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

Supplementary Information

One-step additive crosslinking of conjugated polyelectrolyte interlayers resulting in improved lifetime and performance of fully-solution processed OLEDs

Sebastian Stolz[a,b], Martin Petzoldt[b,c], Naresh Kotadiya[a,b], Tobias Rödlmeier[a,b], Ralph Eckstein[a,b], Jan Freudenberg[b,c], Uwe H. F. Bunz[c,d], Uli Lemmer[a,e], Eric Mankel[b,f], Manuel Hamburger[b,c] and Gerardo Hernandez-Sosa[a,b]

---

[a] *Light Technology Institute, Karlsruhe Institute of Technology, Engesserstrasse 13, 76131 Karlsruhe, Germany.*

[b] *InnovationLab, Speyerer Strasse 4, 69115 Heidelberg, Germany.*

[c] *Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 227, 69120 Heidelberg, Germany.*

[d] *Centre for Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 225, 69120 Heidelberg, Germany.*

[e] *Institute of Microstructure Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.*

[f] *Surface Science Division, Materials Science Institute, Technische Universität Darmstadt, Jovanka-Bontschits-Strasse 2, 64287 Darmstadt, Germany.*

**Correspondence - gerardo.sosa@kit.edu*

UV-Vis absorption spectra of annealed and non-annealed PFN:DIO samples

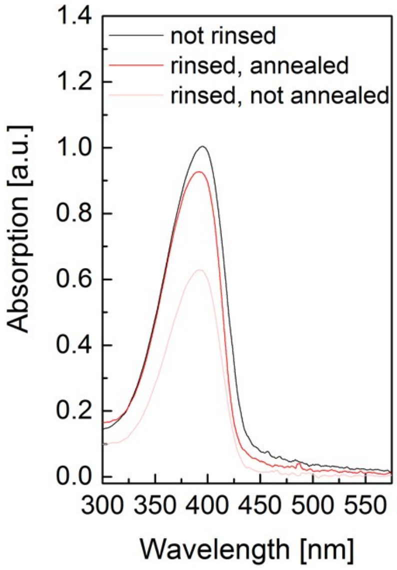


Figure S1. UV-Vis absorption spectra of PFN:DIO films which were rinsed with DCB. It can be observed that an annealing step is required for the crosslinking reaction between PFN and DIO which renders PFN insoluble in DCB.

In Figure S1, UV-Vis absorption spectra of PFN samples on glass analogous to the ones in Figure 2 are shown. It can be seen that samples containing DIO need to be annealed in order to render them insoluble in dichlorobenzene (DCB). The PFN absorption of non-annealed samples gets strongly reduced by the DCB rinsing procedure which indicates a significant decrease in thickness. This can be explained by the proposed crosslinking reaction (Figure 1). During the annealing process, the acetic acid is removed from the film and DIO can only subsequently bind to PFN's amine groups, effectively crosslinking the film.

White light interferometer topography images

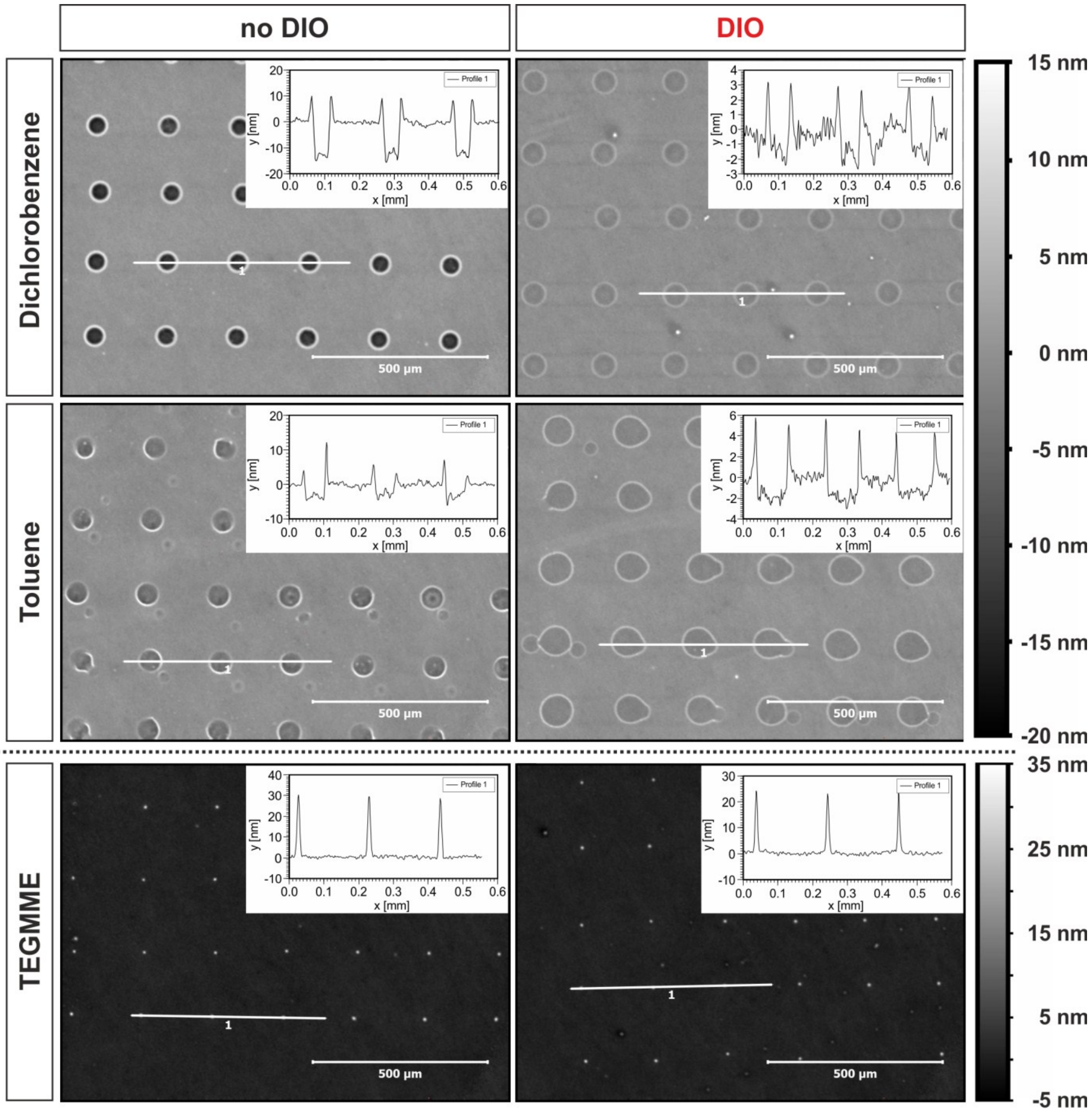


Figure S2. Topography images of PFN films on top of glass substrates which were taken with a white light interferometer. On top of the films, droplets of three different solvents (DCB, toluene and triethylene glycol monomethyl ether (TEGMME)) were inkjet-printed in order to check the susceptibility of the films to the solvents.

In Figure S2, topography images of crosslinked and non-crosslinked PFN films are shown. On top of the films, droplets of three different solvents (DCB, toluene and triethylene glycol monomethyl ether (TEGMME)) were inkjet-printed. In summary, these images confirm the effectiveness of the crosslinking process. As can be seen, particularly DCB caused the formation of deep holes in the non-crosslinked film (~ 15 nm). In contrast, the crosslinked PFN film exhibited only small holes with a depth of < 3 nm. In case of toluene, the situation was similar and the non-crosslinked film was affected significantly more than the crosslinked one (~5 nm in comparison to < 3 nm). When droplets of TEGMME were printed on top of the films, the situation was different. Instead of holes, the solvent caused the formation of spikes. However, the area covered by these spikes was rather small, indicating that the films are only marginally affected by this solvent. In addition, there was no difference observed between the crosslinked and non-crosslinked samples in case of TEGMME.

Synthesis of PFN

General Remarks

All reactions requiring exclusion of oxygen and moisture were carried out in dry glassware under a dry and oxygen free argon or nitrogen atmosphere. For spectroscopic and analytic characterizations the following devices were available:

Analytical thin layer chromatography (TLC) was performed on Macherey-Nagel Polygram® SIL G/UV_{254} and Polygram® ALOX N/UV_{254} precoated sheets. Components were visualized by observation under UV irradiation (254 nm and 365 nm) or with phosphomolybdic acid solution (20 wt. % in ethanol).

Flash column chromatography was carried out on silica gel (0.032 mm-0.062 mm and 0.015-0.040 mm), and ALOX basic (50-200 µm) purchased from Macherey, Nagel & Co., Merck KGaA. and ACROS Organics, with an Isolera™ accelerated chromatographic automated isolation system from Biotage®.

^{1}H NMR and **^{13}C NMR** spectra were recorded at room temperature on Bruker Avance DRX 300 (300 MHz), Bruker Avance III 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) and Bruker Avance III 600 (600 MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to residual undeuterated solvent peak.[1] The following abbreviations are used to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). All NMR spectra were integrated and processed using ACD/Spectrus Processor 2012 of Advanced Chemistry Development Inc.

Ultra performance liquid chromatography with tandem mass spectrometer (UHPLC-MS) were carried out on a Waters® Acquity UHPLC-MS System with SQD2 detector and APCI ionization source.

High resolution mass spectra (HR-MS) were determined at the Organisch-Chemisches Institut of the University of Heidelberg under the direction of Dr. J. Gross. All methods were recorded on Vakuum Generators ZAB-2F (EI^{+}), Finnigan MAT TSQ 700 (ESI^{+}), IonSense Saugus DART-SVP-OS (DART) or JEOL JMS-700 (FAB^{+}) spectrometer.

Absorption spectra were carried out on a JASCO UV-VIS V-660 or JASCO UV-VIS V-670 in solution or in solid state *via* a spin-cast glass-slide (Thin Films for solid state spectroscopy were prepared by a **Spin Coater** SCV-10).

Emission spectra were recorded on a JASCO FP-6500 in solution or in solid state *via* a spin-cast glass-slide.

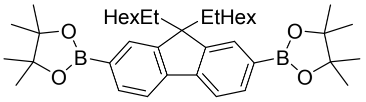
Gel permeation chromatography (GPC) was performed with PSS SecCurity (Agilent Technologies 1260 Infinity, RI, UV 270 nm detectors). Number- (M_n) and weight average (M_w)

molecular weights and polydispersities (PDI) were determined by GPC versus PS, PEO, PMMA, PVP standards. Measurements were carried out at 60° C in DMF (flow rate 1 mL/min) with PSS-SDV columns (8.0×30.0 mm, 10 µm particles, 10^2-, 10^3- and 10^5- Å pore size). All GPC-spectra were analyzed and processed by PSS-WinGPC UniChrom (PSS).

Formulas were drawn with ChemBioDraw Ultra 12.0 and 14.0.

IUPAC names and atom numberings of the compounds described in the experimental section were determined with the program ChemBioDraw Ultra 12.0 and 14.0.

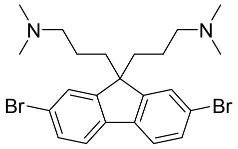
2,7-Bis(4,4,5,5-tetramethyl[1.3.2]dioxaborolan-2yl)-9,9-bis(2-ethylhexyl)fluorene



2,7-Bis(4,4,5,5-tetramethyl[1.3.2]dioxaborolan-2yl)-9,9-bis(2-ethylhexyl)fluorene was synthesized according to a literature procedure (12.0 g, 18.6 mmol, 70 %).[2] The acquired NMR spectra are consistent with the literature.[2]

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ = 7.79 - 7.61 (m, 6H), 1.93 (d, *J*=5.4 Hz, 4H), 1.29 (s, 24H), 0.88 - 0.54 (m, 22H), 0.47 - 0.36 (m, 8H). ^{13}C NMR (75 MHz, CHLOROFORM-d) δ = 150.21, 143.99, 133.51, 130.45, 119.29, 83.58, 54.77, 44.04, 34.68, 33.53, 33.51, 27.87, 27.23, 24.93, 24.87, 24.82, 22.74, 14.09, 10.37.

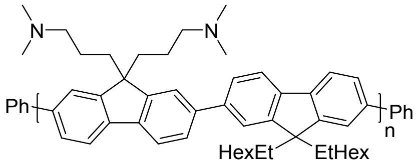
2,7-Dibromo-9,9-bis(3'-(*N*,*N*-dimethylamino)propyl)fluorene



2,7-Dibromo-9,9-bis(3'-(*N*,*N*-dimethylamino)propyl)fluorene was prepared according to a literature procedure.[3] The acquired NMR spectra are consistent with the literature (2.0 g, 4.1 mmol, 58 %).[3]

^{1}H NMR (300 MHz, CHLOROFORM-*d*) δ = 7.78 (d, *J*=8.1 Hz, 2H), 7.65 (d, *J*=1.5 Hz, 2H), 7.51 (dd, *J*=1.7, 8.1 Hz, 2H), 2.04 - 1.83 (m, 20H), 0.67 - 0.46 (m, 4H). ^{13}C NMR (75 MHz, CHLOROFORM-d) δ = 151.89, 139.01, 130.32, 126.10, 121.55, 121.15, 59.46, 55.20, 45.21, 37.47, 21.92.

Poly[(9,9-bis(2-ethylhexyl)-fluorene)-_alt_-(9,9-bis(3'-(_N_,_N_-dimethylamino)propyl)fluorene] (PFN)



Poly[2,7-(9,9-bis(2-ethylhexyl)-fluorene)-*alt*-2,7-(9,9-bis(3'-(*N*,*N*-dimethylamino)propyl)fluorene] **PFN** was prepared by a procedure similar to that in the literature.[4] 2,7-Dibromo-9,9-bis(3'-(*N*,*N*-dimethylamino)propyl)-fluorene (494 mg, 1.00 mmol), 2,7-bis(4,4,5,5-tetramethyl[1.3.2]dioxaborolan-2yl)-9,9-bis(2-ethylhexyl)-fluorene (642 mg, 1.00 mmol) were dissolved in 15 mL of THF. Then tetraethylammonium hydroxide 35 wt. % (4.3 mL, 10 mmol) was added to this solution. This suspension was degassed (via sonication). Then tetrakis(triphenylphosphane)palladium (58 mg, 50 µmol) was added and the suspension was degassed again. The reaction mixture was stirred at 70 °C for 6 h. Then phenylboronic acid (122 mg, 1.00 mmol) was added and the mixture stirred for another 2 h at this temperature. Bromobenzene (105 µL, 1.00 mmol) was added. After 2 h stirring at this temperature the polymer was precipitated in 250 mL of ethyl acetate. The obtained solid was dissolved in chloroform, and then filtered through a syringe filter (0.45 µm, PTFE), concentrated, and precipitated from ethyl acetate to give the polymer **PFN** (500 mg, 690 µmol, 69 %).

^{1}H NMR (600 MHz, CHLOROFORM-*d*) δ = 7.94 - 7.76 (m, 4H), 7.68 (br. s., 8H), 2.07 (br. s., 20H), 1.10 - 0.51 (m, 40H). ^{13}C NMR (150 MHz, CHLOROFORM-d) δ = 151.29, 150.98, 140.93, 140.21, 139.96, 128.78, 127.16, 126.31, 126.17, 122.73, 122.60, 121.27, 120.06, 119.93, 59.66, 55.08, 54.94, 53.03, 45.12, 44.47, 37.81, 34.74, 33.87, 29.68, 28.19, 28.16, 27.18, 22.73, 21.91, 14.16, 14.05, 10.47, 10.43. GPC study (DMF / 60°C, polystyrene standard) M_n = 12000 g/mol, M_w = 18200 g/mol, PDI = 1.52. FTIR: $\tilde{\nu}$ = 2924, 2853, 2765, 1456, 1378, 1263, 1147, 1042, 1013, 905, 812, 732 cm^{-1}.

NMR Spectra of PFN

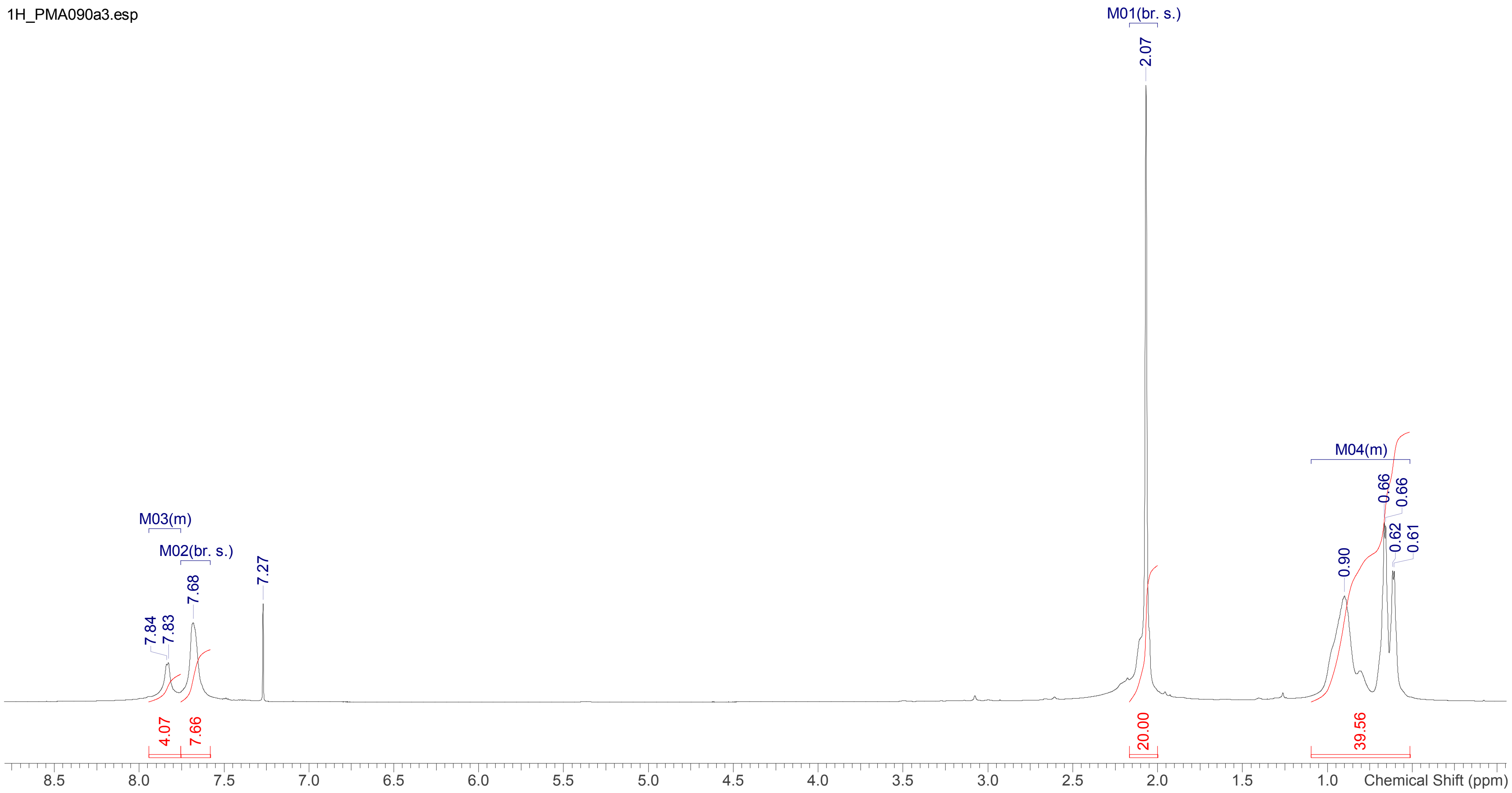


Figure S3. ^{1}H NMR of PFN in CDCl3.

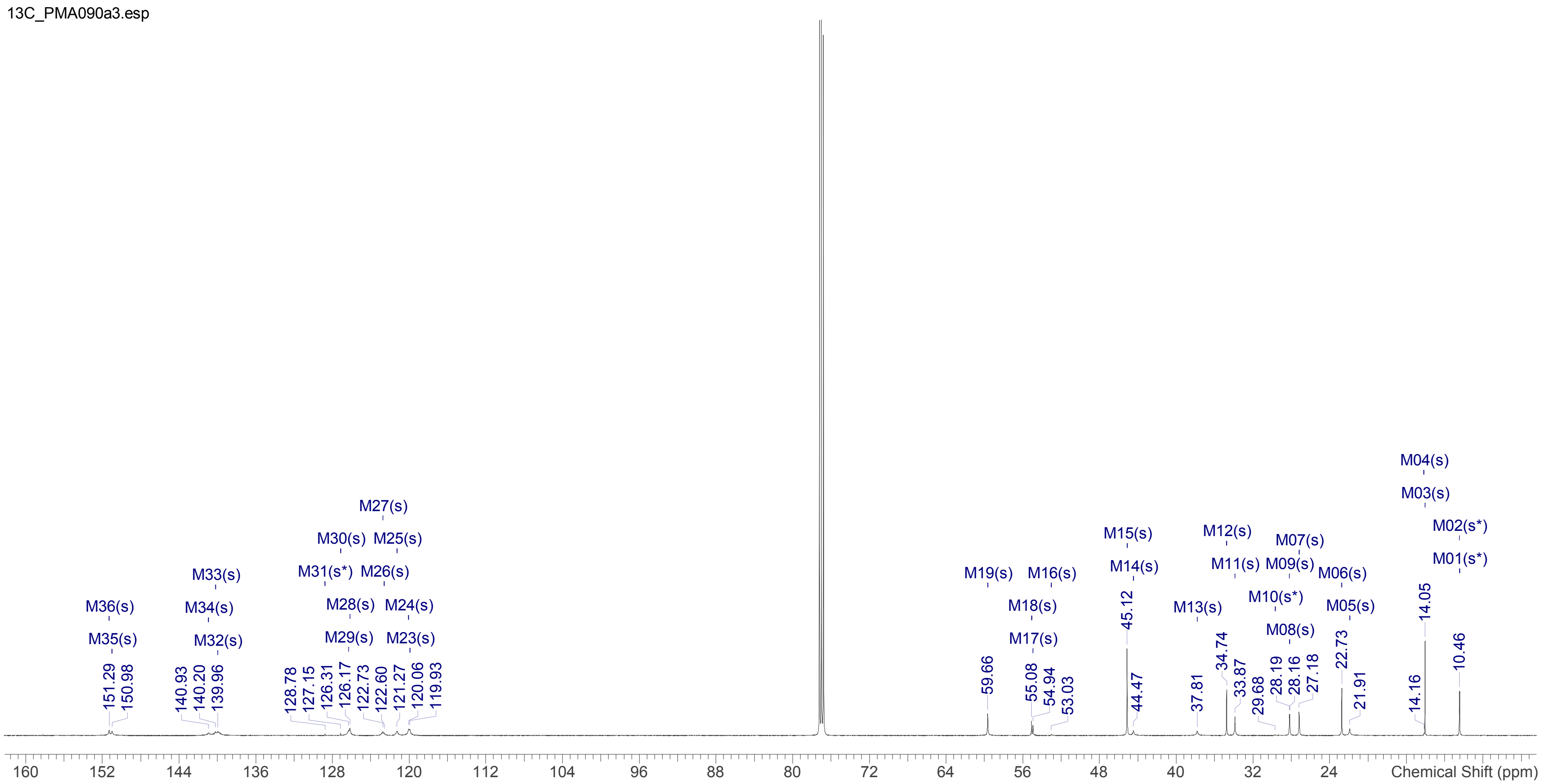


Figure S4. ^{13}C NMR of PFN in CDCl3.

GPC-Analysis

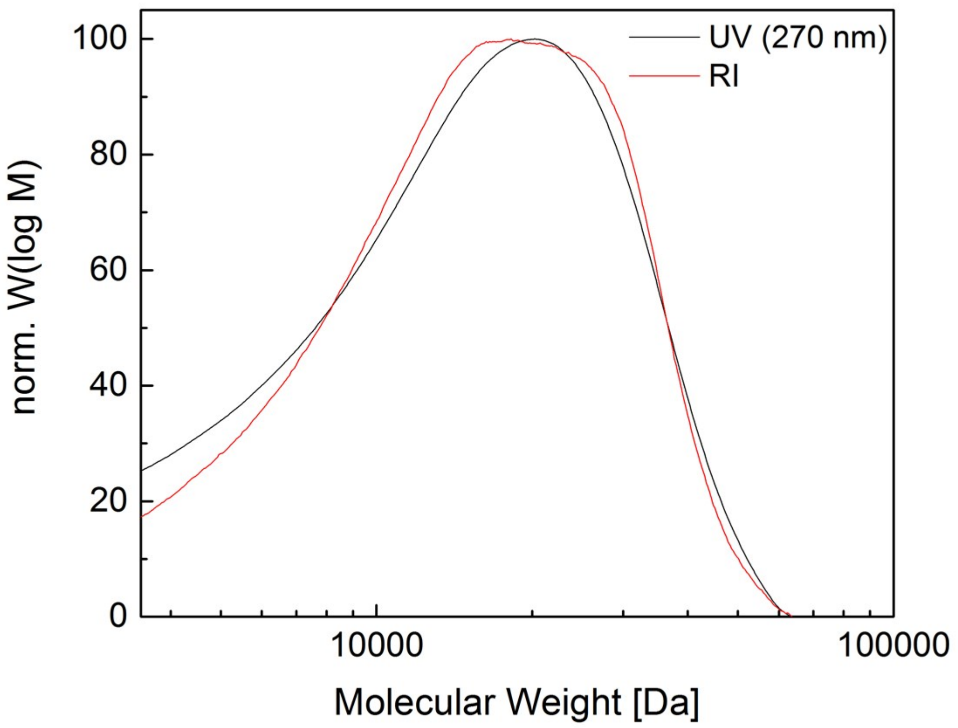


Figure S5. GPC spectra of polymer **PFN** in DMF at 60° C.

Table S1. GPC results

Detector	**M_n [g/mol]**	**M_w [g/mol]**	**D**
UV (270 nm)	11983	18181	1.52
RI	12520	18316	1.46

UV/Vis-Spectra (absorption/emission) of PFN

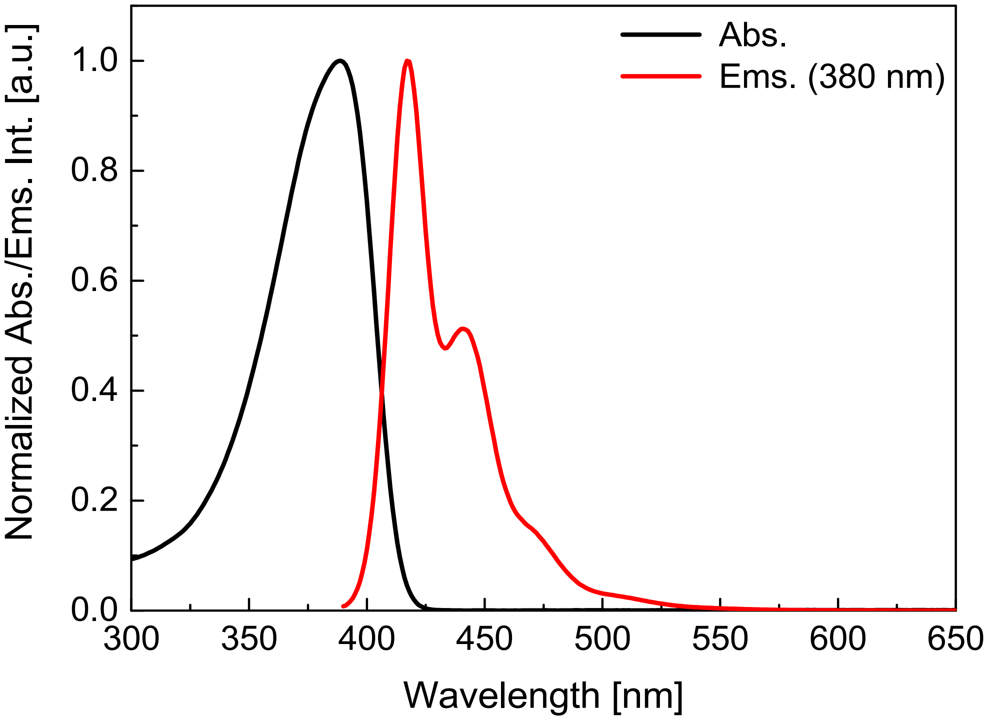


Figure S6. Absorption-/emission-spectra of polymer **PFN** in $CHCl_3$ at a concentration of ~1.5 10^{-6} mol L^{-1}.

Supplemental References

[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179

[2] J. Jo, C. Chi, S. Höger, G. Wegner, D. Y. Yoon, *Chem. - A Eur. J.* **2004**, *10*, 2681.

[3] F. Huang, L. T. Hou, H. B. Wu, X. H. Wang, H. L. Shen, W. Cao, W. Yang, Y. Cao, *J Am Chem Soc* **2004**, *126*, 9845-9853.

[4] X. Guan, K. Zhang, F. Huang, G. C. Bazan, Y. Cao, *Adv Funct Mater* **2012**, *22*, 2846-2854.