): 1,4-Bis(heptan-4-yloxy)-2,5-diiodobenzene (5.0 g, 9.0 mmol) was dissolved in a mixture of toluene (V = 44.8 mL) and piperidine (V = 22.4 mL). After degassing with nitrogen for 45 min the catalysators $Pd(PPh_3)_2Cl_2$ (62.9 mg, 90.0 µmol), CuI (34.1 mg, 180.0 µmol) and TMSA (1.72 g, 2.5 eq., 16.25 mmol) were added. The reaction was stirred over night at room temperature. The crude product was washed with dichloromethane, saturated ammonium chloride solution and brine. Drying over $MgSO_4$, column chromatography (SiO_2, PE: EA, 50:1) led to the isolation of a colorless solid (3.7 g, 82%, 7.4 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm*)*: 6.87 (s, 2H, H_{aryl}), 4.18 (qui, 2H, -C*H*-O-), 1.72-1.38 (m, 16H), 0.93 (t, 6H, *J* = 7.3 Hz, -CH_3), 0.28-0.23 (m, 18H, Si-CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 153.70 (s, 2C, C_{aryl}-O), 119.84 (d, 2C, C_{aryl}-H), 115.51 (s, 2C, C_{aryl}-C≡CH), 101.65 (s, 2C, -C≡C-), 99.56 (d, 2C, -C≡C-), 80.42 (t, 2C, -*C*H-O-), 35.98 (t, 4C, -CH-CH_2-), 18.38 (t, 4C, -CH_2-CH_2-), 14.28 (q, 4C, -CH_3), 0.00 (q, 6C, Si-CH_3). IR (neat): $\tilde{\nu}$ = 2956.34, 2931.27, 2905.24, 2870.52, 2155.06, 1486.85, 1464.67, 1432.85, 1400.07, 1361.50, 1336.43, 1267.00, 1246.75, 1217.83, 1201.43, 1178.29, 1157.08, 1125.26, 1070.30, 1007.62, 990.26, 946.87, 909.27, 884.20, 855.27, 836.95, 756.92, 727.03, 698.10, 679.78, 669.17, 661.46, 624.82, 555.39, 530.32, 485.97, 469.58, 439.69 cm^{-1}. HRMS [DART$^+$] m/z: [M$^+$] calcd for $[C_{30}H_{50}Si_2O_2]^+$, 498.3344, found, 498.3344. Elemental Analysis: calcd for $C_{30}H_{50}Si_2O_2$, 72.23 % C, 10.10 % H, found 72.44 % C, 10.27 % H.

Synthesis of 1,4-diethynyl-2,5-bis(heptan-4-yloxy)benzene: ((2,5-Bis(heptan-4-yloxy)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethyl-silane) (3.5 g, 7.0 mmol) was dissolved in methanol (V = 23.4 mL) and DCM (V = 70.2 mL). After degassing with nitrogen for 30 min, potassium carbonate (9.7 g, 10.0 eq., 70.2 mmol) was added. The reaction was stirred over night at room temperature. The crude product was filtrated with DCM over SiO_2 and dried under reduced pressure to obtain a yellow oil (2.5 g, quant.,7.0 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm*)*: 6.93 (s, 2H, H_{aryl}), 4.18 (qui, 2H, *J* = 5.8 Hz, -C*H*-O-), 3.30 (s, 2H, -C≡C-H), 1.75-1.35 (m, 16H, -CH_2-), 0.93 (t, 6H, *J* = 7.1 Hz, -CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 153.66 (s, 2C, C_{aryl}-O), 120.03 (d, 2C, C_{aryl}-H), 114.54 (s, 2C, C_{aryl}-C≡CH), 82.01 (s, 2C, -C≡C-), 80.31 (d, 2C, -C≡C-), 80.19 (-*C*H-O-), 36.07 (t, 4C, -CH-CH_2-), 18.52 (t, 4C, -CH_2-CH_2-), 14.20 (q, 4C, -CH_3). IR (neat): $\tilde{\nu}$ = 3289.00, 2957.30, 2932.23, 2871.49, 2106.85, 1487.81, 1464.67, 1396.21, 1378.85, 1364.39, 1303.64, 1268.93, 1199.51, 1117.55, 1069.33, 989.30, 946.87, 892.88, 867.81, 811.88, 740.53, 673.99, 643.14, 605.53, 510.08, 492.72, 473.43, 452.22, 434.86, 425.22 cm^{-1}. HRMS [DART$^+$] m/z: [M$^+$] calcd for $[C_{24}H_{34}O_2 + H]^+$, 355.2637; found, 355.2637.

Synthesis of 4-Heptanyloxy-PPE (1hpt): 1,4-Bis(heptan-4-yloxy)-2,5-diiodobenzene (1.7 g, 3.0 mmol) and 1,4-Diethynyl-2,5-bis(heptan-4-yloxy)benzene (1.1 g, 3 mmol) were dissolved in toluene (V = 10.0 mL) and piperidine (V = 8.3 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (42.1 mg, 60.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 22.9 mg, 120 µmol, 4.0 mol% CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs a yellow solid was obtained (1.833 g, 93%, 5.58 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm*)*: 7.00 (s, 2H, H_{aryl}), 4.27 (quin, 2H, *J = 5.5 Hz*, -O-CH-), 1.78-1.69 (m, 4H, -CH_2-), 1.69-1.60 (m, 4H, -CH_2-),1.56-1.42 (m, 8H, -CH_2-), 0.95 (t, 12H, *J = 7.3 Hz*, -CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 153.10 (s, 2C, -C_{aryl}-O), 119.70 (d, 2C, -C_{aryl}-H), 115.76 (s, 2C, C_{aryl}-C≡C-), 91.64 (s, 2C, -*C*≡*C*-), 80.28 (t, 2C, -*C*H_2-O-), 36.16 (d, 4C, -CH-CH_2O-), 18.57 (t, 4C, -*C*H_2-), 14.29 (q, 4C, -CH_3). IR (neat): $\tilde{\nu}$ = 2956.34, 2931.27, 2870.52, 1593.88, 1539.88, 1505.17, 1463.71, 1417.42, 1376.93, 1364.39, 1269.90, 1237.11, 1199.51, 1116.58, 1068.37, 989.30, 945.91, 903.49, 865.88, 750.17, 711.60, 689.43 cm^{-1}. GPC (MDa): M_n = 28969 gmol^{-1}, M_w = 44216 gmol^{-1}, PDI = 1.52, degree of polymerization, n = 97. TGA-DSC: recrystallization at 105.0 °C, melting point T = 189.0 °C and decomposition T = 290.5 °C.

Synthesis of Nonan-5-yl-4-methylbenzenesulfonate: Nonan-5-ol (43.3 g, 300.0 mmol) was dissolved in pyridine (V = 300 mL), ice bath cooled and degassed for 45 min with nitrogen. After adding 4-methylbenzenesulfonyl chloride (57.3 g, 1.0 eq., 300.0 mmol) the mixture was stirred for 1 hour at 0 °C and another 2 hours at room temperature. The reaction mixture was quenched with 1M hydrochloride acid, extracted with ethyl acetate, dryed over $MgSO_4$ and organic solvents were removed under reduced pressure. After column chromatography (SiO_2, PE: EA, 50:1) a colorless oil could be obtained (54.9 g, 61%, 184.0 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm*)*: 7.80 (d, 2H, *J* = 8.2 Hz, H_{aryl}), 7.33 (d, 2H, *J* = 8.0 Hz, H_{aryl}), 4.55 (quin, 1H, *J* = 6.0 Hz, O-C*H*-), 2.45 (s, 3H, -CH_3), 1.63-1.51 (m, 4H, -CH-CH_2-), 1.28-1.13 (m, 4H, -CH_2-CH_2-), 0.82 (t, 6H, *J* = 7.0 Hz, -CH_2-CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$), δ (ppm): 144.29 (s, 1C, -C_{Aryl}-SO_3-), 134.74 (s, 1C, C_{Aryl}-CH_3), 129.60 (d, 2C, -C_{Aryl}H-), 127.69 (d, 2C, -C_{Aryl}H-), 84.57 (d, 1C, -SO_3-*C*H-), 33.78 (t, 2C, -CH-*C*H_2-), 26.79 (t, 2C, -CH_2-*C*H_2-), 22.37 (s, 1C, C_{Aryl}-*C*H_3), 21.59 (t, 2C, -CH_2-*C*H_2-), 13.84 (q, 2C, -*C*H_3). IR (neat): $\tilde{\nu}$ = 2957.06, 2930.31, 2871.73, 2862.09, 1598.7, 1495.53, 1467.32, 1457.68, 1456.23, 1359.09, 1306.05, 1290.14, 1211.32, 1186.97, 1174.68, 1118.75, 1096.57, 1019.44, 951.21, 945.43, 898.42, 888.30, 836.71, 814.05, 761.02, 724.13, 687.01, 667.73, 663.87, 575.40, 553.22 cm^{-1}. HRMS [DART$^+$] m/z: [M$^+$] calcd for $[C_{14}H_{22}O_3S+NH_4]^+$, 316.1941; found, 316.1938. Elemental Analysis: calcd for $C_{16}H_{26}O_3S$ 64.39 % C, 8.78 % H, found 64.74 % C, 8.67 % H.

Synthesis of 1,4-diiodo-2,5-bis(nonan-5-yloxy)benzene: Nonan-5-yl-4-methylbenzenesulfonate (60.0 mmol, 17.9 g) was dissolved in butanone (V = 150 mL) and degassed for 1 hour with nitrogen. After adding 2,5-diiodohydroquinon (30.0 mmol, 10.9 g) and potassium carbonate (300 mmol, 10 eq., 41.5 g) the suspension was stirred at 75 °C for 5 days. The reaction mixture was quenched with water, extracted with ethylacetate and dried over $MgSO_4$. The organic solvent was removed under reduced pressure. Purification via column chromatography (SiO_2, PE:EA 100:1) led to a colorless solid (12.5 g, 68 %, 20.4 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm*)*: 7.14 (s, 2H, H_{aryl}), 4.13 (quin, 2H, *J* = 5.8 Hz, -O-C*H*-), 1.72-1.54 (m, 8H, -CH-CH_2-), 1.45-1.28 (m, 16H, -CH_2-CH_2-), 0.92 (t, 12H, *J* = 7.1 Hz, -CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$), δ (ppm): 152.1 3(s, 2C, C_{aryl}-O), 124.09 (d, 2C, C_{aryl}-H), 87.72 (s, 2C, C_{aryl}-I), 80.88 (t, 2C, -*C*H-O), 33.29 (t, 4C, O-CH-*C*H_2-), 27.44 (t, 4C, -CH_2-*C*H_2-) 22.77 (t, 4C, -CH_2-*C*H_2-), 14.06 (q, 2C, -*C*H_3). IR (neat): $\tilde{\nu}$ = 2953.69, 2930.79, 2870.04, 2858.95, 1460.09, 1378.61, 1343.18, 1282.43, 1258.57, 1200.23, 1131.05, 1119.48, 1045.23, 1019.68, 979.42, 917.95, 880.10, 853.34, 816.70, 757.88, 728.96 cm^{-1}. HRMS [FAB$^+$] m/z: $[M]^{\cdot+}$ calcd for $[C_{24}H_{40}I_2O_2\,]^{\cdot+}$, 614.1112; found, 614.1112. Elemental Analysis: calcd for $C_{24}H_{40}I_2O_2$ 46.92 % C, 6.56 % H, found 47.29 % C, 6.59 % H.

Synthesis of ((2,5-Bis(nonan-5-yloxy)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(tri-methyl-silane): 1,4-diiodo-2,5-bis(nonan-5-yloxy)benzene (6.1 g, 10.0 mmol) was dissolved in a mixture of toluene (V = 25.0 mL) and piperidine (V = 12.5 mL). After degassing with nitrogen for 45 min the catalysators $Pd(PPh_3)_2Cl_2$ (70.2 mg, 10.0 µmol), CuI (38.1 mg, 20.0 µmol) and TMSA (2.45 g, 2.5 eq., 25.0 mmol) were added. The reaction was stirred over night at room temperature. The crude product was washed with dichloromethane, saturated ammonium chloride solution and brine. Drying over $MgSO_4$, column chromatography (SiO_2, PE: EA, 100:1) led to the isolation of a colorless solid (5.4 g, 98%, 9.8 mmol). ^{1}H-NMR (500 MHz, $CDCl_3$), δ (ppm*)*: 6.86 (s, 2H, H_{aryl}), 4.17 (qui, 2H, -C*H*-O-), 1.70-1.54 (m, 8H), 1.46-1.29 (m, 16H) 0.93 (t, 12H, *J* = 7.1 Hz, -CH_3), 0.27-0.24 (m, 18H, Si-CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$), δ (ppm): 153.55 (s, 2C, C_{aryl}-O), 119.79 (d, 2C, C_{aryl}-H), 115.44 (s, 2C, C_{aryl}-C≡CH), 101.65 (s, 2C, -C≡C-), 99.53 (d, 2C, -C≡C-), 80.55 (t, 2C, -*C*H-O-), 33.36 (t, 4C, -CH-*C*H_2-), 27.26 (t, 4C, -*C*H_2- *C*H_2-), 22.86 (t, 4C, -*C*H_2- *C*H_2-), 14.07 (q, 4C, -*C*H_3), 0.00 (q, 6C, Si-*C*H_3). IR (neat): $\tilde{\nu}$ = 2958.27, 2932.23, 2858.95, 2151.20, 1486.85, 1465.63, 1432.85, 1401.03, 1369.21, 1350.89, 1246.75, 1219.76, 1199.51, 1176.36, 1129.12, 1024.02, 980.62, 936.27, 859.13, 835.99, 757.88, 722.21, 699.06, 624.82, 478.26 cm^{-1}. HRMS [DART$^+$] m/z: [M$^+$] calcd for $[C_{34}H_{58}Si_2O_2+H]^+$, 555.4045, found, 555.4048. Elemental Analysis: calcd for $C_{34}H_{58}Si_2O_2$, 73.58 % C, 10.53 % H, found 73.46 % C, 10.41 % H.

Synthesis of 1,4-diethynyl-2,5-bis(nonan-5-yloxy)benzene: ((2,5-Bis(nonan-5-yloxy)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethyl-silane) (2.2 g, 4.0 mmol) was dissolved in methanol (V = 12 mL) and DCM (V = 36 mL). After degassing with nitrogen for 30 min, potassium carbonate (5.5 g, 10.0 eq., 40.0 mmol) was added. The reaction was stirred over night at room temperature. The crude product was filtrated with DCM over SiO_2 and dryed under reduced pressure to obtain a yellow oil (2.5 g, quant., 7.0 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm*)*: 6.93 (s, 2H, H_{aryl}), 4.16 (quin, 2H, -O-C*H*-), 3.30 (s, 2H, -C≡C-H), 1.72-1.54 (m, 8H, -CH-CH_2-), 1.46-1.25 (m, 16H, -CH_2-CH_2-), 0.92 (t, 12H, *J* = 7.1 Hz, -CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 153.63 (s, 2C, C_{aryl}-O), 120.08 (d, 2C, C_{aryl}-H), 114.55 (s, 2C, C_{aryl}-C≡CH), 82.01 (s, 2C, -C≡C-H), 80.76 (t, 2C, -*C*H-O), 80.18 (d, 2C, -C≡C-H), 33.50 (t, 2C, O-CH-*C*H_2-), 27.40 (t, 4C, -*C*H_2- *C*H_2-), 22.79 (t, 4C, -*C*H_2- *C*H_2-), 14.05 (q, 2C, -*C*H_3). IR (neat): $\tilde{\nu}$ = 3313.83, 3291.17, 2954.17, 2930.55, 2870.76, 2859.19, 1739.96, 1487.09, 1467.08, 1396.93, 1378.61, 1365.11, 1299.55, 1269.41, 1215.66, 1196.85, 1161.18, 1130.08, 1120.44, 1019.19, 987.61, 928.79, 889.98, 868.29, 728.96, 644.10, 604.57 cm^{-1}. HRMS [DART$^+$] m/z: [M$^+$] calcd for $[C_{28}H_{42}O_2 + H]^+$, 411.3258; found, 411.3280. Elemental Analysis: calcd for $C_{28}H_{42}O_2$, 81.90 % C, 10.31 % H, found 81.98 % C, 10.58 % H.

Synthesis of 5-Nonanyloxy-PPE (1non): 1,4-diiodo-2,5-bis(nonan-5-yloxy)benzene (921.6 mg, 1.5 mmol) and 1,4-diethynyl-2,5-bis(nonan-5-yloxy)benzene (616.0 g, 1.5 mmol) were dissolved in toluene (V = 5.0 mL) and piperidine (V = 3.9 mL). After degassing the mixture for 45 min with N_2, 0.5 mL of a catalysator stock solution (21.1 mg, 30.0 µmol, 2.0 mol%, $Pd(PPh_3)_2Cl_2$, 11.4 mg, 60 µmol, 4.0 mol% CuI, 5.0 mL piperidine) was added. The reaction mixture was heated up to 75 °C and stirred for 5 days. Followed by the general work up for PPEs a yellow solid was obtained (1.142 g, 99%, 2.97 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm*)*: 7.00 (s, 2H, H_{aryl}), 4.33-4.14 (m, 2H, -O-C*H*-), 1.90-1.60 (m, 4H, -O-CH-CH_2-), 1.60-1.20 (m, 16H, -CH-CH_2-), 0.90 (t, 12H, *J* = 6.0 Hz, -CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$), δ (ppm): 153.18 (s, 2C, C_{aryl}-O), 119.86 (d, 2C, C_{aryl}-H), 115.94 (s, 2C, C_{aryl}-C≡CH), 91.68 (s, 2C, -C≡C-), 80.82 (t, 2C, -*C*H-O), 33.69 (t, 2C, O-CH-*C*H_2-), 27.48 (t, 4C, -*C*H_2- *C*H_2-), 22.88 (t, 4C, -*C*H_2- *C*H_2-), 14.07 (q, 2C, -*C*H_3). IR (neat): $\tilde{\nu}$ = 2955.13, 2931.03, 2870.52, 2858.71, 2363.58, 1503.48, 1485.64, 1465.88, 1415.98, 1377.89, 1270.86, 1197.34, 1119.72, 984.96, 929.52, 864.44, 803.45, 731.13 cm^{-1}. GPC: M_n = 49805 $gmol^{-1}$, M_w = 80687 gmol^{-1}, PDI = 1.62, degree of polymerization P_n = 130. TGA-DSC: melting point 191.1 °C and decomposition 266.3 °C.

Experimental Procedures

Used materials

Burnished ITO coated glas (Kintec, Hong Kong), conductivity 10 Ω/sq, ITO layer thickness 190 nm, Size 150 mm x 150 mm.

PEDOT:PSS aqueous dispersion (Heraeus, Clevios P VP.Al 4083, Charge: 9000481853) solid content 1.3-1.7%, resistivity 500-5000 Ωcm, viscosity 5-12 mPas, particle size distribution d_{50} = 80 nm. PEDOT work function approx.. 5.2 eV, PEDOT:PSS ratio 1:6 (by weight).

TPBi (Ossila), Sublimed (>99.8% purity), HOMO 6.2/6.7 eV, LUMO 2.7 eV

LiF, toluene, acetone and isopropanole purchased from SigmaAldrich.

Syringe filter VWR collection, PES membrane, pore size 0.45 µm, diameter 25 mm

Syringe filter VWR collection, PTFE membrane, pore size 0.45 µm, diameter 25 mm

Preparation of active layer structure for layer thickness tests

For the fabrication of the devices, glass substrates patterned with 190 nm ITO electrodes (Kintec©, Hong Kong) were cleaned subsequently in ultrasonic baths at 40°C of acetone and 2-propanol. After drying the active layer PPEs were filtered (Syringe filter VWR collection, PTFE membrane, pore size 0.45 µm, diameter 25 mm) and spin-coated (4000 rpm, 1000 rpm/s, 30 s) on top from different concentrations of polymer in toluene solution to obtain films of different thicknesses. After drying on a hot plate for 5 min, the layer thickness was measured via profilometry.

Results for layer Thickness test

Spin coating parameter: 4000 rpm (1000 rpm/s, 30 s)

Tested with profilometer measurements

Material	Weight content [mg/mL]	Layer thickness [nm]
Hexyloxy	7.5	43
	9.0	60
	10.5	61
	12.0	62
	13.5	80
	15.0	90
5-Nonanyloxy	7.5	33
	9.0	39
	10.5	39
	12.0	51
	13.5	62
	15.0	81
(*rac*)-Citronellyloxy	7.5	31
	9.0	36
	10.5	53
	12.0	54
	13.5	60
	15.0	82

Device processing for thickness-performance relationship

a) Only PPE layer

For the fabrication of the devices, glass substrates patterned with 190 nm ITO electrodes (Kintec©, Hong Kong) were cleaned subsequently in ultrasonic baths at 40°C of acetone and 2-propanol. After drying, the substrates were O_2 plasma treated for 5 min. Then, the active layer PPEs were filtered (Syringe filter VWR collection, PTFE membrane, pore size 0.45 µm, diameter 25 mm) and spin-coated (4000 rpm, 1000 rpm/s, 30 s) on top from different concentrations of polymer in toluene solution to obtain films of different thicknesses. After drying of the sample overnight under vacuum at room temperature, a 1 nm thick LiF layer was deposited by thermal evaporation at a pressure of 7E-6 mbar at rate of 2 $Ås^{-1}$, followed by a 100 nm thick Al electrode evaporated at 6 $Ås^{-1}$.

b) With hole injection layer PEDOT:PSS

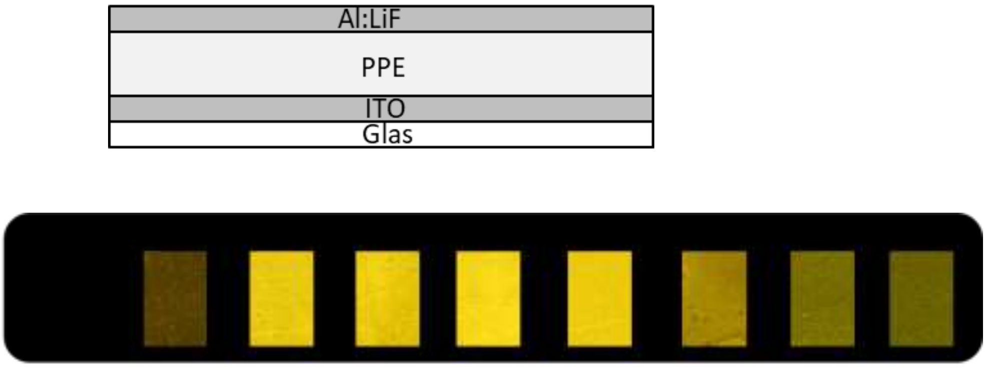
For the fabrication of the devices, glass substrates patterned with 190 nm ITO electrodes (Kintec©, Hong Kong) were cleaned subsequently in ultrasonic baths at 40°C of acetone and 2-propanol. After drying, the substrates were O_2 plasma treated for 5 min. A 40 nm layer of polyethylenedioxythiophene doped with poly(styrene-sulfonate) (PEDOT:PSS) was filtered (Syringe filter VWR collection, PES membrane, pore size 0.45 µm, diameter 25 mm) and coated on top (2500 rpm, 3000 rpm/s, 45 s). The films were annealed for 3 min at 200 °C and 15 min at 120 °C. Then, the active layer PPEs were filtered (Syringe filter VWR collection, PTFE membrane, pore size 0.45 µm, diameter 25 mm) and spin-coated (4000 rpm, 1000 rpm/s, 30 s) on top from different concentrations of polymer in toluene solution to obtain films of different thicknesses. After drying of the sample overnight under vacuum at room temperature, a 1 nm thick LiF layer was deposited by thermal evaporation at a pressure of 7E-6 mbar at rate of 2 $Ås^{-1}$, followed by a 100 nm thick Al electrode evaporated at 6 $Ås^{-1}$.

Device measurement

A setup provided by BOTEST (Botest Systems GmbH, Wertheim, Germany) was used for the analysis of PLED characteristics. Electroluminescence spectra were obtained by an Ocean OPTICS JAZ 200-1100 nm spectrometer module.

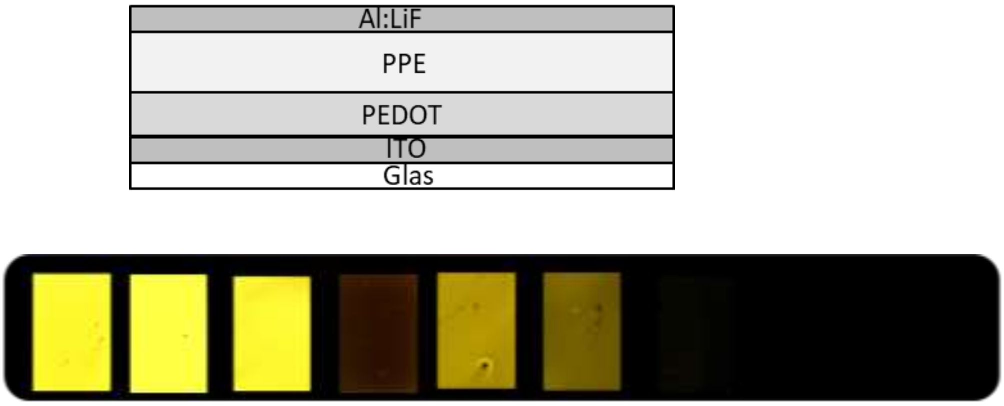
OLED characteristics

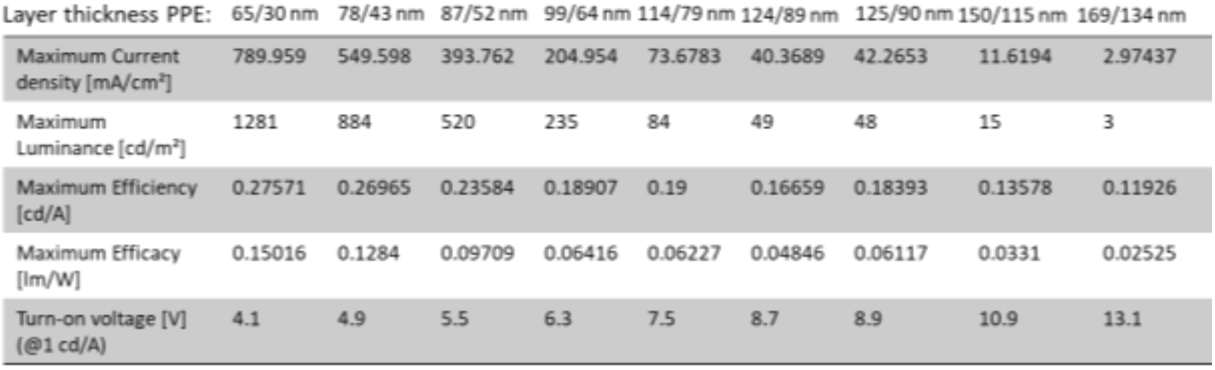
Results for thickness-performance relationship



Layer thickness PPE:	37 nm	45 nm	51 nm	57 nm	70 nm	80 nm	100 nm	123 nm	150 nm
Maximum Current density [mA/cm²]	1263.94	2082.92	635.31	416.627	256.501	136.966	103.014	29.34	
Maximum Luminance [cd/m²]	96	125	261	775	117	78	62	30	<1 cd/A
Maximum Efficiency [cd/A]	0.00766	0.01921	0.04119	0.18608	0.08314	0.11265	0.10154	0.12099	
Maximum Efficacy [lm/W]	0.00204	0.00544	0.01052	0.05324	0.02133	0.10607	0.02369	0.02449	
Turn-on voltage [V] (@1 cd/A)	5.8	7.2	8.1	7.5	8.3	9.5	11.3	13.3	>20

Figure S1. Thickness test of simple **1hex** PLED stacks.





Layer thickness PPE:	65/30 nm	78/43 nm	87/52 nm	99/64 nm	114/79 nm	124/89 nm	125/90 nm	150/115 nm	169/134 nm
Maximum Current density [mA/cm²]	789.959	549.598	393.762	204.954	73.6783	40.3689	42.2653	11.6194	2.97437
Maximum Luminance [cd/m²]	1281	884	520	235	84	49	48	15	3
Maximum Efficiency [cd/A]	0.27571	0.26965	0.23584	0.18907	0.19	0.16659	0.18393	0.13578	0.11926
Maximum Efficacy [lm/W]	0.15016	0.1284	0.09709	0.06416	0.06227	0.04846	0.06117	0.0331	0.02525
Turn-on voltage [V] (@1 cd/A)	4.1	4.9	5.5	6.3	7.5	8.7	8.9	10.9	13.1

Figure S2. Thickness test of **1hex** PLED stacks with hole injection layer.

Device processing for thickness-performance relationship in multi-stack PLEDS

For the fabrication of the devices, glass substrates patterned with 190 nm ITO electrodes (Kintec©, Hong Kong) were cleaned subsequently in ultrasonic baths at 40°C of acetone and 2-propanol. After drying, the substrates were O_2 plasma treated for 5 min. A 40 nm layer of polyethylenedioxythiophene doped with poly(styrenesulfonate) (PEDOT:PSS) was filtered (Syringe filter VWR collection, PES membrane, pore size 0.45 µm, diameter 25 mm) and coated on top (2500 rpm, 3000 rpm/s, 45 s). The films were annealed for 3 min at 200 °C and 15 min at 120 °C. Then, the active layer PPEs were filtered (Syringe filter VWR collection, PTFE membrane, pore size 0.45 µm, diameter 25 mm) and spin-coated (4000 rpm, 1000 rpm/s, 30 s) on top from different concentrations of polymer in toluene solution to obtain films of different thicknesses. After drying of the sample overnight under vacuum at room temperature, a 20 nm thick TPBi layer was deposited by thermal evaporation at a pressure of 7E-6 mbar at a rate of 20 Ås^{-1}, followed by deposition of a 1 nm thick LiF at rate of 2 Ås^{-1} and by a 100 nm thick Al electrode evaporated at 6 Ås^{-1}. The devices were encapsulation with UV hardening adhesive (20 min) and a cover glass.

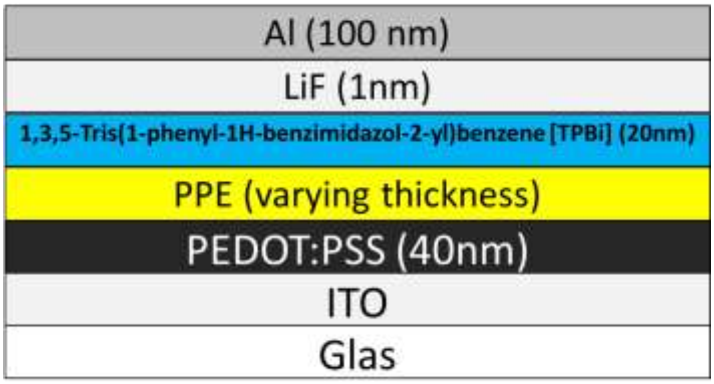


Figure S3. Thickness test of **PPE** PLED stacks with hole and electron injection layer.

Results for thickness-performance relationship in multi-stack PLEDS

Hexyloxy-PPE (1hex)

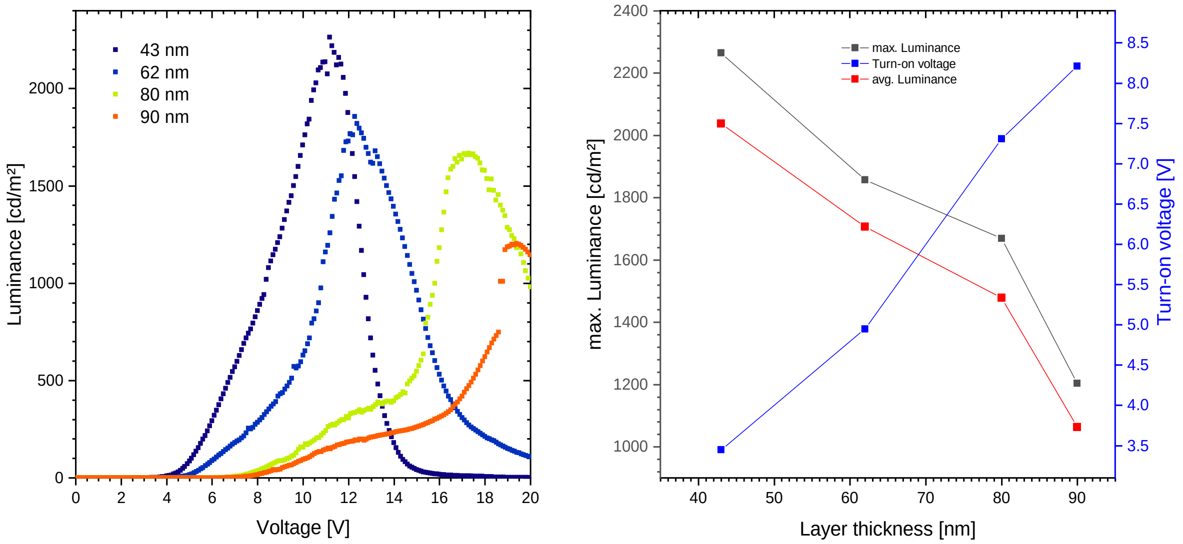


Figure S4. Optimized simple PLED stack and performance metrics for **1hex**.

Table S1. PLED characteristics for **1hex**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
Hexyloxy (1hex)	3.45 V	2264.2 cd/m^2 @ 11.1 V	2037.8 cd/m^2	24.3E-2 cd/A	8.6E-2 lm/W	43 nm
	4.95 V	1856.6 cd/m^2 @ 12.3 V	1706.2 cd/m^2	28.8E-2 cd/A	11.6E-2 lm/W	62 nm
	7.31 V	1668.3 cd/m^2 @ 17.3 V	1478.1 cd/m^2	32.0E-2 cd/A	6.6E-2 lm/W	80 nm
	8.21 V	1203.1 cd/m^2 @ 19.4 V	1063.5 cd/m^2	21.8E-2 cd/A	6.1E-2 lm/W	90 nm

Dodecyloxy-PPE (1dodec)

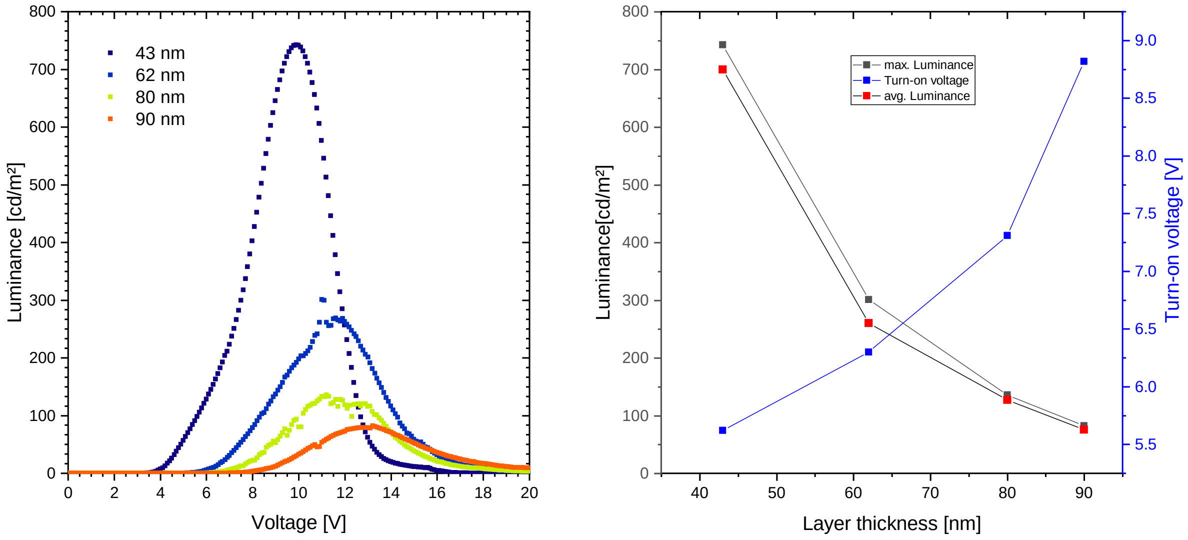


Figure S5. Optimized simple PLED stack and performance metrics for **1dodec**.

Table S2. PLED characteristics for **1dodec**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
Dodecyloxy (1dodec)	5.62 V	742.3 cd/m^2 @ 9.9 V	700.0 cd/m^2	9.7E-2 cd/A	3.1E-2 lm/W	43 nm
	6.30 V	300.9 cd/m^2 @ 11.0 V	260.5 cd/m^2	18.1E-2 cd/A	7.3E-2 lm/W	62 nm
	7.31 V	135.5 cd/m^2 @ 11.2 V	126.9 cd/m^2	14.4E-2 cd/A	5.0E-2 lm/W	80 nm
	8.82 V	82.5 cd/m^2 @ 13.2 V	75.9 cd/m^2	17.3E-2 cd/A	5.4E-2 lm/W	90 nm

Octadecyloxy-PPE (1odec)

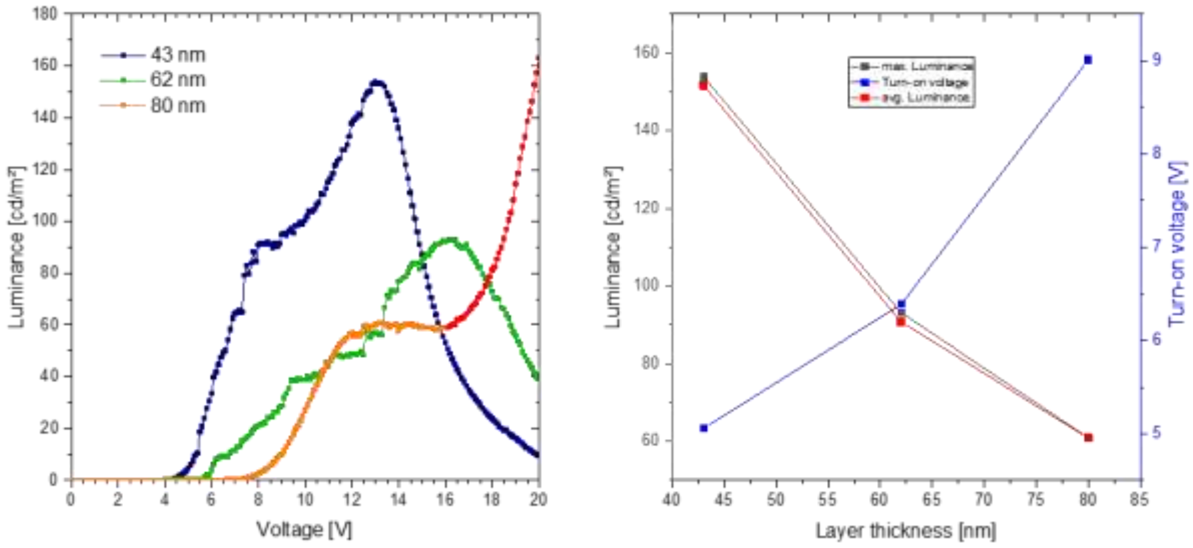


Figure S6. Optimized simple PLED stack and performance metrics for **1odec**.

Table S3. PLED characteristics for **1odec**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
Octadecyloxy (1odec)	5.06 V	153.7 cd/m² @ 13.0 V	151.6 cd/m²	4.4E-2 cd/A	2.6E-2 lm/W	43 nm
	6.39 V	93.1 cd/m² @ 16.4 V	90.7 cd/m²	4.6E-2 cd/A	1.7E-2 lm/W	62 nm
	9.01 V	163.0 cd/m² @ 20.0 V	163.0 cd/m²	9.1E-2 cd/A	3.0E-2 lm/W	80 nm
	9.01 V	60.9 cd/m² @ 13.2 V	60.9 cd/m²	9.1E-2 cd/A	3.0E-2 lm/W	90 nm

Hexyl-PPE (2hex)

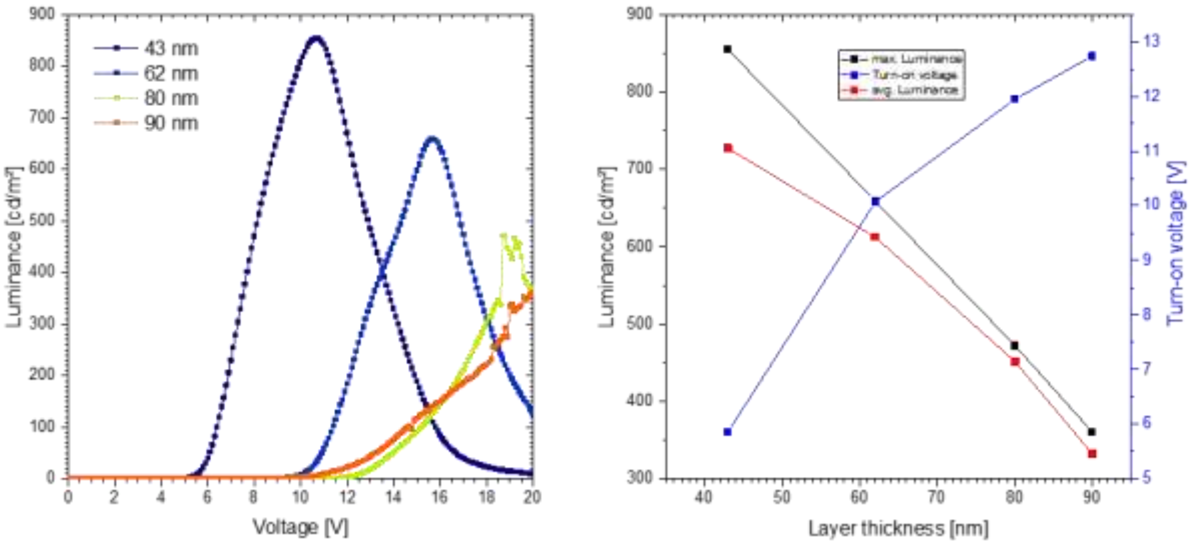


Figure S7. Optimized simple PLED stack and performance metrics for **2hex**.

Table S4. PLED characteristics for **2hex**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
Hexyl (2hex)	5.86 V	854.7 cd/m² @ 10.7 V	726.9 cd/m²	17.1E-2 cd/A	6.3E-2 lm/W	43 nm
	10.07 V	659.3 cd/m² @ 15.7 V	612.6 cd/m²	17.3E-2 cd/A	3.9E-2 lm/W	62 nm
	11.95 V	472.2 cd/m² @ 12.6 V	451.5 cd/m²	15.2E-2 cd/A	3.1E-2 lm/W	80 nm
	12.74 V	360.9 cd/m² @ 20.0 V	332.2 cd/m²	16.8E-2 cd/A	3.8E-2 lm/W	90 nm

Dodecyl-PPE (2dodec)

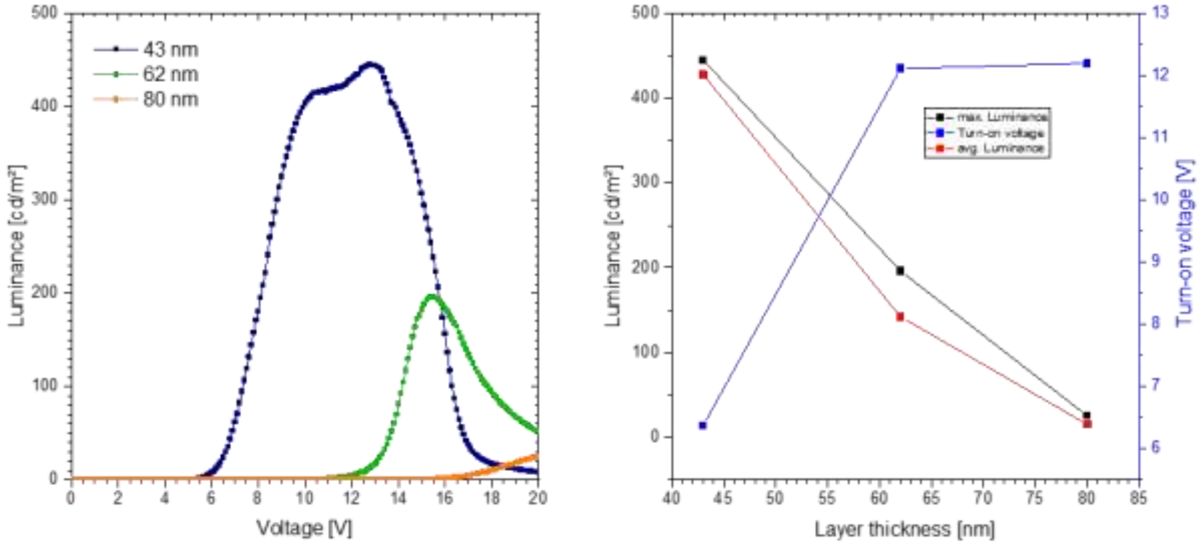


Figure S8. Optimized simple PLED stack and performance metrics for **2dodec**.

Table S5. PLED characteristics for **2dodec**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thicknesses
Dodecyl (2dodec)	6.73 V	444.7 cd/m^2 @ 12.8 V	427.3 cd/m^2	18.5E-2 cd/A	7.7E-2 lm/W	43 nm
	12.11 V	195.9 cd/m^2 @ 15.5 V	142.3 cd/m^2	1.05 cd/A	24.9E-2 lm/W	62 nm
	12.19 V	25.3 cd/m^2 @ 19.9 V	15.3 cd/m^2	24.3 cd/A	4.0E-2 lm/W	80 nm

(rac)-Citronellyloxy-PPE (1racCtr)

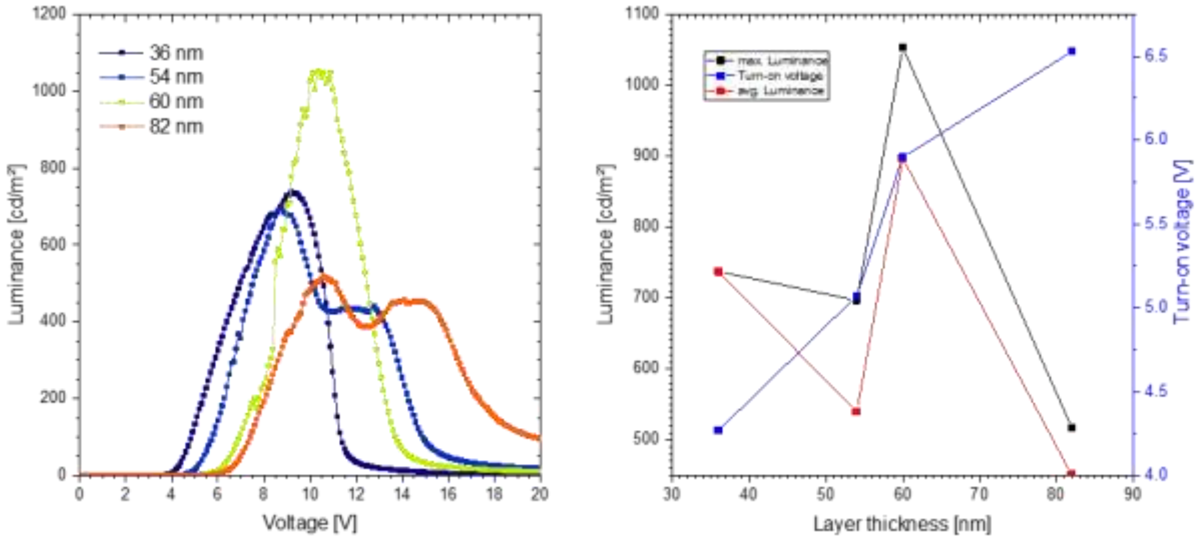


Figure S9. Optimized simple PLED stack and performance metrics for **1racCtr**.

Table S6. PLED characteristics for **1racCtr**.

Material	**Turn-on voltage**	**Max. Luminance**	**Avg. Luminance**	**Avg Efficency**	**Avg. Efficacy**	**Layer Thickness**
(*rac*)-Citronellyloxy (1racCtr)	4.27 V	737.5 cd/m² @ 10.7 V	737.5 cd/m²	22.9E-2 cd/A	14.6E-2 lm/W	36 nm
	5.07 V	696.7 cd/m² @ 8.7 V	539.9 cd/m²	20.9E-2 cd/A	10.5E-2 lm/W	54 nm
	5.90 V	1053.8 cd/m² @ 5.9 V	896.9 cd/m²	43.9E-2 cd/A	19.4E-2 lm/W	60 nm
	6.53 V	517.0 cd/m² @ 10.6 V	450.7 cd/m²	21.6E-2 cd/A	8.9E-2 lm/W	82 nm

(*S*)-(*rac*)-Citronellyloxy-PPE (1SracCtr)

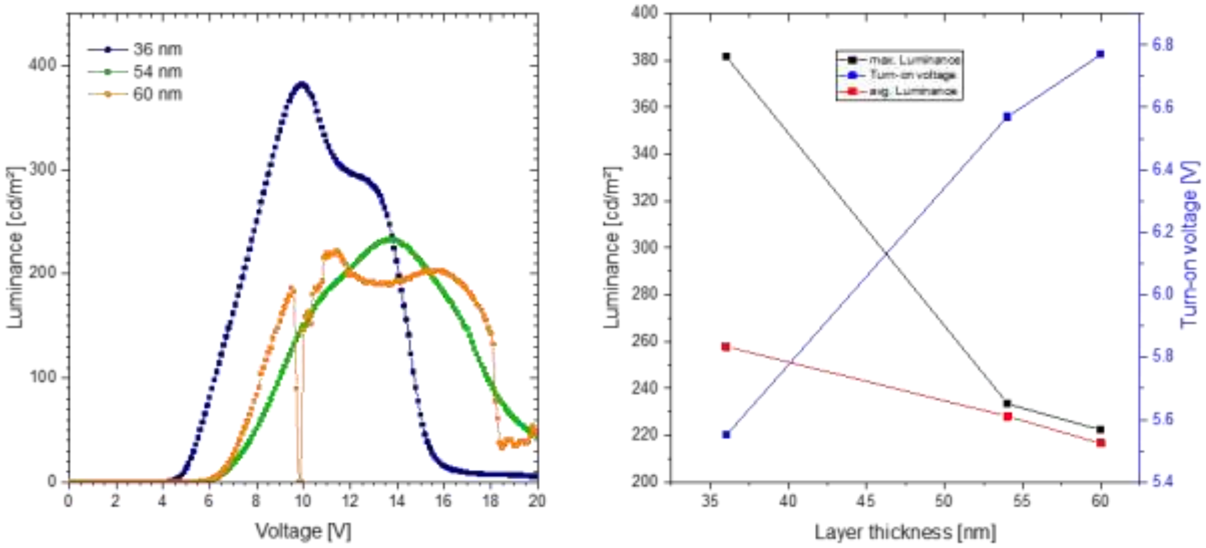


Figure S 10. Optimized simple PLED stack and performance metrics for **1SracCtr**.

Table S7. PLED characteristics for **1SracCtr**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
(*S*)-(*rac*)-Citronellyloxy (1racCtr)	5.55 V	381.8 cd/m² @ 10.0 V	257.8 cd/m²	6.2E-2 cd/A	3.0E-2 lm/W	36 nm
	6.57 V	233.4 cd/m² @ 13.9 V	228.1 cd/m²	9.5E-2 cd/A	4.0E-2 lm/W	54 nm
	6.77 V	222.3 cd/m² @ 11.4 V	216.5 cd/m²	12.4E-2 cd/A	4.5E-2 lm/W	60 nm

(*S*)-Citronellyloxy-PPE (1SCtr)

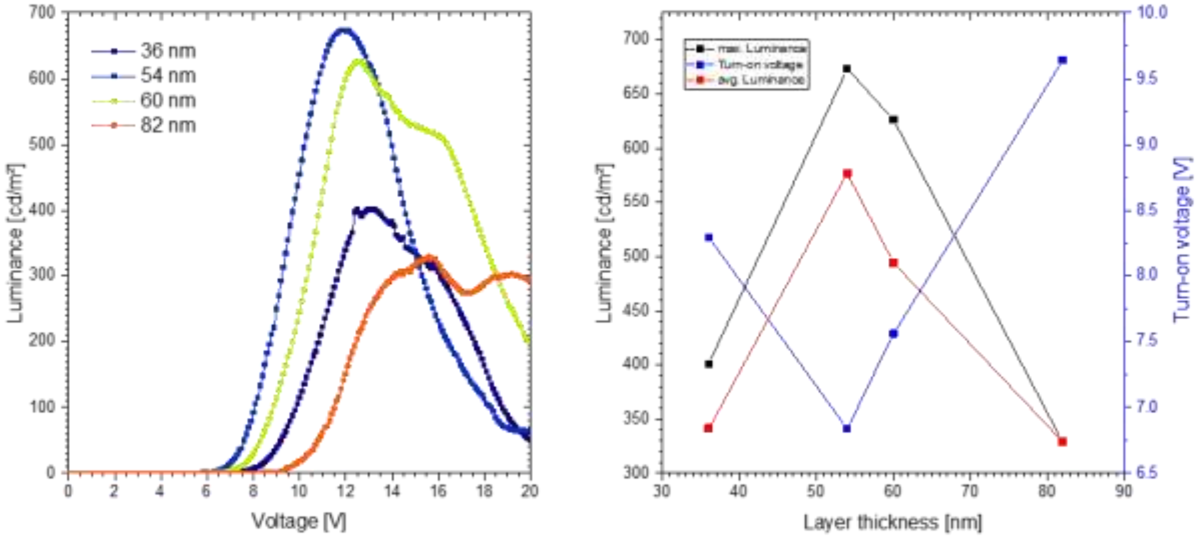


Figure S11. Optimized simple PLED stack and performance metrics for **1SCtr**.

Table S8. PLED characteristics for **1SCtr**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
(*S*)-Citronellyloxy (1SCtr)	8.29 V	400.9 cd/m² @ 13.1 V	341.2 cd/m²	17.9E-2 cd/A	5.6E-2 lm/W	36 nm
	6.84 V	673.5 cd/m² @ 11.8 V	576.7 cd/m²	14.4E-2 cd/A	5.2E-2 lm/W	54 nm
	7.56 V	626.2 cd/m² @ 12.5 V	494.2 cd/m²	16.8E-2 cd/A	5.6E-2 lm/W	60 nm
	9.64 V	328.7 cd/m² @ 15.6 V	328.7 cd/m²	15.3E-2 cd/A	3.0E-2 lm/W	82 nm

Farnesanyloxy-PPE (1Fs)

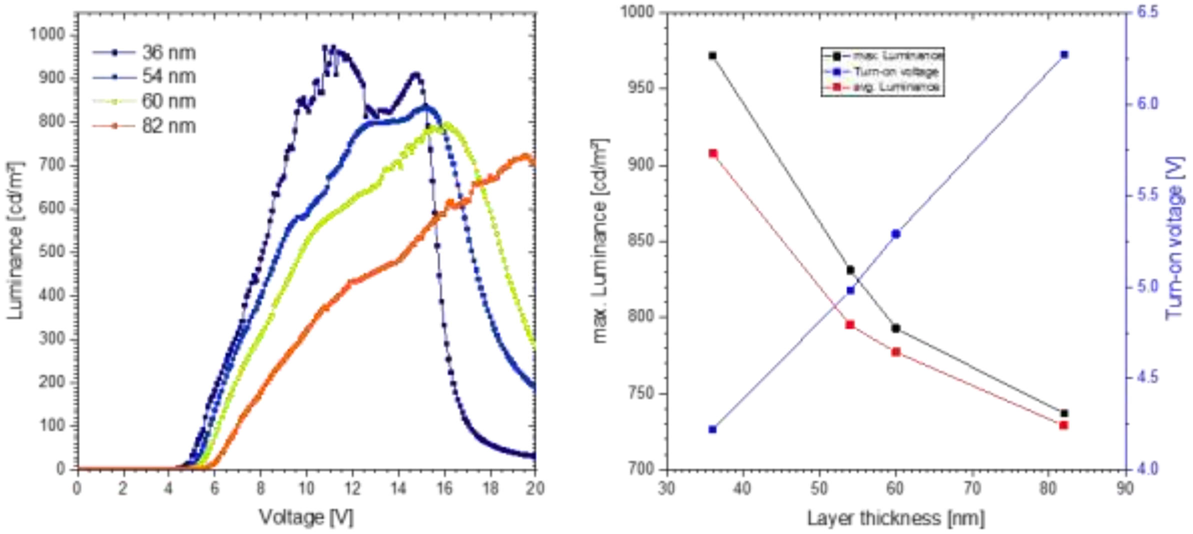


Figure S12. Optimized simple PLED stack and performance metrics for **1Fs**.

Table S9. PLED characteristics for **1Fs**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
Farnesanyloxy (1Fs)	4.22 V	971.7 cd/m² @ 11.2 V	907.4 cd/m²	26.5E-2 cd/A	16.6E-2 lm/W	36 nm
	4.98 V	831.3 cd/m² @ 15.2 V	795.1 cd/m²	29.0E-2 cd/A	14.5E-2 lm/W	54 nm
	5.29 V	792.8 cd/m² @ 16.1 V	777.0 cd/m²	38.2E-2 cd/A	19.3E-2 lm/W	60 nm
	6.27 V	736.8 cd/m² @ 13.7 V	729.1 cd/m²	45.8E-2 cd/A	18.9E-2 lm/W	82 nm

Phytanyloxy-PPE (1Pt)

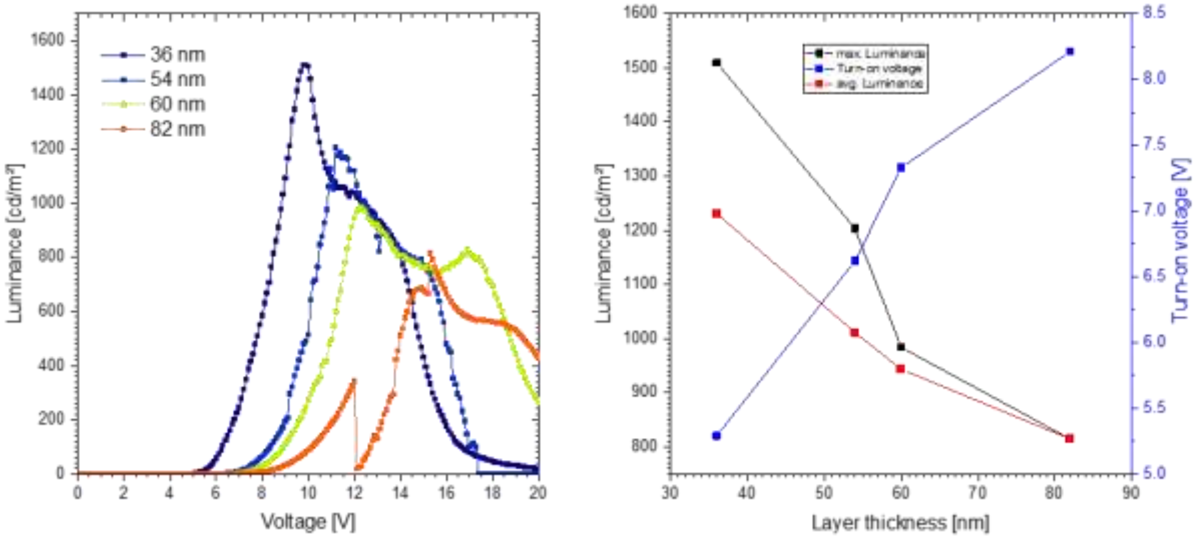


Figure S13. Optimized simple PLED stack and performance metrics for **1Fs**.

Table S10. PLED characteristics for **1Pt**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
Phytanyloxy (1Pt)	5.29 V	1509.2 cd/m² @ 9.8 V	1230.7 cd/m²	38.4E-2 cd/A	17.3E-2 lm/W	36 nm
	6.62 V	1203.7 cd/m² @ 11.2 V	1011.5 cd/m²	36.8E-2 cd/A	12.2E-2 lm/W	54 nm
	7.33 V	984.1 cd/m² @ 12.3 V	943.0 cd/m²	42.1E-2 cd/A	14.0E-2 lm/W	60 nm
	8.21 V	814.7 cd/m² @ 15.3 V	814.7 cd/m²	61.9E-2 cd/A	17.7E-2 lm/W	82 nm

2-Ethylhexyloxy-PPE (1Ethex)

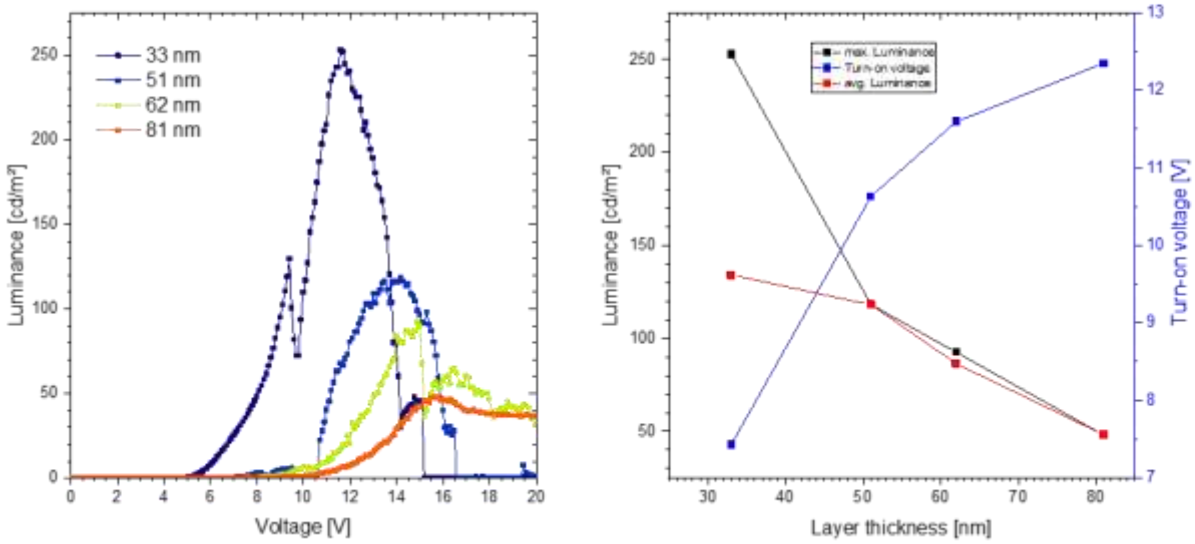


Figure S14. Optimized simple PLED stack and performance metrics for **1Ethex**.

Table S11. PLED characteristics for **1Ethex**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
2-Ethylhexyloxy (1Ethex)	7.43 V	252.9 cd/m² @ 11.6 V	134.1 cd/m²	3.1E-2 cd/A	1.3E-2 lm/W	33 nm
	10.63 V	1118.3 cd/m² @ 14.2 V	118.3 cd/m²	3.4E-2 cd/A	0.8E-2 lm/W	51 nm
	11.60 V	92.5 cd/m² @ 14.9 V	86.5 cd/m²	2.0E-2 cd/A	0.4E-2 lm/W	62 nm
	12.35 V	48.1 cd/m² @ 15.7 V	48.1 cd/m²	4.9E-2 cd/A	0.8E-2 lm/W	81 nm

4-Heptanyloxy-PPE (1hpt)

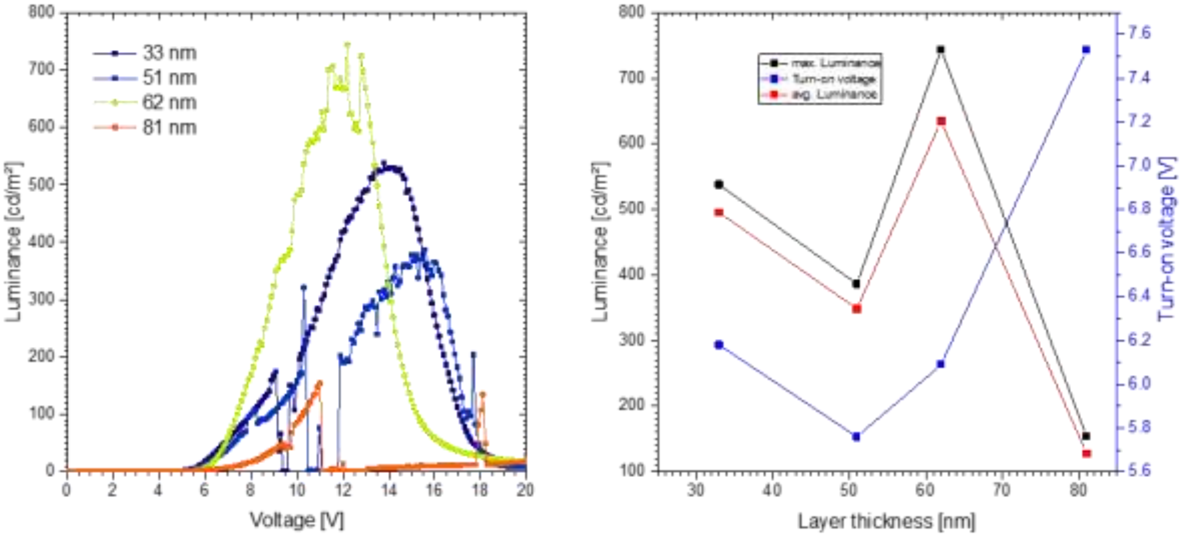


Figure S15. Optimized simple PLED stack and performance metrics for **1hpt**.

Table S12. PLED characteristics for **1hpt**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
4-Heptanyloxy (1hpt)	6.18 V	537.8 cd/m² @ 13.8 V	494.8 cd/m²	12.2E-2 cd/A	5.6E-2 lm/W	33 nm
	5.76 V	386.3 cd/m² @ 15.6 V	348.6 cd/m²	12.9E-2 cd/A	5.9E-2 lm/W	51 nm
	6.09 V	744.1 cd/m² @ 12.2 V	634.1 cd/m²	32.9E-2 cd/A	12.5E-2 lm/W	62 nm
	7.53 V	153.8 cd/m² @ 11.0 V	127.3 cd/m²	13.7E-2 cd/A	4.8E-2 lm/W	81 nm

5-Nonanyloxy-PPE (1non)

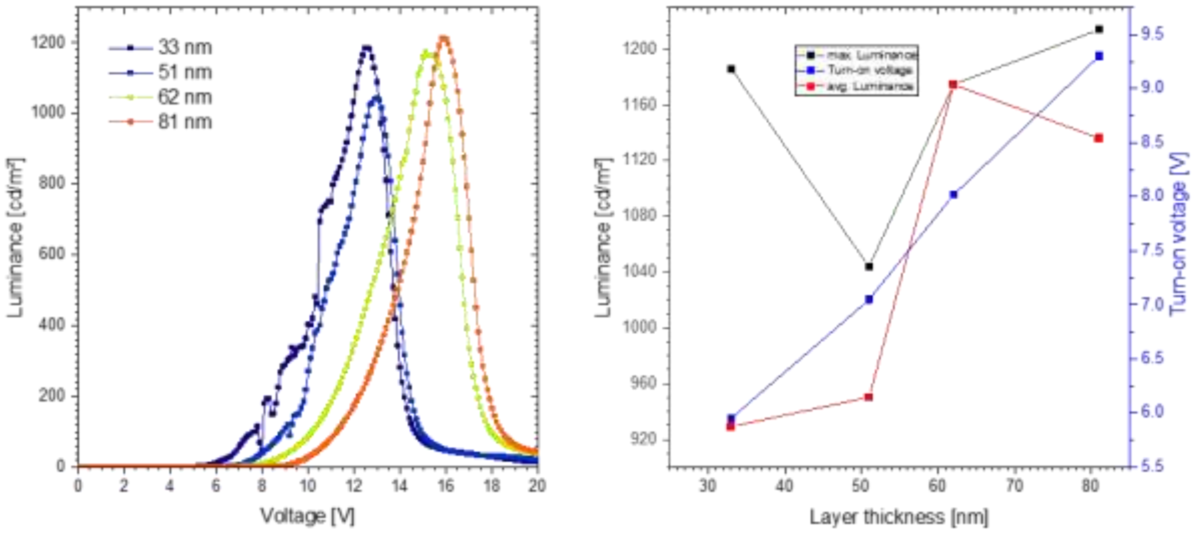


Figure S16. Optimized simple PLED stack and performance metrics for **1non**.

Table S13. PLED characteristics for **1non**.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
5-Nonanyloxy (1non)	5.95 V	1185.9 cd/m² @ 12.5 V	929.3 cd/m²	19.4E-2 cd/A	9.7E-2 lm/W	33 nm
	7.05 V	1043.9 cd/m² @ 13.0 V	950.3 cd/m²	24.1E-2 cd/A	10.1E-2 lm/W	51 nm
	8.02 V	1174.9 cd/m² @ 15.1 V	1174.9 cd/m²	29.3E-2 cd/A	10.1E-2 lm/W	62 nm
	9.30 V	1214.1 cd/m² @ 15.9 V	1214.1 cd/m²	31.9E-2 cd/A	9.6E-2 lm/W	81 nm

Device processing for electron injection-performance relationship in PLEDS

For the fabrication of the devices, glass substrates patterned with 190 nm ITO electrodes (Kintec©, Hong Kong) were cleaned subsequently in ultrasonic baths at 40°C of acetone and 2-propanol. After drying, the substrates were O$_2$ plasma treated for 5 min. A 40 nm layer of polyethylenedioxythiophene doped with poly(styrenesulfonate) (PEDOT:PSS) was filtered (Syringe filter VWR collection, PES membrane, pore size 0.45 µm, diameter 25 mm) and coated on top (2500 rpm, 3000 rpm/s, 45 s). The films were annealed for 3 min at 200 °C and 15 min at 120 °C. Then, the active layer PPEs were filtered (Syringe filter VWR collection, PTFE membrane, pore size 0.45 µm, diameter 25 mm) and spin-coated (4000 rpm, 1000 rpm/s, 30 s) on top from different concentrations of polymer in toluene solution to obtain films of different thicknesses. After drying of the sample overnight under vacuum at room temperature, a 20 nm thick LiF layer was deposited by thermal evaporation at a pressure of 7E-6 mbar at a rate of 2 Ås^{-1}, followed by deposition of a 100 nm thick Al electrode evaporated at 6 Ås^{-1}. The devices were encapsulation with UV hardening adhesive (20 min) and a cover glass.

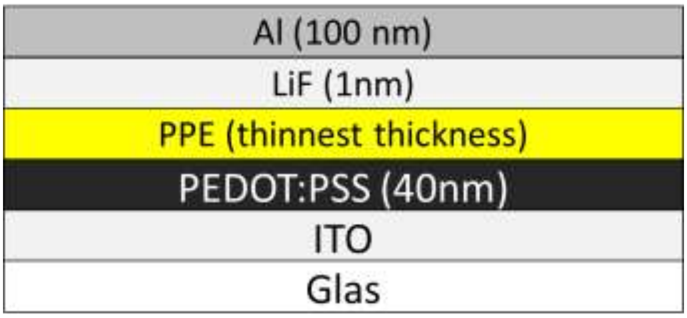


Figure S17. PLED architecture for performance test without electron injectionlayer.

Results for electron injection-performance relationship in PLEDS

Table S14. PLED characteristics for simple PPE stack without electron injection layer TPBi.

Material	Turn-on voltage	Max. Luminance	Avg. Luminance	Avg Efficency	Avg. Efficacy	Layer Thickness
Hexyloxy (1hex)	5.72 V	1140.3 cd/m^2 @ 13.5 V	1009. 8 cd/m^2	1.323 cd/A	0.627 lm/W	43 nm
Dodecyloxy (1dodec)	5.63 V	315.0 cd/m^2 @ 17.9 V	288.4 cd/m^2	0.333 cd/A	0.186 lm/W	43 nm
Octadecyloxy (1odec)	6.60 V	166.8 cd/m^2 @ 10.9 V	140.0 cd/m^2	0.362 cd/A	0.362 lm/W	43 nm
Hexyl (2hex)	9.00 V	400.8 cd/m^2 @ 17.4 V	356.8 cd/m^2	1.053 cd/A	0.341 lm/W	43 nm
Dodecyl (2dodec)	8.33 V	69.7 cd/m^2 @ 11.0 V	66.2 cd/m^2	1.498 cd/A	0.529 lm/W	43 nm
(*rac*)-Citronellyloxy (1racCtr)	5.98 V	581.3 cd/m^2 @ 9.7 V	444.7 cd/m^2	0.663 cd/A	0.315 lm/W	36 nm
(*S*)-(*rac*)-Citronellyloxy (1SracCtr)	5.93 V	253.4 cd/m^2 @ 14.5 V	211.56 cd/m^2	0.337 cd/A	0.164 lm/W	36 nm
(*S*)-Citronellyloxy (1SCtr)	6.01 V	322.8 cd/m^2 @ 9.7 V	282.2 cd/m^2	0.457 cd/A	0.220 lm/W	36 nm
Farnesanyloxy (1Fs)	5.94 V	560.0 cd/m^2 @ 8.9 V	440.4 cd/m^2	1.618 cd/A	0.753 lm/W	36 nm
Phytanyloxy (1Pt)	6.50 V	279.3 cd/m^2 @ 11.9 V	246.3 cd/m^2	1.581 cd/A	0.709 lm/W	36 nm
2-Ethylhexyloxy (1Ethex)	6.43 V	1102.4 cd/m^2 @ 6.9 V	961.4 cd/m^2	0.433 cd/A	0.204 lm/W	33 nm
4-Heptanyloxy (1hpt)	4.79 V	636.0 cd/m^2 @ 11.9 V	536.1 cd/m^2	0.761 cd/A	0.480 lm/W	33 nm
5-Nonanyloxy (1non)	5.12 V	1260.1 cd/m^2 @ 13.1 V	1094.6 cd/m^2	1.400 cd/A	0.787 lm/W	33 nm

OLED electroluminescence spectra

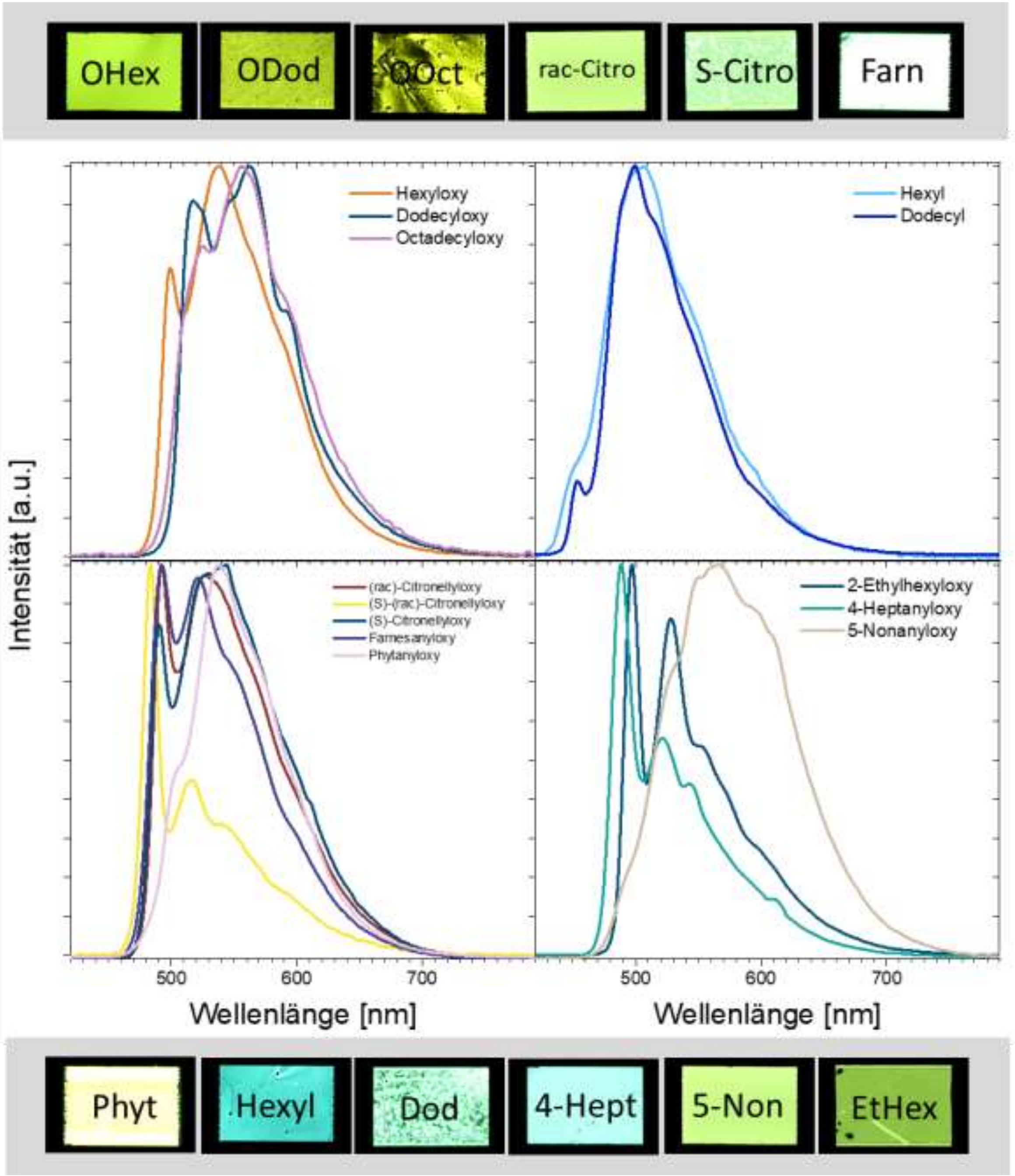


Figure S18. Electroluminescence spectra of PPE PLEDs and pictures of working devices.

UV-vis and emission spectra of PPE films

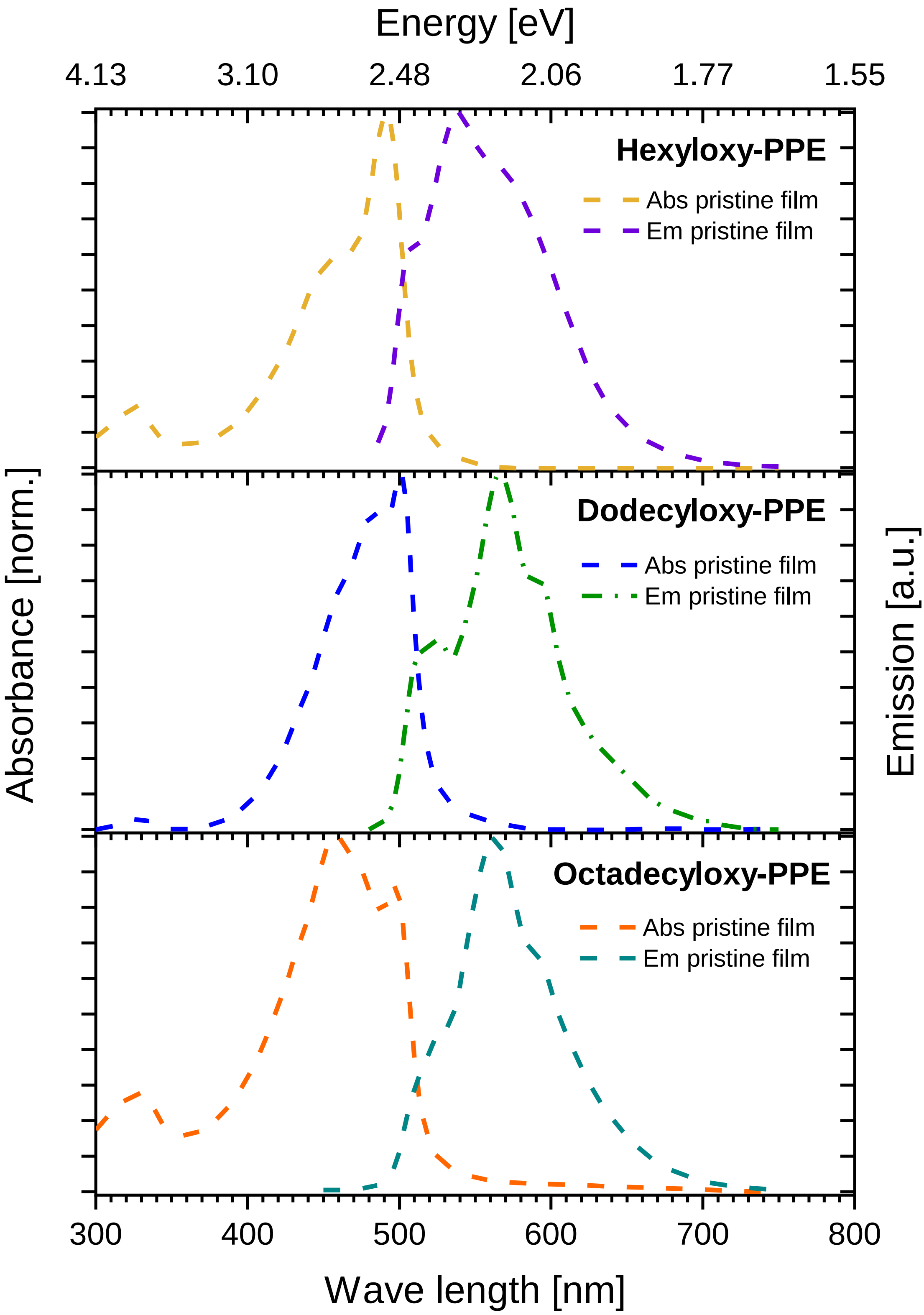


Figure S19. UV-vis and emission spectra of pristine films of **1hex**, **1dodec** and **1odec**.

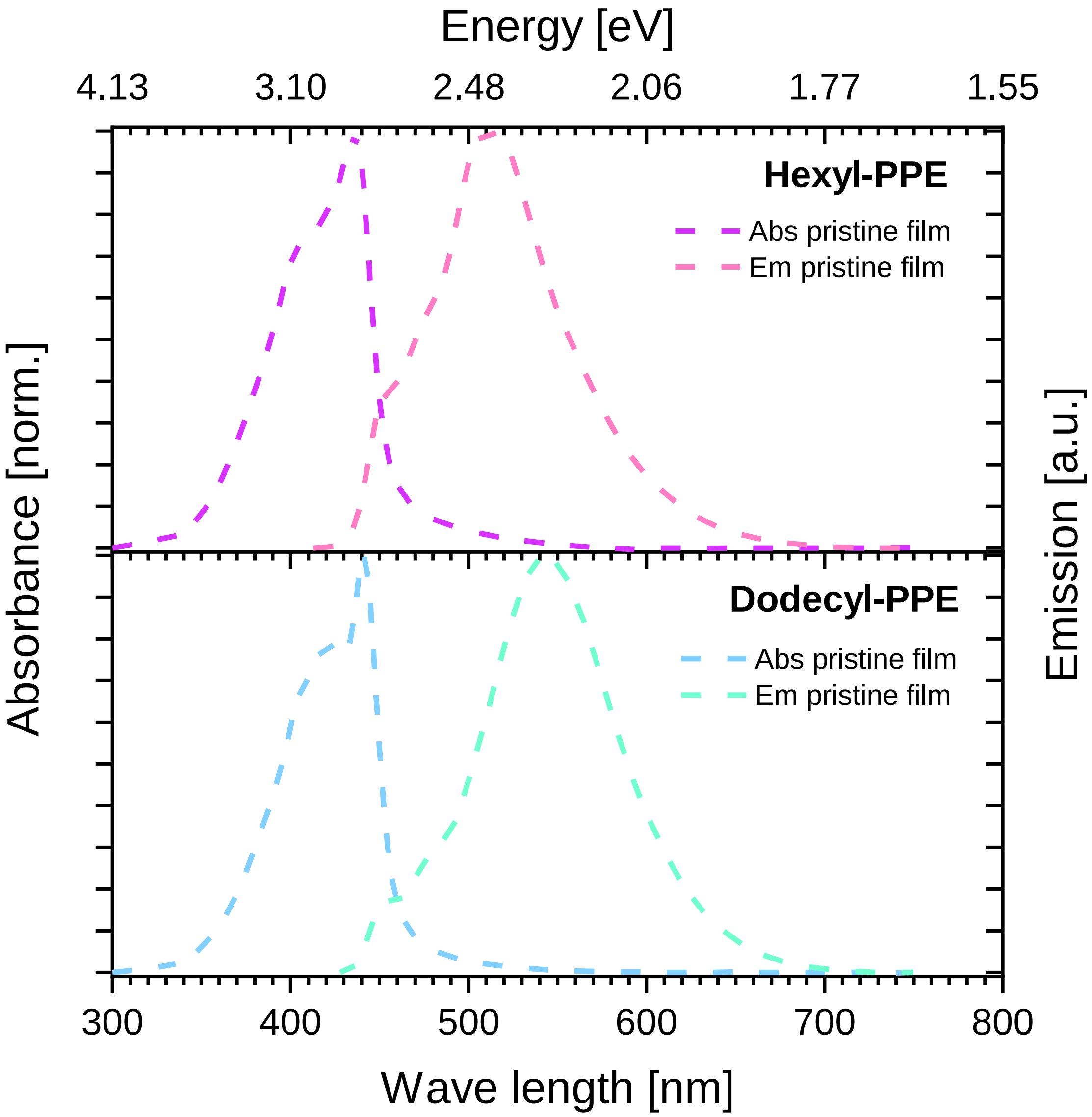


Figure S20. UV-vis and emission spectra of pristine films of **2hex** and **2dodec**.

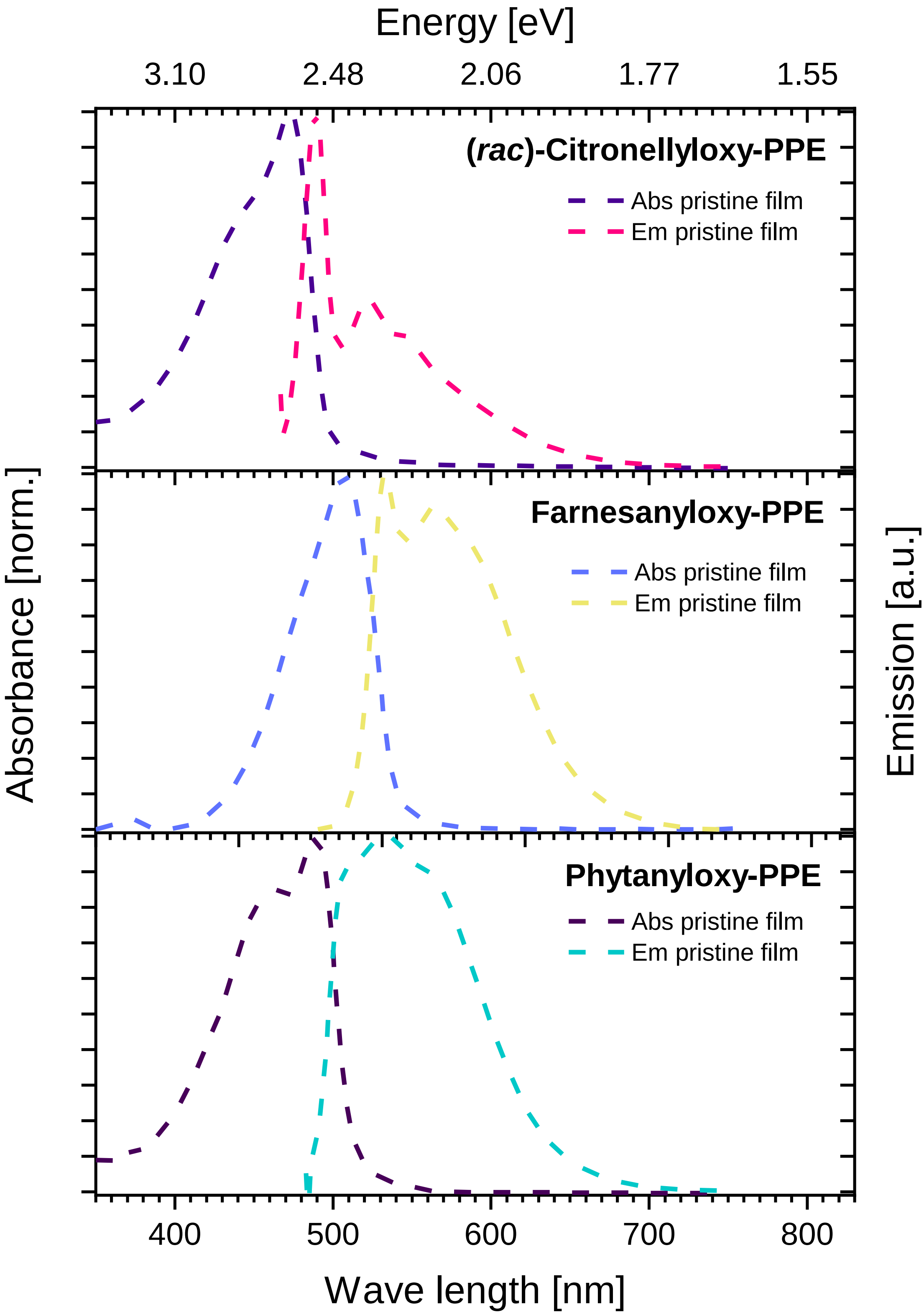


Figure S21. UV-vis and emission spectra of pristine films of **1racCtr**, **1Fs** and **1Pt**.

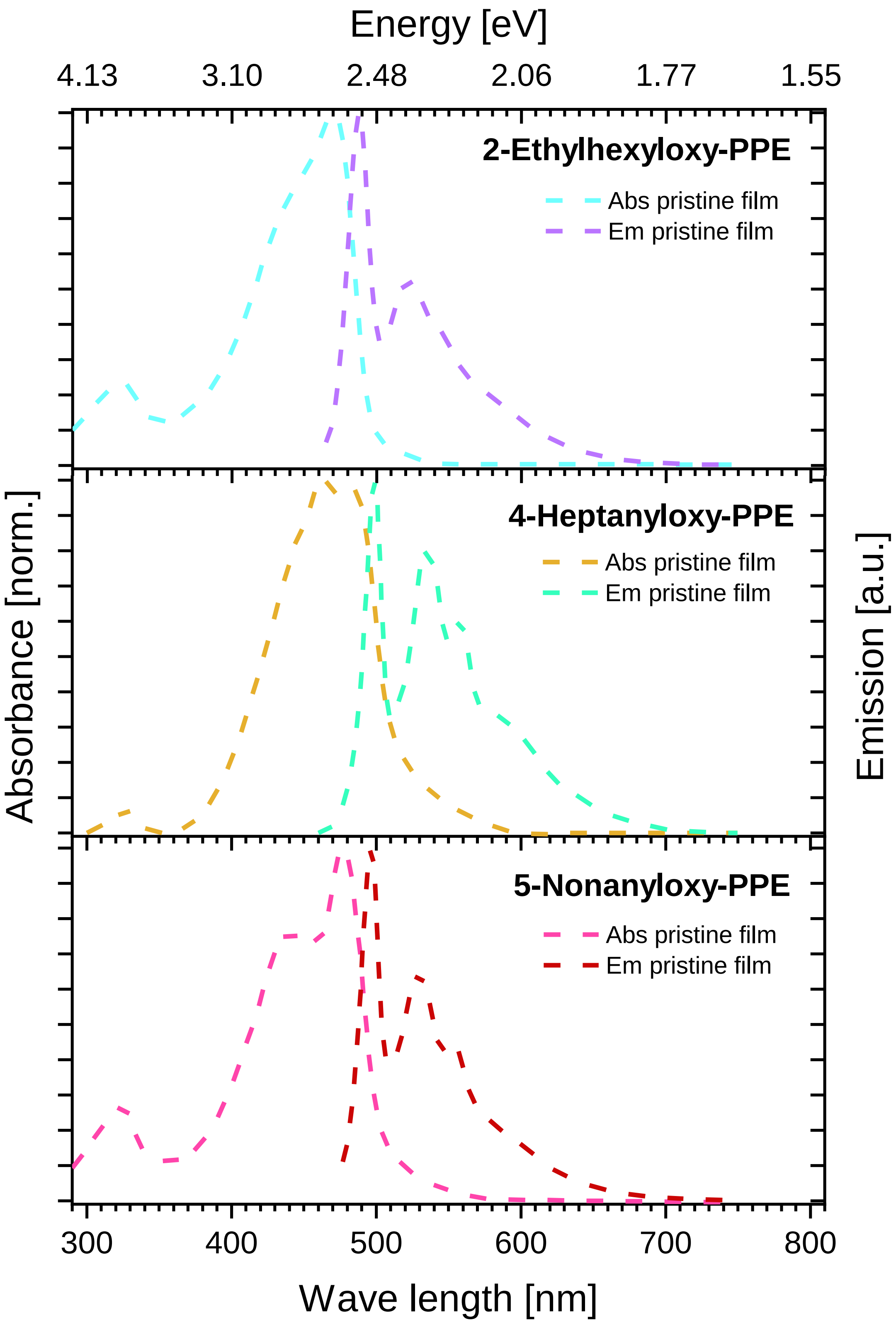


Figure S22. UV-vis and emission spectra of pristine films of **1Ethex**, **1hpt** and **1non**.

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