Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

A Printable Thermally Activated Delayed Fluorescent Polymer Light Emitting Diode

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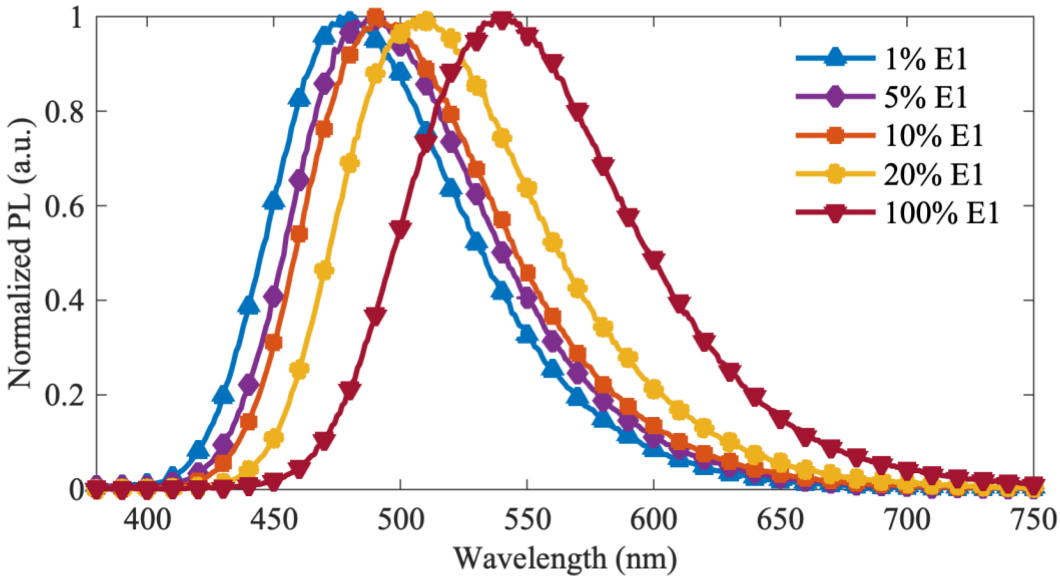


Figure S1. Photoluminescence spectra of pure **E1** and **E1**:PMMA with different weight percentages of **E1**.

Table S2. Averages and best performance parameters of OLEDs.

	P1 OLED	***P5 OLED***
L_{MAX} (cd m^{-2})	2487	4690
L_{AVG} (cd m^{-2})	2087 ± 262	4219 ± 357
EQE_{MAX} (%)	0.24	1.05
EQE_{AVG} (%)	0.22 ± 0.02	0.54 ± 0.31
CE_{MAX} (cd A^{-1})	0.71	3.46
CE_{AVG} (cd A^{-1})	0.65 ± 0.06	1.78±1.01
$V_{turn\text{-}on\text{-}AVG}$ (V)	8.12 ± 0.08	8.1±0.2

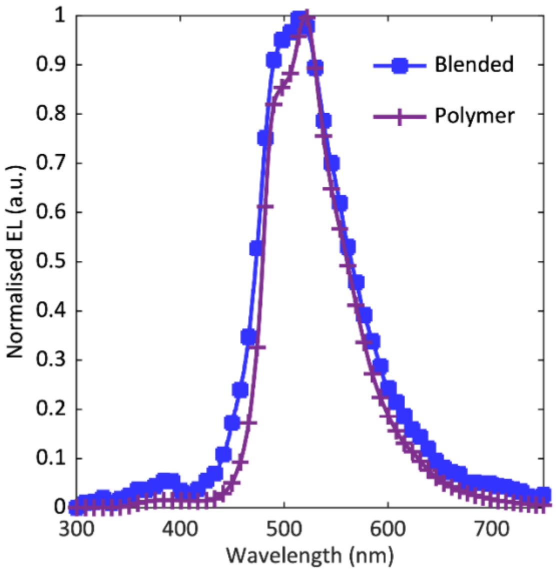


Figure S3. Electroluminescence spectra comparison between a blended EML ((**E1**(5mol%):PMMA)(30 wt%):26DCzPPy) and a polymer EML (**P5**(30wt%):26DCzPPy) OLED. The structure of the OLEDs was ITO/PEDOT:PSS/EML/TPBi/Ba/Ag.

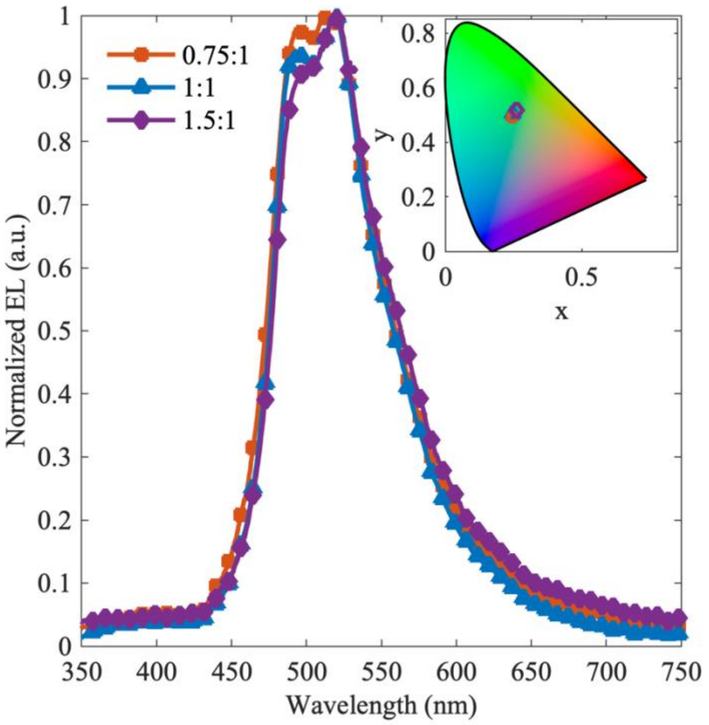


Figure S4. Electroluminescence spectra of the standard (**P5**(30wt%):26DCzPPy) OLEDs with different thickness ratios of EML to ETL, whilst keeping the overall device thickness constant. Insert of CIE coordinates (CIE: 0.25, 0.59 for 0.75:1, 0.25,0.50 for 1:1 and 0.26, 0.56 for 1.5:1).

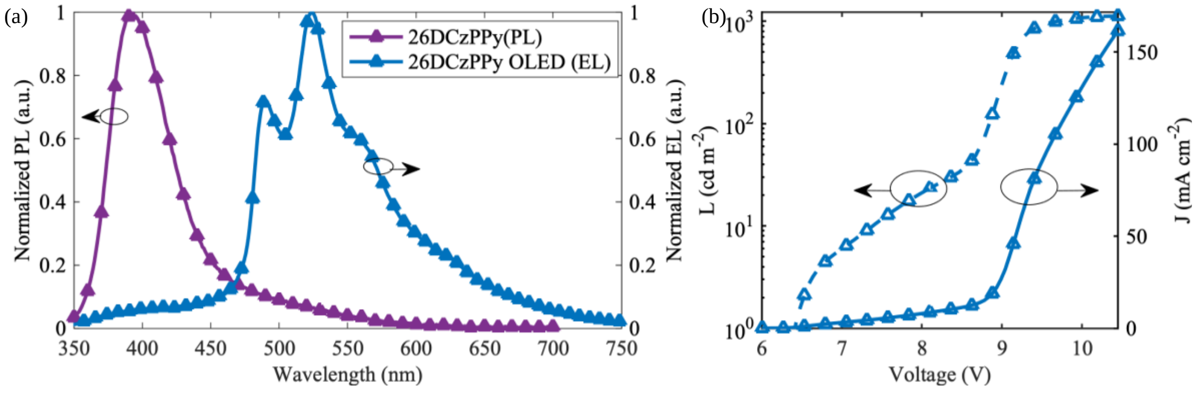


Figure S5. (a) Photoluminescence spectrum of 26DCzPPy and electroluminescence spectrum of OLED with structure ITO/PEDOT:PSS/26DCzPPy/TPBi/Ba/Ag (CIE: 0.31, 0.52). (b) Current density and luminance with respect to voltage for ITO/PEDOT:PSS/26DCzPPy/TPBi/Ba/Ag (Emitter-Free) OLED. (Pixel sizes for these OLEDs were 10 mm^2).

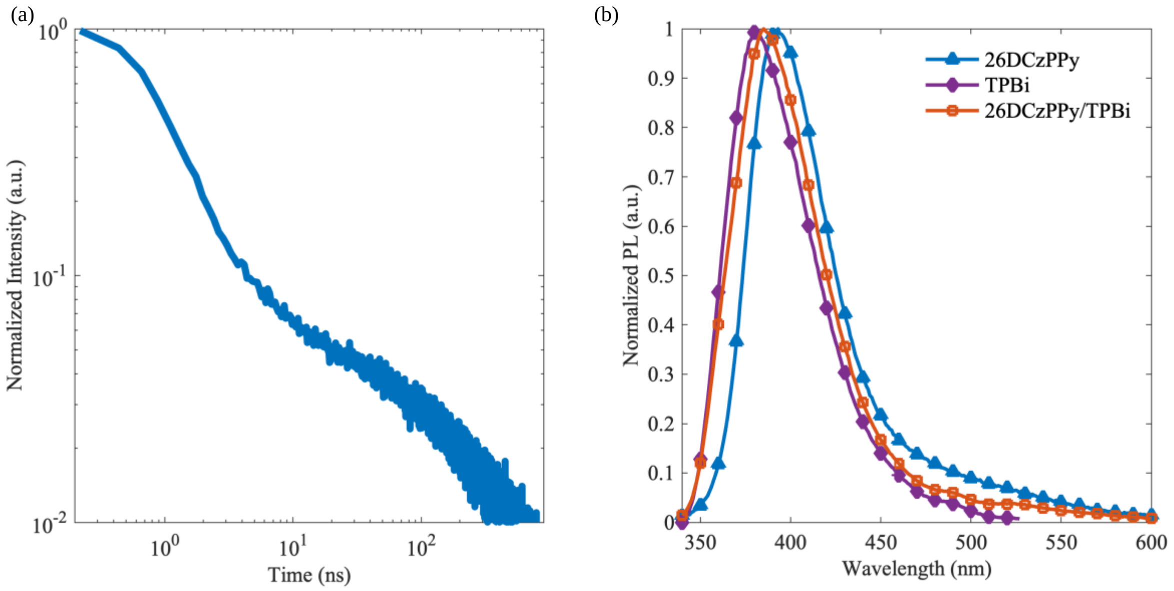


Figure S6. (a) Time resolved photoluminescence of TPBi:26DCzPPy, and (b) Photoluminescence of TPBi, 26DCzPPy and a TPBI/26DCzPPy film.

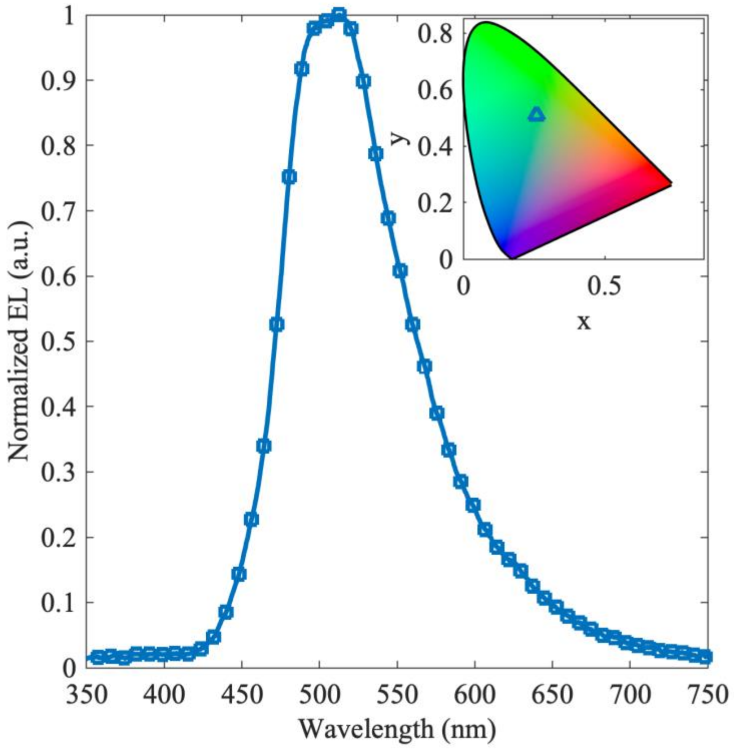


Figure S7. Electroluminescence spectrum of a standard OLED (shown in figure 4) without a TPBi layer. Insert of CIE coordinates (CIE: 0.26, 0.48).

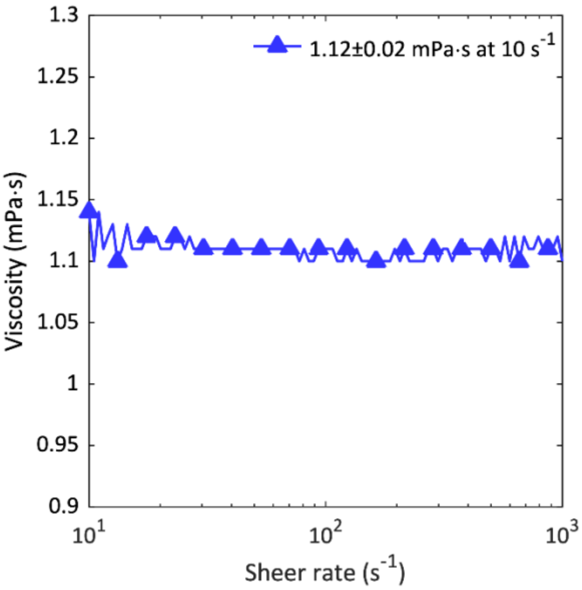


Figure S8. Viscosity measurements of **P5**(30%):26DCzPPy in 10 mg mL$_{-1}$ of 5 vol% propylene carbonate and 95 vol% anisole.

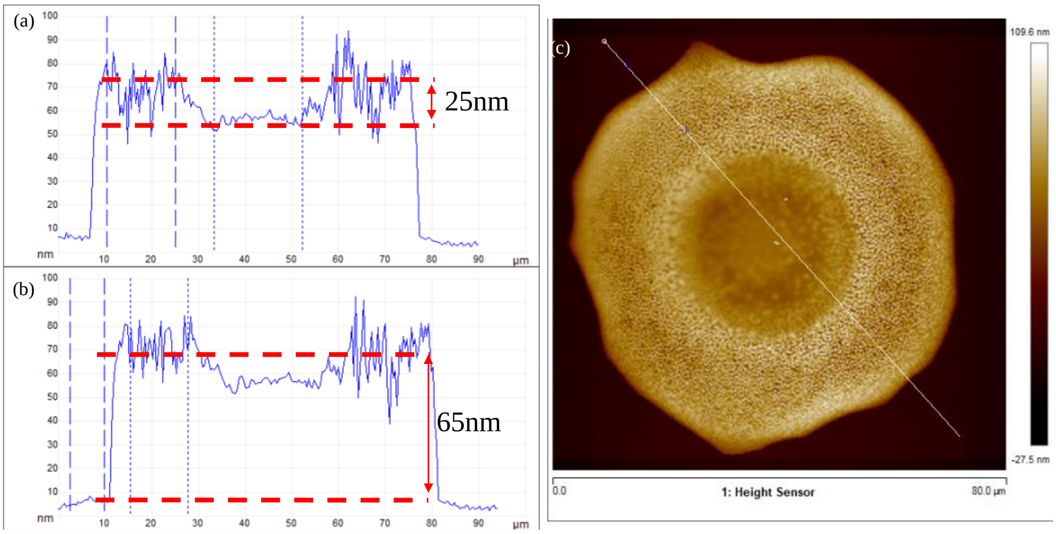


Figure S9. Cross-sectional height variation on the printed droplet. (a) Difference in height between edge and mid-section of droplet. (b) Height of the highest part of the droplet. (c) Cross section for the height profile in (a) and (b).

Photophysical calculations

The equations used to determine the prompt (Φ_{PF}) and delayed fluorescent (Φ_{DF}) yields and the reverse intersystem crossing rate (k_{rISC}) used the method shown by Dias, F. B. et al. (2017).[1] Firstly, the TRPL curves were fitted using a triple exponential fit (**Equation (1)**) where the delayed component is determine from the second two components (**Equation (2)**) . From TRPL fitting the Φ_{DF} and Φ_{PF} components were determined using **Equation (3)**. Using this ratio and the measured Φ_F, the values for Φ_{DF} and Φ_{PF} were found. **Equation (4)** was used to determine the k_{rISC}.

$$\boldsymbol{I(t)} = A\,e^{-\frac{1}{\tau_1}(\boldsymbol{t})} + Be^{-\frac{1}{\tau_2}(\boldsymbol{t})} + Ce^{-\frac{1}{\tau_3}(\boldsymbol{t})} \qquad (\mathbf{1})$$

$$\boldsymbol{\tau_{DF}} = \frac{B\tau_2^2 + C\tau_3^2}{B\tau_2 + C\tau_2} \qquad (\mathbf{2})$$

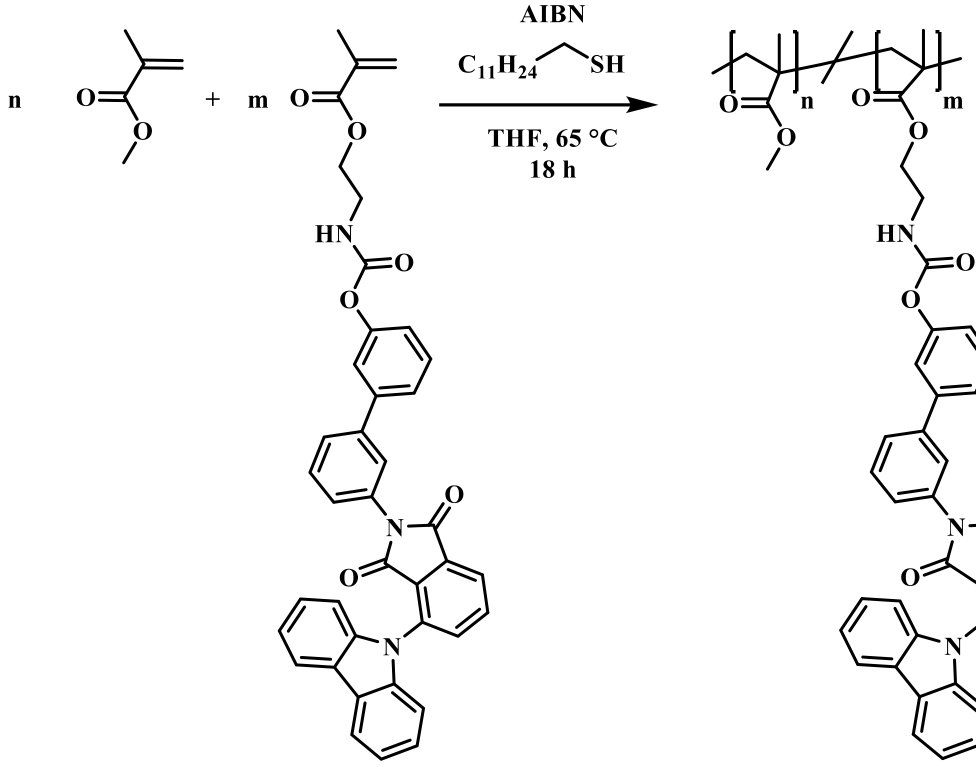
$$\frac{\boldsymbol{\Phi_{DF}}}{\boldsymbol{\Phi_{PF}}} = \frac{B\tau_2 + C\tau_2}{A\tau_1} \qquad (\mathbf{3})$$

$$\boldsymbol{\kappa_{rISC}} = \frac{1}{\tau_{DF}}\left(\frac{\Phi_{PF} + \Phi_{DF}}{\Phi_{PF}}\right) \qquad (\mathbf{4})$$

Polymer synthesis

The polymer was synthesized in a free radical polymerization of MMA and the emitter methacrylate monomer in a feed ratio of 95:5 using azobisisobutyronitrile (AIBN) as a thermally decomposing radical initiator. The content of the emitter in the final building block was confirmed by ^{1}H-NMR spectroscopy.

P5:



M1 **P5**

The emitter methacrylate monomer **M1** was synthesized as reported in the literature.[2]

Methyl methacrylate and THF were passed over basic alumina prior to utilization. The emitter methacrylate monomer **M1** (96.7 mg, 0.15 mmol, 5 eq.) and AIBN (5.0 mg, 0.03 mmol, 1 eq.) were carefully weighed in a dry headspace vial. Methyl methacrylate (308 µL, 289.6 mg, 2.9 mmol, 95 eq.), dodecane-1-thiol (7.3 µL, 6.2 mg, 0.03 mmol, 1 eq.) and THF (2 mL) were added, the vial sealed airtight and degassed by purging with argon for 5 min. The polymerization mixture was then placed in a preheated oil bath and stirred at 65 °C for 18 h. The polymerization was quenched by opening to oxygen and cooling the mixture to -18 °C. Afterwards, the polymer was precipitated in ice-cold methanol (10% water). After filtration the yellow powder was dried in vacuo (yield: 380 mg, 95%).

SEC (THF): M_n = 6 800 g mol^{-1}, M_w = 11 100 g mol^{-1}, $Đ$ = 1.62 (p(MMA) calibration)

^{1}H-NMR (400 MHz, CD_2Cl_2) δ [ppm] = 8.21-8.15 (m, 2H, Ar-H), 8.15 – 8.11 (m, 1H, Ar-H), 8.09 – 8.03 (m, 1H, Ar-H), 8.00– 7.95 (m, 1H, Ar-H), 7.66 -7.58 (m, 2H, Ar-H), 7.57 - 7.51 (m, 1H, Ar-H), 7.48 – 7.29 (m, 8H, Ar-H), 7.27 - 7.21 (m, 2H, Ar-H), 7.17 - 7.09 (m, 1H, Ar-H), 4.19 - 4.02 (m, 2H, CH_2-O), 3.58 (m, 66H, CH_3-O p(MMA)), 2.53 – 2.40 (m, 2H, CH_2), 2.06 - 1.75 (m, 38H, CH_3 p(MMA)), 1.08 - 1.53 (m, 20H, p(MMA)), 0.99 (s, 23H, p(MMA)), 0.92 – 0.64 (m, 40H, p(MMA)).

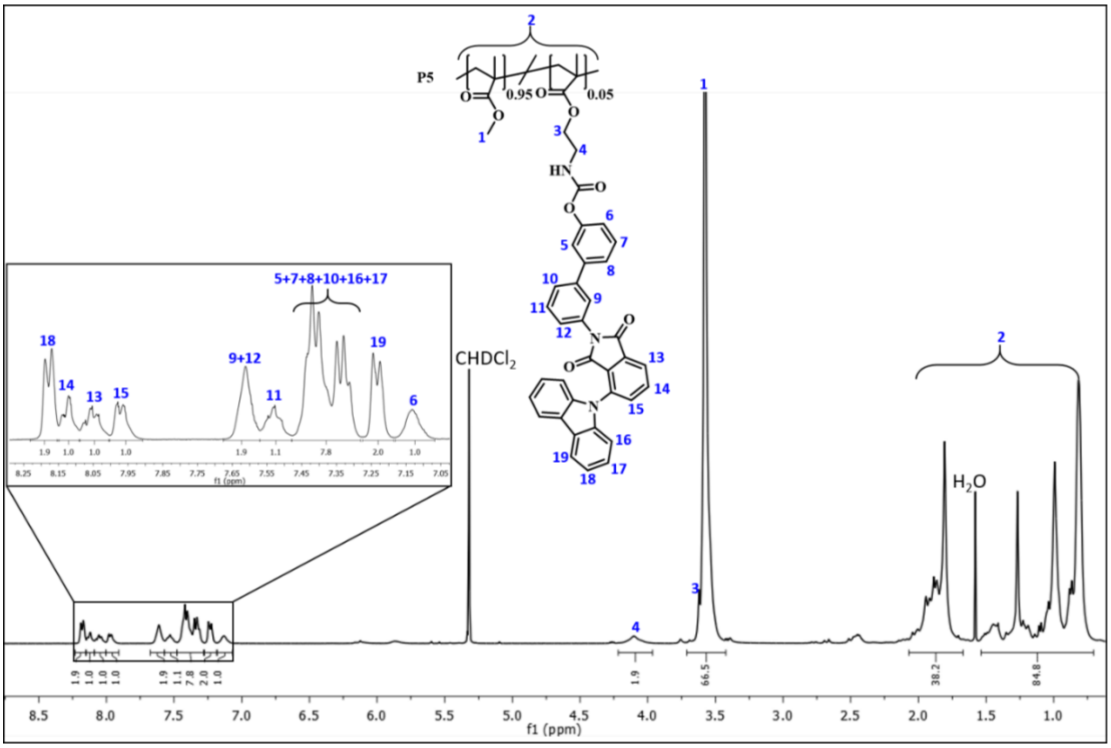


Figure S10. ^{1}H-NMR spectrum of **P5** in CD_2Cl_2.

P1:

Methyl methacrylate and THF were passed over basic alumina prior to utilization. The emitter methacrylate monomer **M1** (19.3 mg, 0.03 mmol, 1 eq.) and AIBN (5.0 mg, 0.03 mmol, 1 eq.) were carefully weighed in a dry headspace vial. Methyl methacrylate (321 µL, 301.8 mg, 3.0 mmol, 99 eq.), dodecane-1-thiol (7.3 µL, 6.2 mg, 0.03 mmol, 1 eq.) and THF (2 mL) were added, the vial sealed airtight and degassed by purging with argon for 5 min. The polymerization mixture was then placed in a preheated oil bath and stirred at 65 °C for 18 h. The polymerization was quenched by opening to oxygen and cooling the mixture to -18 °C. Afterwards, the polymer was precipitated in ice-cold methanol (10% water). After filtration the yellow powder was dried in vacuo (307 mg, yield: 92%).

SEC (THF): M_n = 10 200 gmol^{-1}, M_w = 16 300 gmol^{-1}, $Đ$ = 1.60 (p(MMA) calibration)

^{1}H-NMR (400 MHz, CD_2Cl_2) δ [ppm] = 8.21-8.15 (m, 2H, Ar-H), 8.15 – 8.11 (m, 1H, Ar-H), 8.09 – 8.03 (m, 1H, Ar-H), 8.00– 7.95 (m, 1H, Ar-H), 7.66 -7.58 (m, 2H, Ar-H), 7.57 - 7.51 (m, 1H, Ar-H), 7.48 – 7.29 (m, 8H, Ar-H), 7.27 - 7.21 (m, 2H, Ar-H), 7.17 - 7.09 (m, 1H, Ar-H), 4.19 - 4.02 (m, 2H, CH_2-O), 3.58 (m, 302H, CH_3-O p(MMA)), 2.53 – 2.40 (m, 5H, CH_2), 2.06 - 1.75 (m, 177H, CH_3 p(MMA)), 1.08 - 1.53 (m, 64H, p(MMA)), 0.99 (s, 103H, p(MMA)), 0.92 – 0.64 (m, 186H, p(MMA)).

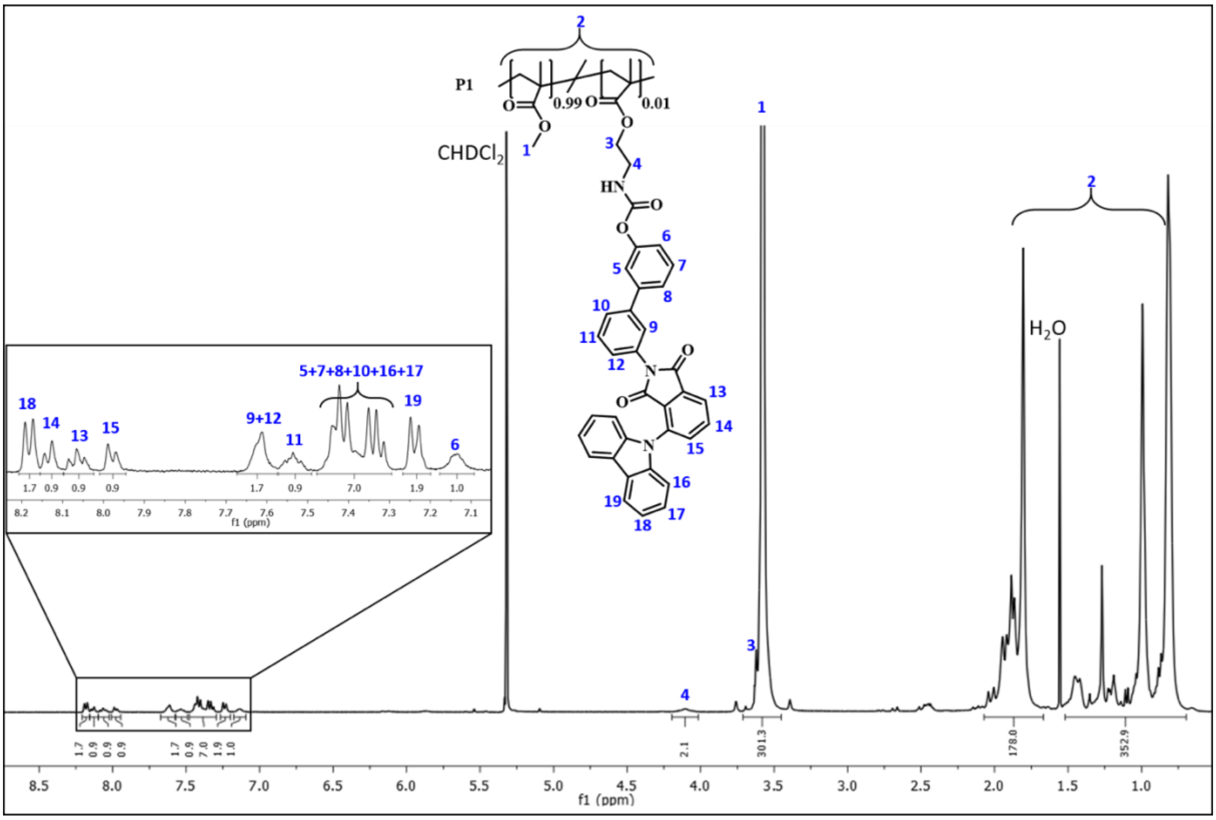


Figure S11. ^{1}H-NMR spectrum of **P1** in CD_2Cl_2.

The content of the emitter building block in the polymer was calculated from the ^{1}H-NMR resonances of the emitter at 7.17 - 7.09 ppm (1 H) and the methoxy group of p(MMA) at 3.58 ppm (3 H).

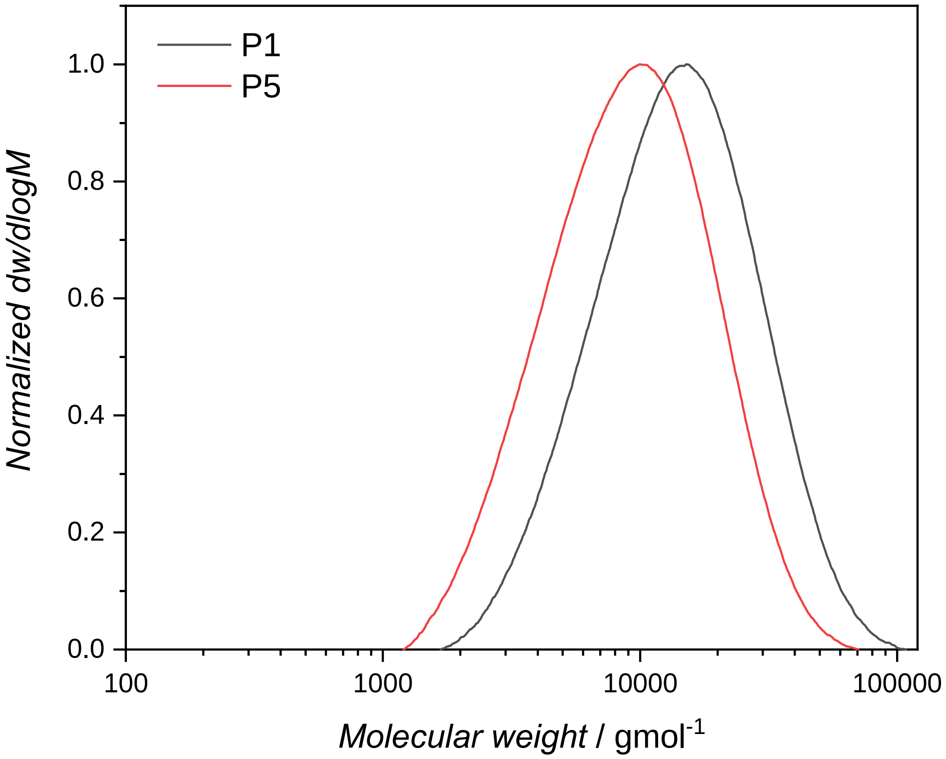


Figure S12. Polymer synthesis Molecular weight distribution determined by size exclusion chromatography in THF of **P1** (black) and **P5** (red).

References

1 F. B. Dias, T. J. Penfold and A. P. Monkman, *Methods Appl. Fluoresc.* **2017**, *5*, 012001

2 S. V. Kunz, C. M. Cole, A. Welle, P. E. Shaw, P. Sonar, N. P. Thoebes, T. Baumann, S. D. Yambem, E. Blasco, J. P. Blinco and C. Barner-Kowollik, *Macromolecules* **2019**, *52*, 9105