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Solubility Modulation of Polyfluorene Emitters by Thermally Induced (Retro)-Diels-Alder-Crosslinking of Cyclopentadienyl Substituents

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Abstract

For cost-efficient organic electronic devices the consecutive deposition of active layers by solution-based processes is a key merit. We report a synthetic approach enabling solubility reduction of bis(cyclopentadienyl)-substituted polyfluorenes as emissive layers in OLEDs. Thermally induced retro-Diels-Alder reaction liberates free cyclopentadiene as “protecting group” and pending cyclopentadienyl units, which crosslink the polymer strands upon cooling via [4+2] cycloadditions. The activation temperature is tuned in the range of 180 °C to 250 °C through alkyl, alkoxy or ester linkages. Ultimately, macrocyclic self-protected bis(cyclopentadienylene) moieties avoid extrusion of volatile cyclopentadiene (Cp) during activation. The solvent resistance of the emissive layers after crosslinking is examined by absorption spectroscopy and white-light scanning interferometry. The influence of the desolubilization procedure on the performance of solution-processed OLEDs is investigated.

Introduction

Both organic light-emitting diodes (OLEDs) and organic solar cells (OPVs) rely upon multi-layer architectures.[1,2] Sequential deposition of different layers by vacuum techniques offers defined interfaces, but is restricted to small organic molecules or inorganics[3] and not applicable to polymers. The latter exhibit superior properties for future applications, e.g. in terms of morphological robustness, flexibility[4,5,6,7] and self-healing ability,[8,9] but have to be deposited from solution.[10] Polymers and small molecules can be cast into films by high-throughput printing technologies, advantageous for large area fabrication at low production costs.[3,11] Thus, the development of protocols for solution-based consecutive layer deposition is vital. Each material must exhibit resistance to the subsequently used solvent while retaining or improving device characteristics. Strategies involve orthogonal solvents,[12] or transformation of soluble precursors into immobilized active layers by external stimuli such as (UV-)light, heat or treatment with additives. Solubility is reduced either by cleavage of solubilizing side-chains,[1] as demonstrated by our group[13] and others[14,15] on polyfluorenes[13] and polythiophenes,[14] or by formation of insoluble covalently crosslinked networks (Figure 1).[1,2,16]

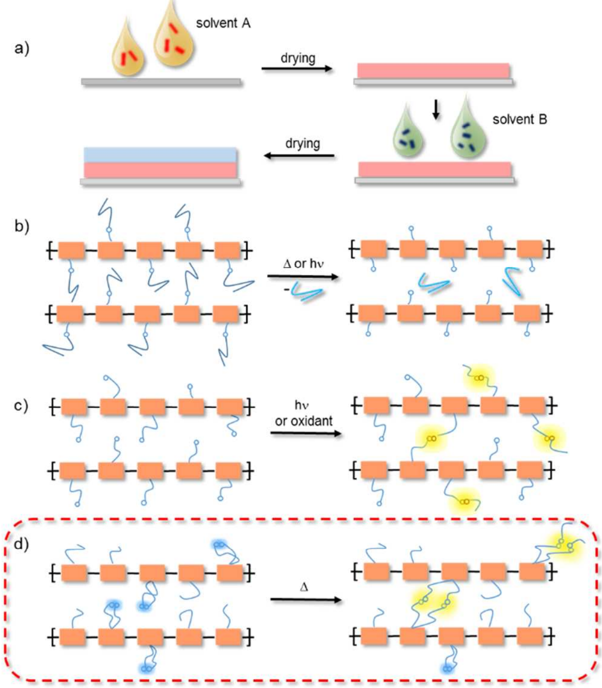
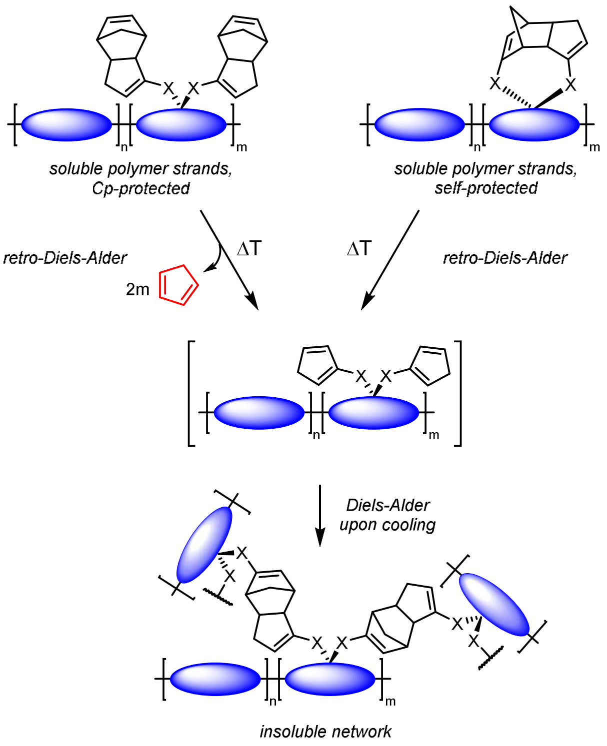


Figure 1: Concepts for solution processing of consecutive layers (selection). a) orthogonal coating utilizing solubility/insolubility in solvents of varying polarity, b) thermal/photochemical removal of side-chains, c) photochemical/oxidative crosslinking, d) additive-free, thermal crosslinking without byproducts (this work).

Removal of solubilizing groups (Figure 1b) necessitates the cleavage products either to leave the thin film as volatiles, possibly changing the film morphology, or to be tolerated under device operation. In contrast, crosslinking is a more (atom-)economical approach: prominent examples include dimerization of cinnamic esters[17] induced by UV-irradiation. The radiation dose employed is crucial, as adverse photochemical processes can occur upon over-exposure which compromise device performance.[18],[19] Other protocols involve additives, i.e. diiodooctane as cross-linking reagent for amines,[20] in-situ generated nitrenes by UV-irradiation,[21],[22] or (photo)acids inducing cationic ring-opening polymerization (CROP) of oxetanes.[23] Thermal, additive-free crosslinking of polymers for organic electronics remains challenging, as the utilized functional groups should not decrease the material's performance.[24] Benzocyclobutene-derived monomers applied as additives for polyethylene undergo conversion to *ortho*-xylylenes at 200 °C, which irreversibly dimerize to inert dibenzocyclooctane linkers without noticeable byproducts.[25] Desolublization, however, required rather long annealing periods of 4 h. Additionally, benzocyclobutadiene-derived building blocks are scarce and expensive due to their reactive nature,[26] and are not universally applicable if additional olefinic bonds are present in the active material. Reaction kinetics of less reactive and more selective Diels-Alder partners (*vide supra*) can be gained from dynamic covalent chemistry,[27,28] well-explored for self-healing polymers.[8,9,29,30] The activation barrier of the [4+2] cycloaddition is tuned by changing the electron demand of dienophile and diene components, allowing for adjustment of crosslinking temperatures and annealing times.



Scheme 1: Schematic illustration of the crosslinking process of different polymer strands through Diels-Alder reaction of cyclopentadienyl groups. Top left: Retro-Diels-Alder reaction liberating protective cyclopentadiene as volatile by-product to furnish cyclopentadienyl groups for dimerization. Top right: Cleavage of a macrocyclic self-protected bis(cyclopentadienylene) *via* retro-Diels-Alder reaction to avoid formation of volatile side-products. X denotes the variable linkers (-CH_2-, -O-, -COO-).

In this contribution, we establish cyclopentadienyl groups as crosslinking moieties in organic electronics, at the same time choosing easily accessible polyfluorenes (PFs) as common emitters in OLEDs. Bis(cyclopentadienyl)-substituted fluorene monomers were synthesized and copolymerized with conventional ethylhexyl-substituted fluorene monomers in different ratios through statistic Yamamoto coupling. A thermal stimulus applied to the polyfluorenes leads to retro-Diels-Alder reactions, liberating cyclopentadiene used as a “protecting group” for the cyclopentadienyl-functionalized polymer strands (Scheme 1). The pending cyclopentadienyl units undergo dimerization or trimerization via [4+2] cycloadditions upon cooling, causing the desired network formation and solubility decrease. This process tolerates various functional groups. The cleavage temperature of the retro-Diels-Alder reaction is determined by the electron demand of the bis(cyclopentadienyl)s and tuned through linkage *via* C-C-bond, ether, or ester group. Self-protected macrocyclic bis(cyclopentadienylene) units avoid the necessity of sacrificial protecting units, leading to purely thermal, additive-free and comparably fast modulation of solubility without extrusion of any byproducts (Scheme 1, top right and Figure 1d). We examine the solvent resistance of thin films after their annealing at elevated temperature to evaluate the degree of crosslinking. The self-protected polyfluorene exhibits superior performance in solution-processed proof-of-concept OLEDs in comparison to their Cp-protected counterparts. In contrast to other successful and benign immobilization strategies, e.g. CROP employing oxetanes, additional post-treatment steps like washing are precluded, rendering our process compatible with roll-to-roll techniques.[16]

Experimental

Synthesis

All reactions requiring exclusion of oxygen and moisture were carried out in dried glassware under a dry and oxygen free nitrogen or argon atmosphere using Schlenk techniques. Commercially available monomer building blocks for Yamamoto polymerization were purified before usage applying column chromatography and the procedure described by Meijer *et al*.[31]

2,7-Dibromo-9,9-bis(6-bromohexyl)-9*H*-fluorene (2):[32] 2,7-Dibromo-9*H*-fluorene **1** (2.50 g, 7.72 mmol, 1.00 eq.) and tetrabutylammonium iodide (291 mg, 772 µmol, 98 wt%, 0.10 eq.) were suspended in 40 mL of aqueous 50 wt% NaOH solution. Applying three freeze-pump-thaw-cycles the suspension was degassed. Thereafter 1,6-dibromohexane (8.57 mL, 13.6 g, 54.0 mmol, 97 wt%, 7.00 eq.) was added and the resulting mixture was stirred at 70 °C for 4.5 h. The aqueous suspension was extracted with chloroform, the combined organic layers were washed three times with deionized water and dried over $MgSO_4$. The remaining 1,6-dibromohexane was distilled off at 70 °C at 1 mbar and purified by flash column chromatography (SiO_2, PE : EA 9 : 1). **2** was isolated as a colorless solid (3.61 g, 5.55 mmol, 72.0 %). ^1H-NMR (301 MHz, $CDCl_3$): δ 0.52 - 0.66 (m, 4 H), 1.01 - 1.15 (m, 4 H), 1.15 - 1.27 (m, 4 H), 1.61 - 1.73 (m, 4 H), 1.88 - 1.97 (m, 4 H), 3.30 (t, *J* = 6.8 Hz, 4 H), 7.42 - 7.49 (m, 4 H), 7.50 - 7.55 (m, 2 H).

2,7-Dibromo-9,9-bis(1-(3a,4,7,7a-tetrahydro-1*H*-4,7-methanoinden-3-yl)-1l5,6l3-hexyl)-9*H*-fluorene and its stereoisomers (F-C-Cp$_2$): Sodium cyclopenta-2,4-dien-1-ide (271 mg, 3.08 mmol, 2.00 eq.) was suspended in 40 mL freshly degassed, anhydrous THF and 5.00 mL of freshly distilled cyclopentadiene. Then 2,7-dibromo-9,9-bis(6-bromohexyl)-9*H*-fluorene **2** (1.00 g, 1.54 mmol, 1.00 eq.) was added slowly at 0 °C and the resulting mixture was stirred at room temperature for 6 h and thereafter at 50 °C for 120 h. The mixture was filtrated over Celite, the solvent was removed under reduced pressure and the crude product was absorbed on Celite. After flash column chromatography (SiO_2, PE) a crude mixture of **F-C-Cp$_2$** was isolated as a slightly yellow oil (1.04 g, 1.38 mmol, 90.0 %). To eliminate not fully reacted sideproducts crude **F-C-Cp$_2$** (650 mg, 864 µmol, 1.00 eq.) was dissolved in 10mL anhydrous DCM in a heatgun dried Schlenk tube under an atmosphere of nitrogen. To scavenge unreacted cyclopentadienyl groups, 4-phenyl-3H-1,2,4-triazole-3,5(4H)-dione was added at -78 °C and the resulting mixture was stirred at -78 °C for 30 min. Then the reaction mixture was allowed to warm to room temperature and was stirred for another 1 h. The solvent was removed under reduced pressure and the crude product was absorbed on Celite. After flash column chromatography (SiO_2, PE), gel permeation chromatography (toluene) and high pressure liquid chromatography (PE, 5 mLmin^{-1}) **F-C-Cp$_2$** was isolated as a highly viscous, colorless oil (578 mg, 768 µmol, 80.1 %). ^1H-NMR (500 MHz, CD_2Cl_2): δ 0.49 - 0.66 (m, 4 H), 0.92 - 2.23 (m, 30 H), 2.51 - 3.47 (m, 8 H), 4.95 - 5.08 (m, 1 H), 5.34 - 5.43 (m, 2 H), 5.66 - 6.43 (m, 3 H), 7.41 - 7.48 (m, 4 H), 7.49 - 7.55 (m, 2 H). ^{13}C-NMR (126 MHz, CDCl3): δ 23.7, 23.7, 26.6, 27.0, 27.4, 27.6, 27.7, 29.0, 29.3, 29.4, 29.8, 29.9, 29.9, 30.1, 30.3, 31.1, 31.6, 32.6, 33.2, 33.8, 34.3, 34.8, 35.0, 37.1, 40.3, 41.3, 41.5, 41.7, 43.6, 44.5, 45.5, 45.8, 46.2, 46.3, 46.4, 49.2, 50.1, 50.2, 53.8, 54.4, 54.7, 55.8, 56.3, 57.1, 59.6, 121.3, 121.6, 123.5, 124.4, 125.1, 126.3, 130.2, 131.4, 131.8, 132.0, 132.3, 132.3, 133.2, 135.5, 136.4, 139.2, 139.4, 145.4, 146.6, 151.2, 152.6. IR (cm^{-1}): 3042, 2925, 2853, 1448, 1416, 1339, 1248, 1130, 1061, 876, 807, 743, 722, 687, 667. HRMS (DART+): calc. for $C_{45}H_{53}{}^{79}Br_2^+$ $[M+H]^+$: 751.2514, found: 751.2563.

3a,4,7,7a-Tetrahydro-1*H*-4,7-methanoinden-1-ol (4):[33] Monopotassium phosphate (780 mg, 5.67 mmol, 99 wt%, 0.15 eq.) was suspended in 9 mL 1,4-dioxane and 1 mL deionized water. Freshly distilled cyclopentadiene **3** (5.10 mL, 5.00 g, 37.8 mmol, 1.00 eq.) was added and the mixture was heated to 90 °C. Thereafter selenium dioxide (2.14 g, 18.9 mmol, 98 wt%, 0.50 eq.) were added in portions over a period of 45 min. Stirring was continued at 90 °C for 1 h and then at 105 °C for 3 h. The mixture was allowed to cool to room temperature, filtrated and the residue washed twice with diethyl ether. The organic layer was washed twice with 20mL saturated $NaHCO_3$-solution each, 20mL brine and was dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was absorbed on Celite. After flash column chromatography (SiO_2, PE : EA 10 : 1) **4** was isolated as a yellow solid (3.02 g, 20.4 mmol, 53.9 %). ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 1.38 - 1.42 (m, 2 H), 2.48 - 2.52 (m, 1 H), 2.76 - 2.80 (m, 1 H), 3.02 - 3.05 (m, 1 H), 3.34 - 3.39 (m, 1 H), 4.00 - 4.05 (m, 1H), 5.57 (td, *J* = 5.7 Hz, *J* = 1.9 Hz, 1 H), 5.75 - 5.77 (m, 1 H), 5.83 (dd, *J* = 5.7 Hz, *J* = 3.1 Hz, 1 H), 5.93 (dd, *J* = 5.7 Hz, *J* = 3.0 Hz, 1 H).

1-((6-Iodohexyl)oxy)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoindene (5): Sodium hydride (425 mg, 10.6 mmol, 60wt% in mineral oil, 1.05 eq.) was suspended in 10 mL anhydrous DMF. **4** (1.50 g, 10.1 mmol, 1.00 eq.) in 10 mL anhydrous DMF was added dropwise over a period of 20 min at 0 °C and then the reaction mixture was stirred at 0 °C for 1 h. Thereafter 1,6-diiodohexane (2.58 mL, 5.29 g, 15.2 mmol, 97 wt%, 1.50 eq.) in 5 mL anhydrous DMF were added at 0 °C and the resulting mixture was stirred at 0 °C for 30 min. Stirring was continued at room temperature for 24 h. The mixture was quenched with 30 mL ice water and then extracted twice with diethyl ether. The combined organic layers were washed with deionized water and were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was absorbed on Celite. After flash column chromatography (SiO_2, PE : EA 100 : 1) **5** was isolated as a slightly yellow oil (820 mg, 2.29 mmol, 22.6 %). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.36 - 1.44 (m, 5 H), 1.54 - 1.59 (m, 3 H), 1.79 - 1.87 (m, 2 H), 2.58 - 2.62 (m, 1 H), 2.77 - 2.80 (m, 1 H), 2.97 - 3.01 (m, 1 H), 3.19 (t, *J* = 7.1 Hz, 2 H), 3.34 - 3.40 (m, 2 H), 3.45 - 3.50 (m, 1 H), 3.75 - 3.78 (m, 1 H), 5.58 (td, *J* = 5.7 Hz, *J* = 1.8 Hz, 1 H), 5.80 - 5.82 (m, 1 H), 5.86 (dd, *J* = 5.8 Hz, *J* = 2.9 Hz, 1 H), 5.95 (dd, *J* = 5.8Hz, *J* = 3.0 Hz, 1 H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 8.0, 26.1, 30.7, 31.1, 34.2, 45.3, 46.0, 50.8, 52.1, 55.5, 69.0, 87.3, 133.0, 133.2, 136.2, 139.0. IR (cm^{-1}): 3054, 2957, 2929, 2854, 1726, 1452, 1427, 1361, 1339, 1204, 1108, 1084, 909, 848, 807, 770, 728. HRMS (DART+): calc. for $C_{16}H_{24}IO^+$ $[M+H]^+$ 359.0866, found: 359.0871.

2,7-Dibromo-9,9-bis(6-((3a,4,7,7a-tetrahydro-1*H*-4,7-methanoinden-1-yl)oxy)hexyl)-9*H*-fluorene (F-O-Cp$_2$): 2,7-Dibromo-9*H*-fluorene (355 mg, 1.06 mmol, 97 wt%, 1.00 eq.) and **5** (800 mg, 2.23 mmol, 2.10 eq.) were dissolved in 30 mL anhydrous THF. Applying three freeze-thaw-cycles the solution was degassed. Thereafter potassium *tert*-butoxide (274 mg, 2.39 mmol, 98 wt%, 2.25 eq.) in 50 mL freshly degassed, anhydrous THF were added over a period of 1 h and the resulting mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the crude product redissolved in 40 mL DCM. The organic layer was washed three times with deionized water, dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was absorbed on Celite. After flash column chromatography (SiO_2, PE : EA 100 : 1) **F-O-Cp$_2$** was isolated as a highly viscous, colorless oil (534 mg, 681 µmol, 64.0 %). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.53 - 0.63 (m, 4 H), 1.03 - 1.13 (m, 8 H), 1.35 - 1.41 (m, 6 H), 1.53 - 1.57 (m, 2 H), 1.87 - 1.94 (m, 4 H), 2.52 - 2.56 (m, 2 H), 2.74 - 2.78 (m, 2 H), 2.93 - 2.96 (m, 2 H), 3.22 - 3.28 (m, 2 H), 3.31 - 3.38 (m, 4 H), 3.68 - 3.72 (m, 2 H), 5.58 (td, *J* = 5.7 Hz, *J* = 1.8 Hz, 2 H), 5.77 (d, *J* = 5.4 Hz, 2 H), 5.84 (dd, *J* = 5.7 Hz, *J* = 3.0 Hz, 2 H), 5.92 (dd, *J* = 5.7 Hz, *J* = 3.0 Hz, 2 H), 7.41 - 7.46 (m, 4 H), 7.51 (d, *J* = 8.0 Hz, 2 H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 24.4, 26.7, 30.5, 30.7, 40.9, 45.2, 45.9, 50.7, 52.1, 55.4, 56.4, 69.1, 87.2, 121.9, 122.2, 126.8, 130.9, 133.0, 133.1, 136.2, 138.8, 139.8, 151.1. IR (cm^{-1}): 3050, 2928, 2855, 1449, 1415, 1361, 1339, 1251, 1108, 1081, 1060, 1003, 909, 848, 807, 770, 724, 666, 432. HRMS (DART+): calc. for $C_{45}H_{56}{}^{79}Br_2NO_2^+$ $[M+NH_4]^+$: 800.2672, found: 800.2691.

General procedure for nucleophilic substitution: Under a nitrogen atmosphere, 2,7-dibromo-9*H*-fluorene (1.00 eq.) and tetrabutylammonium iodide (0.10 eq.) were suspended in an aqueous 50 wt%

NaOH solution and toluene. Applying three freeze-thaw-cycles the suspension was degassed. Thereafter the bromide (2.50 – 2.60 eq.) was added and the resulting mixture was stirred at 110 °C for 18 h. The reaction mixture was diluted with water and extracted with water/EA. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated before further purification steps were carried out.

2,2'-(((2,7-Dibromo-9*H*-fluorene-9,9-diyl)bis(ethane-2,1-diyl))bis(oxy))bis(tetrahydro-2*H*-pyran) (6a):[34] According to the general procedure, 2,7-dibromo-9*H*-fluorene **1** (2.38 g, 7.33 mmol, 1.00 eq.), tetrabutylammonium iodide (276 mg, 733 µmol, 98 wt%, 0.10 eq.) and 2-(2-bromoethoxy) tetrahydro-2*H*-pyran (3.00 mL, 4.15 g, 19.1 mmol, 96 wt%, 2.60 eq.) were reacted in 20 mL of aqueous 50 wt% NaOH and 20 mL toluene. The crude product was purified by column chromatography (SiO_2, PE : EA 10 : 1) to yield **6a** as a colorless solid (4.10 g, 7.06 mmol, 96.4 %). ^{1}H-NMR (301 MHz, $CDCl_3$): δ 1.25 - 1.65 (m, 12H), 2.36 (t, *J* = 6.9 Hz, 4 H), 2.67 - 2.77 (m, 2 H), 3.09 - 3.20 (m, 2 H), 3.21 - 3.30 (m, 2 H), 3.43 - 3.52 (m, 2 H), 4.09 - 4.14 (m, 2 H), 7.42 - 7.47 (m, 2 H), 7.48 - 7.52 (m, 2 H), 7.53 - 7.57 (m, 2 H).

2,2'-(((2,7-Dibromo-9*H*-fluorene-9,9-diyl)bis(hexane-2,1-diyl))bis(oxy))bis(tetrahydro-2*H*-pyran) (6b):[35] According to the general procedure, 2,7-dibromo-9*H*-fluorene **1** (2.44 g, 7.54 mmol, 1.00 eq.), tetrabutylammonium iodide (284 mg, 754 µmol, 98 wt%, 0.10 eq.) and 2-((6-bromohexyl)oxy)tetrahydro-2*H*-pyran (4.14 mL, 5.00 g, 18.9 mmol, 2.50 eq.) were reacted in 20 mL of aqueous 30 wt% NaOH and 30 mL toluene. The crude product was purified by column chromatography (SiO_2, PE : EA 20 : 1) to yield **6b** as a colorless solid (4.97 g, 7.18 mmol, 95.2 %). ^{1}H-NMR (301 MHz, $CDCl_3$): δ 0.52 - 0.67 (m, 4 H), 1.03 - 1.19 (m, 8 H), 1.35 - 1.45 (m, 4 H), 1.46 - 1.59 (m, 8 H), 1.69 (td, *J* = 12.4 Hz, *J* = 3.0 Hz, 2 H), 1.73 - 1.84 (m, 2 H), 1.86 - 1.96 (m, 4 H), 3.27 (td, *J* = 9.7 Hz, *J* = 6.6Hz, 2 H), 3.41 - 3.51 (m, 2 H), 3.62 (td, *J* = 9.5 Hz, *J* = 6.9 Hz, 2 H), 3.76 - 3.87 (m, 2 H), 4.48 - 4.54 (m, 2 H), 7.41 - 7.47 (m, 4 H), 7.49 - 7.54 (m, 2 H).

General procedure for deprotection: The THP-protected alcohol (1.00 eq.) was suspended in 40 mL ethanol, 10 mL of hydrochloric acid (10% HCl in water, v/v) were added and the resulting mixture was stirred at 100 °C for 1 h. The organic solvent was removed *in vacuo* and the residue extracted with water/chloroform. The combined organic layers were washed with concentrated $NaHCO_3$ solution, dried over $MgSO_4$ and the solvent was evaporated to yield the corresponding alcohol.

2,2'-(2,7-Dibromo-9*H*-fluorene-9,9-diyl)bis(ethan-1-ol) (7a):[34] According to the general procedure, **6b** (4.10 g, 7.06 mmol, 1.00 eq.) was reacted in 40 mL ethanol and 10 mL of hydrochloric acid (10% HCl in water, v/v). **7a** was isolated as a colorless solid (2.53 g, 6.15 mmol, 87.1 %). ^{1}H-NMR (301 MHz, $CDCl_3$): δ 0.89 (bs, 2 H), 2.34 (t, *J* = 7.4 Hz, 4 H), 3.03 (t, *J* = 7.4 Hz, 4 H), 7.47 - 7.52 (m, 2 H), 7.52 - 7.59 (m, 4 H).

2,2'-(2,7-Dibromo-9*H*-fluorene-9,9-diyl)bis(hexan-1-ol) (7b):[35] According to the general procedure, **6b** (4.97 g, 7.18 mmol, 1.00 eq.) was reacted in 40 mL ethanol and 10 mL of hydrochloric acid (10% HCl in water, v/v). **7b** was isolated as a slightly yellow solid (3.70 g, 7.06 mmol, 98.2 %). ^{1}H-NMR (301 MHz, $CDCl_3$): δ 0.52 - 0.67 (m, 4 H), 1.03 - 1.20 (m, 8 H), 1.33 - 1.44 (m, 4 H), 1.88 - 1.96 (m, 4 H), 3.53 (t, *J* = 6.5 Hz, 4 H), 7.42 - 7.48 (m, 4 H), 7.49 - 7.54 (m, 2 H).

3a,4,7,7a-Tetrahydro-1*H*-4,7-methanoindene-2,5-dicarboxylic acid (8):[30] Freshly prepared sodium cyclopenta-2,4-dien-1-ide (11.5 g, 14.5 mmol, 1.00 eq.) was transferred to a beaker containing a slurry of dry ice and 300 mL anhydrous THF and was stirred at -78 °C for 2 h before the mixture was allowed to slowly warm to room temperature over night. The residue was dissolved in 400 mL deionized water and then extracted three times with DCM. The crude product was precipitated by acidifying the solution with hydrochloric acid (10% HCl in water, v/v), filtrated and washed three times with deionized water. The crude product was recrystallized from methanol and dried *in vacuo* to yield **8** as a colourless solid (9.60 g, 42.8 mmol, 32.8 %). ^{1}H-NMR (301 MHz, DMSO-d_6): δ 1.36 (d, *J*

= 8.0 Hz, 1 H), 1.54 (td, *J* = 8.4 Hz, *J* = 1.5 Hz, 1 H), 1.84 - 1.95 (m, 1 H), 2.30 (tdd, *J* = 17.2 Hz, *J* = 10.2 Hz, *J* = 2.1 Hz, 1 H), 2.82 - 2.94 (m, 1 H), 3.07 - 3.13 (m, 1 H), 3.15 - 3.19 (m, 1 H), 3.41 - 3.53 (m, 1 H), 6.39 (d, *J* = 2.1 Hz, 1 H), 6.72 (d, *J* = 3.2Hz, 1 H), 12.11 (bs, 2 H).

3a,4,7,7a-Tetrahydro-1*H*-4,7-methanoindene-2,5-dicarbonyl dichloride (9):[30] **8** (1.35 g, 6.14 mmol, 1.00 eq.) was suspended in 20 mL oxalyl chloride. The resulting mixture was stirred at 55 °C for 36 h until clear solution was obtained and formation of CO_2 had ceased. Thereafter it was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product was used without further purification.

General procedure for macrocycle formation: Under an argon atmosphere, pyridine (5.00 eq.) was dissolved in 60 mL anhydrous THF. Thereafter a solution of the diol (1.00 eq.) in 100 mL anhydrous THF and a solution of the carbonyl chloride (1.00 eq.) in 100mL anhydrous THF were added at approximately equal rates at room temperature over a period of 5 h. The solvent was removed under reduced pressure, the residue was dissolved in 100 mL of hydrochloric acid (10% HCl in water, v/v) and extracted three times with DCM. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated before further purification steps were carried out.[30]

CF-COO-Cp$_2$a: According to the general procedure, pyridine (3.97 mL, 3.90 g, 49.3 mmol, 5.00 eq.), **7a** (4.06 g, 9.86 mmol, 1.00 eq.) and **9** (2.54 g, 9.86 mmol, 1.00 eq.) were reacted in 260 mL of anhydrous THF. The crude product was purified by column chromatography (SiO_2, PE : EA 20 : 1) to yield **CF-COO-Cp$_2$a** as a colorless solid (379 mg, 636 µmol, 6.5 %). MP: 173 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.40 (d, *J* = 8.5 Hz, 1 H), 1.65 (td, *J* = 8.7 Hz, *J* = 1.6 Hz, 1 H), 1.85 (ddd, *J* = 15.3 Hz, *J* = 6.5 Hz, *J* = 3.2 Hz, 1 H), 2.01 (ddd, *J* = 14.9 Hz, *J* = 8.9 Hz, *J* = 3.5 Hz, 1 H), 2.24 - 2.35 (m, 2 H), 2.55 (tdd, *J* = 17.7 Hz, *J* = 10.5 Hz, *J* = 2.3 Hz, 1 H), 2.64 (ddd, *J* = 14.3 Hz, *J* = 8.7 Hz, *J* = 5.4 Hz, 1 H), 2.85 - 2.91 (m, 1 H), 2.97 - 3.04 (m, 1H), 3.24 - 3.28 (m, 1 H), 3.48 - 3.52 (m, 1 H), 3.55 - 3.61 (m, 1 H), 3.95 - 4.00 (m, 1 H), 4.16 - 4.23 (m, 1 H), 4.68 - 4.74 (m, 1 H), 6.70 (d, *J* = 2.0 Hz, 1 H), 6.82 (d, *J* = 2.9 Hz, 1 H), 7.46 (d, *J* = 1.5 Hz, 1 H), 7.52 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 2 H), 7.56 (dd, *J* = 8.1 Hz, *J* = 5.7 Hz, 2 H), 7.62 (d, *J* = 1.4 Hz, 1 H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 33.3, 37.6, 37.8, 41.0, 46.8, 47.9, 48.6, 52.6, 53.6, 53.8, 61.4, 63.1, 121.7, 121.7, 121.7, 122.1, 127.3, 127.9, 131.3, 131.3, 137.7, 138.5, 138.5, 138.7, 144.6, 148.7, 149.8, 151.6, 166.0, 166.4. IR (cm^{-1}): 2980, 2916, 2861, 1722, 1693, 1625, 1588, 1447, 1380, 1263, 1213, 1158, 1076, 894, 804, 770,733, 670, 442. HRMS (DART+): calc. for $C_{29}H_{28}{}^{79}Br_2NO_4^+$ $[M+NH_4]^+$: 612.0380, found: 612.0372.

CF-COO-Cp$_2$b: According to the general procedure, pyridine (2.84 mL, 2.79 g, 35.3 mmol, 5.00 eq.), **7b** (3.70 g, 7.06 mmol, 1.00 eq.) and **9** (1.81 g, 7.06 mmol, 1.00 eq.) were reacted in 260 mL of anhydrous THF. The crude product was purified by column chromatography (SiO_2, gradient PE : EA 20 : 1 to 10 : 1) to yield **CF-COO-Cp$_2$b** as a colorless solid (103 mg, 145 µmol, 2.1 %). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.25 - 1.82 (m, 22H), 2.03 - 2.16 (m, 1 H), 2.59 (tdd, *J* = 17.7 Hz, *J* = 10.5 Hz, *J* = 1.9 Hz, 1 H), 3.06 (ddd, *J* = 14.8 Hz, *J* = 8.9 Hz, *J* = 4.2 Hz, 1 H), 3.14 - 3.20 (m, 1 H), 3.37 - 3.43 (m, 1 H), 3.48 - 3.57 (m, 1 H), 3.94 - 4.04 (m, 1 H), 4.06 - 4.31 (m, 3 H), 6.59 (d, *J* = 2.0 Hz, 1 H), 6.95 (d, *J* = 3.2 Hz, 1 H), 7.46 (dd, *J* = 8.1 Hz, *J* = 1.7 Hz, 2 H), 7.50 - 7.57 (m, 4 H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 23.5, 23.7, 24.8, 25.0, 28.2, 28.3, 28.5, 28.7, 33.3, 36.7, 37.5, 41.6, 46.8, 47.5, 51.7, 54.5, 54.6, 64.3, 64.7, 64.7, 64.3, 121.3, 121.4, 127.3, 127.3, 130.4, 138.2, 138.6, 138.6, 139.8, 142.9, 147.2, 153.6, 153.7, 165.3, 165.3. IR (cm^{-1}): 2933, 2855, 1705, 1450, 1394, 1348, 1268, 1232, 1156, 1089, 1004, 905, 809, 763, 729. HRMS (DART+): calc. for $C_{37}H_{44}{}^{79}Br_2NO_4^+$ $[M+NH_4]^+$: 724.1632, found: 724.1644.

General procedure for *Yamamoto* polymerization: Under a nitrogen atmosphere in a glovebox were suspended bis(1,5-cyclooctadiene)nickel(0) (2.25 eq.), 2,2'-bipyridine (2.25 eq.) and (1Z,5Z)-cycloocta-1,5-diene (2.25 eq.) in anhydrous DMF and stirred at 60 °C for 20 min. Thereafter 2,7-dibromo-9,9-bis(2-ethylhexyl)-9*H*-fluorene (0.80 - 1.00 eq.), the dibrominated crosslinker monomer (0.00 - 0.20 eq.) and 4-bromo-*N*,*N*-di-p-tolylaniline (1.5 mol%) in anhydrous THF (final solvent ratio: DMF:THF 1:3, v/v) were added. The resulting reaction mixture was stirred at 60 °C for 36 h. The crude polymer was precipitated in an excess of a mixture of methanol/hydrochloric acid (2:1, v/v, 3 $molL^{-1}$). Crosslinker monomers prone to decomposition in acidic media were precipitated in an excess of a mixture of methanol/hydrochloric acid (2:1, v/v, 1 $molL^{-1}$) and the resting time in the acidic non-solvent mixture was minimized. The precipitate was collected by filtration, filtered through a PTFE filter (0.45 µm, THF or chloroform) and then purified by preparative gel permeation chromatography (toluene) to yield the desired statistical copolymer.

Optical and Photoluminescence Spectroscopy

Absorption spectra were recorded on a Jasco UV-Vis V-660 or Jasco UV-Vis V-670. Fluorescence spectra were recorded on a Jasco FP-6500. Quantum yields were determined by an Ulbricht sphere (6 inch) using a PTI QuantaMaster 40 equipped with a Hamamatsu R928P photomultiplier. For all measurements in THF the solvent was purchased from Sigma Aldrich in the quality CHROMASOLV PLUS (purity ≥ 99.9 %). For films the substance was dissolved in chloroform (1 mg/mL). The solution was spin-coated with a Spin 150 from S.P.S. with a rotational speed of 1000 rpm for 10 s followed by 3000 rpm for 5 s.

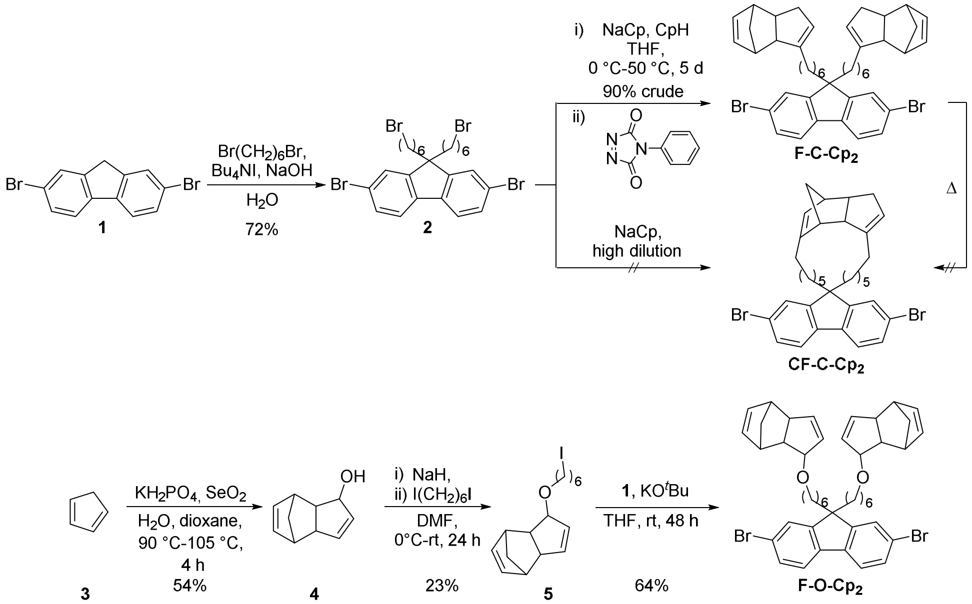
OLED Fabrication and Characterization

Glass/ITO substrates (Kintec) were cleaned in an ultrasonic bath for 10 min in acetone and isopropanol consecutively and treated with O_2 plasma for 5 min. For a regular device architecture, a PEDOT:PSS solution (Heraeus P VP AI 4083) was filtered through a 0.45 µm PVDF filter, spin-coated in ambient conditions with $\omega = 3800$ rpm and $a = 800$ rpm s^{-1} for 45 s and afterwards annealed on a hotplate for 20 min at 135 °C. The film thickness averages at 25 nm. The further film preparation was performed under nitrogen atmosphere. The PF derivatives were separately dissolved in toluene (VWR >99.8%) with a concentration of 10 mg ml^{-1}. The solutions were spin-coated with $\omega = 1250$ rpm and $a = 1000$ rpm s^{-1} for 60 s. The films were either annealed at 80 °C for 5 min (dried) or at 200 (PF-EtHex) 180 (PF-COO-CP 10%), 200 (PF-C-CP 10%) or 250 °C (PF-O-CP 10%) for 30 min to obtain a film thickness of 60 nm. TPBi (Ossila), LiF and Al (45 nm / 1 nm / 100 nm) were thermally evaporated at a pressure of 10^{-6} mbar yielding an active area of 24 mm^2. The OLEDs were characterized under nitrogen atmosphere with a calibrated Botest LIV functionality test system. The electroluminescence was examined with an OceanOptics 2000+ spectrometer. The film thicknesses were determined with a Vecco Dektak 150 profilometer.

Results and Discussion

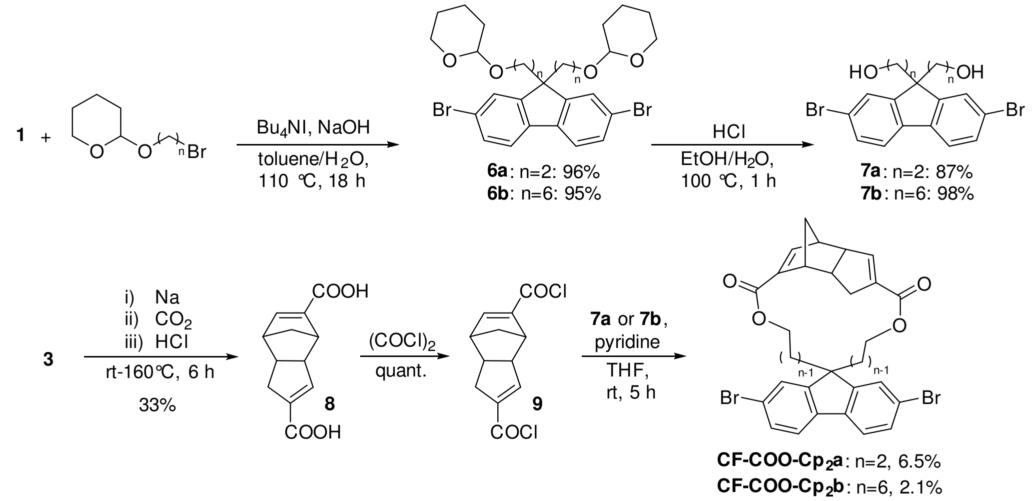
We first synthesized two bis(cyclopentadienyl)-substituted fluorene monomers **F-C-Cp$_2$** and **F-O-Cp$_2$** with covalently bound cyclopentadienyl groups masked as their Diels-Alder adducts with cyclopentadiene, *via* alkyl or alkoxy linkers, respectively (Scheme 2). Nucleophilic substitution of 2,7-dibromofluorene (**1)** with 1,6-dibromohexane yielded bis(bromohexyl)fluorene **2**. Addition of sodium cyclopentadienide in THF in the presence of an excess of Cp furnished crude **F-C-Cp$_2$** as a mixture of several stereoisomers in 90% yield. Traces of monomers with unprotected diene functionalities were trapped with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and the resulting polar cycloadducts were removed *via* column chromatography on silica. GPC analysis (see Supporting Information) confirmed the monomeric nature of **F-C-Cp$_2$**. **F-O-Cp$_2$** was obtained after dimerization and subsequent Riley oxidation of cyclopentadiene **3** to vinyl alcohol **4**, which in turn was reacted with 1,6-diiodohexane to obtain vinylether **5** in 23% yield. Final nucleophilic substitution with dibromofluorene **1** furnished **F-O-Cp$_2$** in 64% yield. To avoid liberation of Cp from the target polymers during thermal activation, possibly compromising electronic properties and morphology of the emissive layer, we aimed for synthesis of cyclic and thus self-protected **CF-C-Cp$_2$**. Reaction of **2** with sodium cyclopentadienide in

THF in high dilution (150 µM) was not successful, as only oligomeric species or unreacted starting material were observed. After a controlled retro-Diels-Alder reaction of highly diluted **F-C-Cp$_2$** in 1,2,5- trichlorobenzene at 200 °C and subsequent intramolecular Diels-Alder reaction upon cooling to 50 °C, only traces of **CF-C-Cp$_2$** were detected (Scheme 2).



Scheme 2: Synthesis of crosslinkable fluorene monomers **F-C-Cp$_2$** (as mixture of endo/exo and constitutional isomers) and **F-O-Cp$_2$**.

To circumvent the need for an intramolecular Diels-Alder reaction, Thiele's acid **8**[30,32] was utilized as a readily available Cp dimer. The conversion of **8** into the corresponding acid chloride **9**[32] and subsequent alcoholysis with fluorenediol **7a**, after reaction of **1** with THP-protected 6-bromoethanol, afforded cyclic **CF-COO-Cp$_2$a** (Scheme 3). **CF-COO-Cp$_2$a** was obtained as the isomerically pure *endo*-product as confirmed *via* the X-ray single crystal structure (Figure 2). The hexamethylene-based macrocycle **CF-COO-Cp$_2$b** was prepared from **7b** and **9** by the same synthetic protocol. These intramolecular macrocyclizations only occurred in low yields due to competing polymerization processes despite working at low concentrations (7% and 2% for **CF-COO-Cp$_2$a** and **CF-COO-Cp$_2$b**, respectively). However, as the crosslinkable monomers are added into the statistic polymerization with only a share of 5% to 20%, the amount of **CF-COO-Cp$_2$a**, obtained on a 400 mg scale, was sufficient for polymer syntheses.



Scheme 3: Synthesis of macrocyclic monomers **CF-COO-Cp$_2$a** and **CF-COO-Cp$_2$b** for crosslinking.

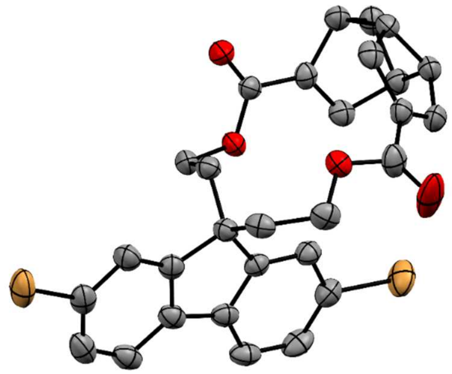
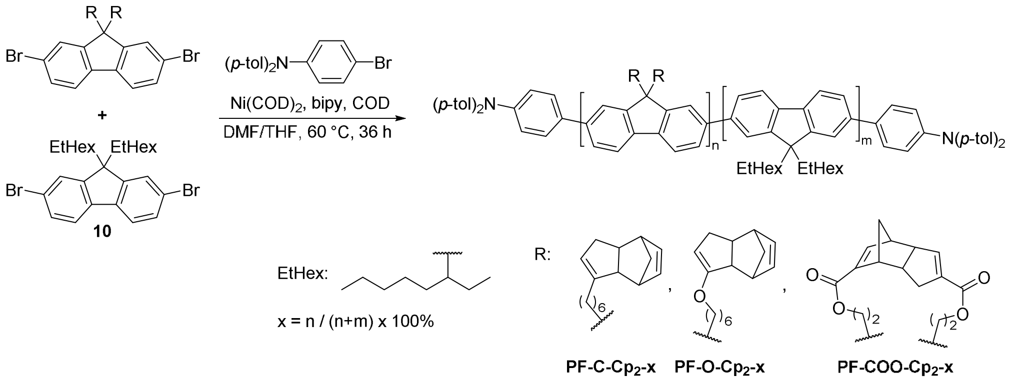


Figure 2: ORTEP representation of **CF-COO-Cp2a**.

We investigated the retro-Diels-Alder reactions of the monomers by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC, see Supporting Information). For **F-C-Cp$_2$** and **F-O-Cp$_2$** cleavage temperatures were estimated to be 200 °C and 250 °C, respectively. The measured mass loss is in the range of the theoretically expected one with two Cp units per monomer – in a further cooling/heating cycle no mass loss was observed. The DSC trace of macrocyclic monomer **CF-COO-Cp$_2$a** revealed a transition at 180 °C, attributed to the retro-Diels-Alder reaction of the Cp dimer to its open form without any loss of mass (TGA), supporting the validity of our concept. To demonstrate monomer crosslinking, we heated all monomers (**F-C-Cp$_2$**, **F-O-Cp$_2$** and **CF-COO-Cp$_2$a**) to their respective retro-Diels-Alder temperature for a period of 5 to 60 minutes under inert atmosphere. Subsequent analysis by gel permeation chromatography (GPC) suggested the formation of oligomeric Diels-Alder-adducts after only five minutes of heating (see Supporting Information).

Polymerization under standard Yamamoto conditions requires reaction temperatures between room temperature and 120 °C.[36] Control experiments conducted in the aforementioned manner show that our monomers are inert towards retro-Diels-Alder reactions up to 80 °C (see Supporting Information). Thus, monomers **F-C-Cp$_2$**, **F-O-Cp$_2$** and **CF-COO-Cp$_2$a** were subjected to statistic co-polymerization with 1,6-dibromo-9,9-(2-ethylhexyl)fluorene (**10**) by Yamamoto coupling at 60 °C, using 5, 10 or 20% of the crosslinkable dibromofluorenes to yield polyfluorenes **PF-C-Cp$_2$-x**, **PF-O-Cp$_2$-x** and **PF-COO-Cp$_2$-x** (x denotes the molar percentage of crosslinkable monomer).[37] As a reference, the homopolymer of **10** (**PF-EtHex**) was prepared under the same conditions (Scheme 3). The polymers were end-capped with 4-bromo-*N,N*-di-*para*-tolylaniline, increasing stability and efficiency of polyfluorenes in OLEDs without affecting electronic properties of the backbone.[38] All polymers were obtained in yields between 37% and 82% by precipitation from a mixture of methanol/3 M hydrochloric acid (2:1, v/v) and subsequent purification by preparative size exclusion chromatography. They were fully characterized *via* analytical gel permeation chromatography versus polystyrene standards in THF, TGA/DSC and optical spectroscopy, both in solution and thin films (Table 1, Table 2, Figure 3 and Supporting Information).



Scheme 4: Nickel-mediated statistic Yamamoto polymerization yielding crosslinkable polyfluorenes using 5%, 10% and 20% of crosslinkable monomers.

Table 1: Yield, molecular weights and thermal properties of polyfluorenes prepared by statistic Yamamoto coupling.

	yield (%)	M_n (10^4 g/mol)	n+m[a]	M_w (10^4 g/mol)	$Đ$	T_{onset}[b] (°C)	Δm_{theo}[c] (%)	Δm[c] (%)
PF-EtHex	66	4.7	121	10.4	2.2	-[d]	0.0	0.0
PF-C-Cp$_2$-5%	67	3.7	92	10.2	2.8	205	1.7	1.3
PF-C-Cp$_2$-10%	63	4.1	100	20.8	6.0	202	3.2	2.4
PF-C-Cp$_2$-20%	37	1.7	40	10.2	5.1	200	6.2	3.7
PF-O-Cp$_2$-5%	63	2.4	61	4.7	1.9	240	1.7	1.2
PF-O-Cp$_2$-10%	65	2.0	49	3.6	1.8	225	3.2	2.6
PF-O-Cp$_2$-20%	56	1.4	32	2.1	1.5	225	6.1	3.5
PF-COO-Cp$_2$-5%	81	6.0	152	22.9	3.8	-[d]	0.0	0.0
PF-COO-Cp$_2$-10%	82	4.6	117	17.6	3.8	-[d]	0.0	0.0
PF-COO-Cp$_2$-20%	76	4.2	105	27.1	6.5	-[d]	0.0	0.0

[a] Number of repeat units calculated from M_n. [b] Onset temperature of retro-Diels-Alder reaction determined via TGA (scanning rate 10 K/min). [c] (Theoretical/observed) mass loss after retro-Diels-Alder reaction and complete Cp expulsion. [d] No mass loss detected.

Table 2: Optical properties of polymers in THF and thin films at room temperature.

	in solution			thin film before ΔT[a]			thin film after ΔT[b]		
	$\lambda_{max, abs}$ (nm)	$\lambda_{max, em}$ (nm)	Φ (%)	$\lambda_{max, abs}$ (nm)	$\lambda_{max, em}$ (nm)	Φ (%)	$\lambda_{max, abs}$ (nm)	$\lambda_{max, em}$ (nm)	Φ (%)
PF-EtHex	377	414	80.1	380	422	22.8	379	422	17.4
PF-C-Cp$_2$-5%	379	414	83.3	383	422	20.9	383	423	13.3

PF-C-Cp$_2$-10%	385	415	80.2	385	424	26.7	385	422	21.4
PF-C-Cp$_2$-20%	383	415	81.4	384	423	22.5	384	422	14.5
PF-O-Cp$_2$-5%	384	415	86.9	385	423	25.9	385	423	12.3
PF-O-Cp$_2$-10%	383	415	85.1	385	422	23.6	385	422	11.3
PF-O-Cp$_2$-20%	380	415	86.0	380	422	32.8	380	422	11.8
PF-COO-Cp$_2$-5%	385	415	84.7	387	424	25.9	388	422	31.0
PF-COO-Cp$_2$-10%	385	415	85.2	386	423	25.7	385	422	25.4
PF-COO-Cp$_2$-20%	386	415	78.9	389	422	23.6	389	423	25.4

[a] Before application of a thermal stimulus. [b] After application of a thermal stimulus ΔT, where ΔT exceeds the determined retro-Diels-Alter temperature.

The number of repeat units of all polyfluorenes well exceeded the effective conjugation length ($n > 12$).[39] With increasing amount of crosslinkable units, dispersity increases deviating from the value expected for polycondensations (Đ = 2). These characteristics are due to minor dimeric impurities (<1%) in the starting materials, resulting in decreased solubility and lower yields of the polymers containing 20% of crosslinker. The DSC peaks attributed to the retro-Diels-Alder reaction in addition to the weight loss observed in the mass trace (see Supporting Information) are in agreement with the cleavage temperatures of the monomers. The absorption spectra measured from solutions in THF exhibit absorption maxima at $\lambda_{max,em}$ = 377 - 386 nm typical of polyfluorenes (see Table 2, Figure 3 and Supporting Information). The fluorescence spectra reveal emission maxima at $\lambda_{max,em}$ = 414 - 415 nm with fluorescence quantum yields in the range of Φ = 79-87%. The emission spectra of thin films do not exhibit bands at lower energies attributed to fluorenone units. Even after thermal treatment at 250 °C, necessary for the activation of **PF-O-Cp$_2$**, the solid-state emission spectrum does not show any sign of keto-defect formation.[40,41]

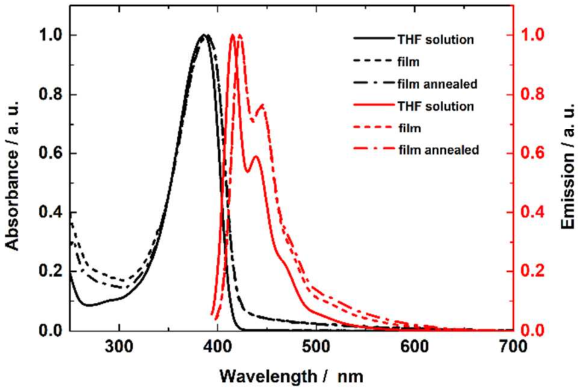


Figure 3: Representative absorption and fluorescence spectra of **PF-COO-Cp$_2$-10%** in solution (THF) and thin films on glass before and after annealing at 180 °C.

Effective crosslinking was demonstrated by rinsing drop-cast polymer films with toluene as a good solvent before and after thermal annealing at 200 °C for 30 min (see Supporting Information). For process optimization, 50-70 nm thick polymer films containing 10 mol% of crosslinker were spun-cast from polymer solutions (8 mg/mL) in toluene. These films were annealed thermally (180 °C, 200 °C and 250 °C for **PF-COO-Cp$_2$**, **PF-C-Cp$_2$** and **PF-C-Cp$_2$**, respectively) for different time periods and stored over night at room temperature. After treatment with 150 µL toluene for 5 seconds before spinning off the solvent, the absorption spectra were recorded. The changes in absorption were quantified and compared to those of the samples before thermal treatment (see Figure 4 and Supporting Information).

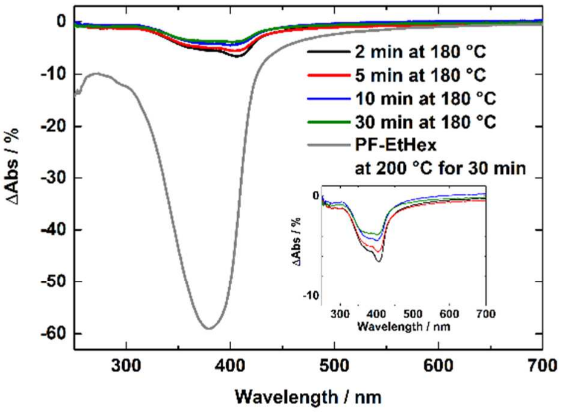


Figure 4: Differential absorption spectra of reference polymer **PF-EtHex** and **PF-COO-Cp$_2$-10%** before and after annealing at 180 °C for a given amount of time. Smaller changes correspond to a higher degree of desolubilization and crosslinking.

For non-crosslinkable **PF-EtHex**, absorbance was reduced by ca. 60%-70%, independent of the annealing time. Heating films of **PF-O-Cp$_2$-10%, PF-C-Cp$_2$-10%** and **PF-COO-Cp$_2$-10%** resulted in complete desolubilization: After 30 minutes at the respective cleavage temperatures, a change of only max. 3% in absorbance was observed for all polymers – even 10 min sufficed to form insoluble networks. Films of higher crosslinking content were even more solvent resistant, whereas a lower crosslinking content of 5% appeared to be insufficient. Additionally, since the above method is susceptible to potential errors from film inhomogenieties, we investigated crosslinking with white light interferometry, visualizing changes of film thickness in the nanometer range. Droplets of various solvents were placed on 50-70 nm thin polymer films by inkjet-printing before and after thermal treatment for 30 min (Figure 5, chlorobenzene as solvent). Changes in height profiles are summarized in the Supporting Information. Both methods showed that untreated polymer layers were re-dissolved by chlorobenzene, whereas annealed films exhibited excellent solvent resistivity. Utilizing 10% and 20% of crosslinker, only a small coffee ring effect[42] as a result of swelling was observed.[43,44,45] **PF-C-Cp$_2$** (20% crosslinker content) were an exception in our series: A small amount of already crosslinked moieties within the monomer (*vide supra*) might explain solvent persistence already after drying at room temperature. Solvent resistance was not limited to chlorobenzene as demonstrated for non-crosslinkable **PF-EtHex** and **PF-COO-CP$_2$-10%** for five additional organic solvents utilizing the same experimental setup (see Supporting Information). The shorter connection of the Cp to the polymer backbone of **PF-COO-CP$_2$-10%** in terms of linker length (4 atoms vs 6 or 7 in **PF-C-Cp$_2$-10%** or **PF-O-Cp$_2$-10%**, respectively) and the resulting decreased flexibility do not prevent desolublization for the crosslinker ratios and conditions investigated.

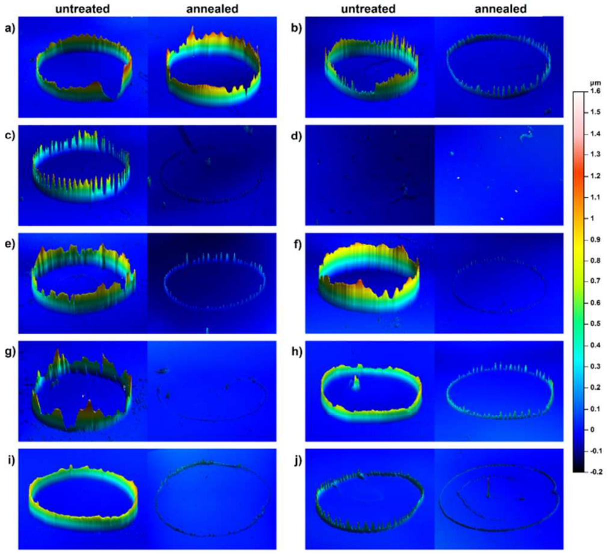


Figure 5: Surface profiles of chlorobenzene droplets on thin films before and after thermal treatment. a) **PF-EtHex**, b) **PF-C-Cp$_2$-5%**, c) **PF-C-Cp$_2$-10%**, d) **PF-C-Cp$_2$-20%**, e) **PF-O-Cp$_2$-5%**, f) **PF-O-Cp$_2$-10%**, g) **PF-O-Cp$_2$-20%**, h) **PF-COO-Cp$_2$-5%,** i) **PF-COO-Cp$_2$-10%** j) **PF-COO-Cp$_2$-20%**.

Solution processed proof-of-concept OLEDs were fabricated to evaluate the influence of the crosslinked side chains. Pristine **PF-EtHex** was chosen as the reference and compared to polyfluorenes with 10% crosslinker, representing optimum desolubilization as previously discussed. Device performances of OLEDs with active layers treated at the respective crosslinking procedure (see Experimental) were evaluated against dried layers (i.e. 80 °C, 5 min). Figure 6 displays the LIV-characteristics of the devices showing turn-on voltages < 7 V and luminance up to 10^4 cd m^{-2}. The OLEDs' figures of merit are summarized in Table 3. As a note, all the dried (80 °C) samples revealed comparable device performances (see Supporting Information).

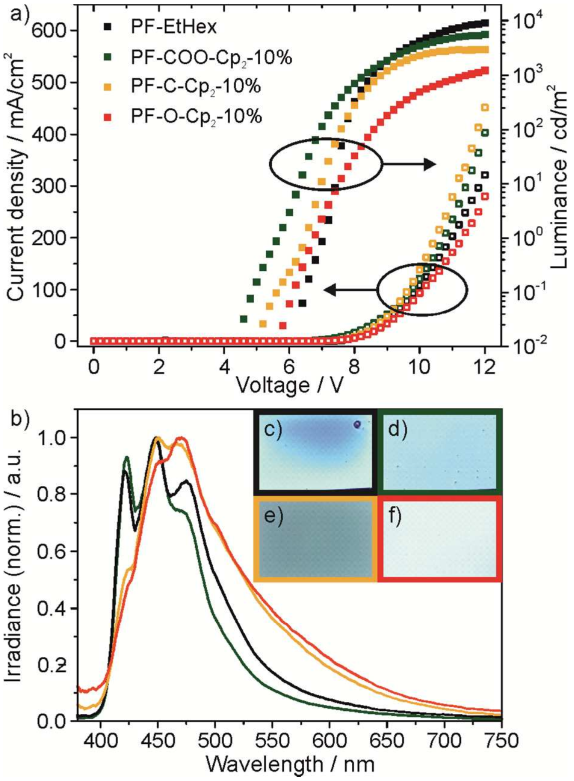


Figure 6: LIV-characteristics of the pixel closest to average of at least 4 samples of each polymer (a), electroluminescence spectra (b) and micrographs of the light emission (c-f) of annealed polyfluorene layers.

Table 3: LIV parameters from measurements of dried and annealed OLEDs.

	PF-COO-Cp$_2$-10%		**PF-C-Cp$_2$-10%,**		**PF-O-Cp$_2$-10%**		**PF-EtHex**	
	Dried	Annealed	Dried	Annealed	Dried	Annealed	Dried	Annealed
Luminance[a] [cd/m^2]	2972.1 ± 1980.3	5041.9 ± 1061.1	1382.7 ± 59.8	2715.8 ± 940.9	4572.9 ± 478.2	1350.6 ± 198.0	1316.5 ± 227.5	12071.2 ± 3516.9
Efficiency[b] [cd/A]	5.1 ± 0.3	4.6 ± 0.2	3.9 ± 0.2	2.8 ± 1.5	3.7 ± 0.5	0.5 ± 0.1	3.5 ± 1.9	5.1 ± 0.6
Efficacy [lm/W]	2.6 ± 0.4	2.0 ± 0.1	1.5 ± 0.1	1.2 ± 0.7	1.6 ± 0.2	0.2 ± 0.0	1.5 ± 0.9	2.4 ± 0.2
Turn-On-Voltage[c] [V]	5.4 ± 0.2	5.6 ± 0.0	7.1 ± 0.1	6.9 ± 0.8	6.5 ± 0.2	6.7 ± 0.0	6.9 ± 0.4	5.9 ± 1.5

[a] Maximum luminance. [b] Maximum value (not a defined luminance). [c] @ 1 cd.

In terms of performance, a clear trend is observed among the crosslinkable polyfluorenes: self-protected **PF-COO-Cp$_2$-10%** exhibits the best behavior in terms of luminance, efficiency, efficacy as well as turn-on voltage after high-temperature annealing. Compared to the dried devices, an increase in luminance with a slight reduction in efficacy was observed for the crosslinked **PF-COO-CP$_2$-10**% (180 °C) and **PF-C-Cp$_2$-10%** (200 °C). The higher crosslinking temperature of 250 °C required for activation of **PF-O-Cp$_2$-10%** lead to a decrease in device efficiency down to 0.5 cd A^{-1} emphasizing the need of lowering annealing temperatures. The best performing crosslinked devices were prepared on the basis of **PF-COO-CP$_2$-10%** achieving a luminance of 0.5x10^4 cd m^{-2}, current (power) efficiency of 4.6 cd A^{-1} (2.0 lm W^{-1}) and a turn-on voltage of 5.6 V. These might compete with the reference device after further optimization, which exhibits the highest efficiency and efficacy after a thermal annealing (200°C, 30 min) with 5.1 cd A^{-1} and a maximum luminance of ~$1.2x10^4$ cd m^{-2}. To gain an explanation for the decrease in device performance, morphological changes in the active layers were investigated. Comparing the surface topologies of dried and thermally crosslinked films by AFM measurements (see Supporting Information) indicated that thermal treatment lead to morphological changes resulting in holes which were also observed in the treated reference sample **PF-EtHex**. Nevertheless, short-contacts did not occur in any device. We assume that the cavities do not extend through the entire layer and that they are fully covered by TPBi. Figure 6b presents the typical electroluminescence-spectra (EL) and micrographs of devices under operation for the annealed devices. The EL spectra correspond to the photoluminescence spectra presented in Figure 3. The integrity of the emission properties is preserved after desolubilization.

As **PF-COO-Cp_2-10%** exhibits superior device performance compared to **PF-C-Cp_2-10%**, which has only been treated at slightly higher temperatures also employed for annealing **PF-EtHex**, we conclude that extrusion of Cp during desolubilization has to be avoided. Incorporation of macrocyclic **CF-COO-Cp_2a** or **CF-COO-Cp_2b** into other functional polyfluorenes or synthesis of structurally related macrocyclic monomers seems promising to facilitate production of purely thermally and by-product free crosslinkable polymeric layers for organic electronics. These could be directly employed after a short heat stimulus without the need of further steps, like annealing or washing, and are thus compatible with roll-to-roll processes.

Conclusion

Thermally induced solubility modulation based on reversible Diels-Alder reactions of cyclopentadienes attached to polyfluorenes was utilized to form solvent-resistant emissive layers in OLEDs. The semi-conducting polymers were synthesized *via* statistic nickel-mediated Yamamoto polymerization of conventional ethylhexyl-substituted fluorene monomers with crosslinkable bis(cyclopentadienyl)-functionalized bis(bromo)fluorenes in different ratios (5%, 10% and 20% of crosslinker). These bis(cyclopentadiene)s, incorporated into the polymer side-chains through different linkages (C-C bonds, ether or ester groups), are thermally activated by retro-Diels-Alder reaction in the temperature range of 180 °C – 250 °C, controllable *via* their electron demand. The generated pending cyclopentadienyl units crosslink by additive-free [4+2] cycloadditions upon cooling with high functional group tolerance. Two polyfluorenes bearing macrocyclic self-protected bis(cyclopentadienylene) units were synthesized to avoid extrusion of Cp as sacrificial protecting groups during network formation. The solvent resistance of the resulting PF layers was examined by absorption spectroscopy and white-light scanning interferometry – a comparably short heat stimulus of 10 to 30 min at the respective activation temperatures is sufficient to render these films insoluble. Among the crosslinkable PFs applied in proof-of-concept OLED devices, the macrocyclic self-protected bis(cyclopentadienylene) demonstrated superior performances over their externally Cp-protected counterparts. Thus, the necessity of by-product free immobilization processes was emphasized. In the future, we will extend our concept of self-protected macrocyclic systems to higher performing polymeric and monomeric semiconductors for fully printed organic electronic devices. The relatively low activation temperature additionally allows application of our process to a variety of flexible plastic substrates. The reversibility of the dimer formation offers further opportunities to increase stability of layers at their interfaces or for patterning.

Supporting Information Description

General remarks, synthetic details and compound characterization, ^{1}H, ^{13}C NMR and GPC spectra, TGA/DSC measurements, UV-Vis and PL spectra, further information on crosslinking tests, single crystal structure analysis and AFM measurements of films.

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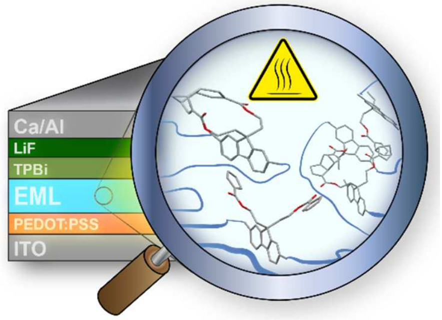
TOC



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