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# Photocrosslinkable Polymer Inks for Solution-Based OLED Fabrication

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ABSTRACT. We introduce a catalyst-free, highly efficient, ambient temperature Diels-Alder reaction employing *o*-methylbenzaldehyde derivatives as photo-caged dienes as an ideal approach for forming three-dimensional insoluble networks for inkjet printing of OLED emissive layer. Herein, poly(methyl methacrylate) based polymers containing 4-(9H-carbazol-9-yl)-2-(3'-

hydroxy-[1,1'-biphenyl]-3-yl)isoindoline-1,3-dione as a blue-green ( $\lambda_{\text{max}} = 495\text{-}500\text{ nm}$ ) Thermally Activated Delayed Fluorescence (TADF) emitter and a photochemically active maleimide/*o*-methylbenzaldehyde crosslinker couple were synthesized and their photocrosslinking behavior was studied. Time resolved fluorescence measurements confirm that the TADF properties are maintained upon integration in a polymer network and HOMO/LUMO levels of the emitter species remain unchanged by the photocrosslinking at 365 nm of the polymer chains. The network formation of the fluorescent films is evidenced by solvent resistance tests and monitored by Fourier Transform Infrared (FT-IR) spectroscopy as well as Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS), showing the consumption of maleimide and *o*-methylbenzaldehyde groups with increasing irradiation time. The surface roughness is investigated via Atomic Force Microscopy (AFM) and found to be unchanged by a solvent wash after the crosslinking. Furthermore, confirmation that the polymer solution can be printed on an inkjet-printer and subsequently photocrosslinked for multilayer OLED device fabrication is achieved.

**INTRODUCTION.** Since their discovery in 1987,<sup>1</sup> Organic Light Emitting Diodes (OLEDs) have conquered our everyday life in display applications for mobile phones, large area OLED television and solid-state lighting. Next-generation metal-free emitter materials for efficient OLED electroluminescence are based on a Thermally Activated Delayed Fluorescence (TADF) mechanism, harvesting the energy of both singlet and triplet excitons and therefore, achieving internal quantum efficiencies up to 100%.<sup>2,3</sup> Further efficiency optimization can be realized by fabricating multilayered devices in which each layer has distinct functions, for example targeted charge injection and transport compared to a single layer architecture of the emissive layer sandwiched between two electrodes.<sup>4</sup>

Currently, small molecule multilayered OLED devices are fabricated by vacuum deposition techniques,<sup>5</sup> which face limitations including high materials waste, confined vacuum chamber sizes and high production costs when it comes to manufacturing of large-area displays.<sup>6</sup> In particular, high molecular weight compounds, such as oligomers and polymers are difficult to process using vapor-deposition, however, are more desirable as they show better film forming abilities as well as morphological stability in the device compared to the small molecule analogues. Preferable solution-based fabrication methods such as ink-jet printing are to date still very limited as the deposition of a new layer partly dissolves the previously deposited layer and there are only few OLED materials with orthogonal solubility available.<sup>7-9</sup>

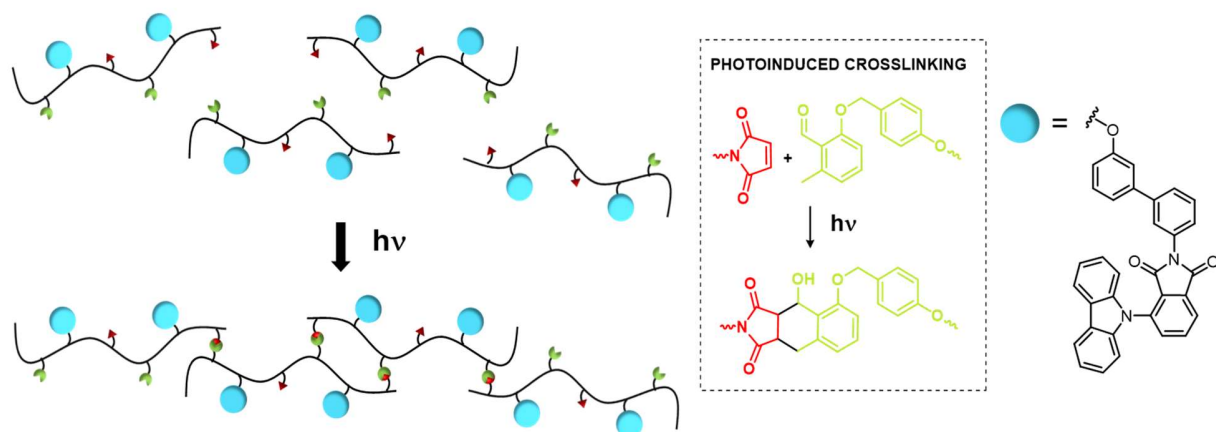
Polymers with TADF active units have previously been synthesized in different architectures<sup>10</sup> such as in the central core or peripheral branches of dendrimers,<sup>11-13</sup> on conjugated<sup>14-16</sup> or non-conjugated<sup>17-19</sup> polymer backbones with the TADF unit as a pendant side group or with the TADF property incorporated in the lateral chain.<sup>16</sup> An advantage of the polymer bearing the emitter functionality as a pendant side group is the preservation of the original emitter characteristics whilst improving the solubility, ink forming ability, large area processing capability and thermal stability of the material.

One approach to prepare organic materials with solvent resistance for solution processing is the crosslinking of a polymer precursor to form insoluble three-dimensional networks.<sup>20</sup> For example, hole transporting materials equipped with various crosslinkable moieties such as oxetane groups were reported to undergo cationic polymerization upon UV irradiation with a photoinitiator.<sup>21-23</sup> Photoinduced [2+2] cycloaddition of cinnamate polymer side groups with UV light leads to network formation with the emitter function being covalently attached to the polymer.<sup>24,25</sup>

More commonly employed is the thermal crosslinking of polymers that are end functionalized with styrene groups at the  $\alpha$ - and  $\omega$ -chain end.<sup>26,27</sup> Other crosslinkable groups that are induced by temperature are benzocyclobutenes dimerizing above 180 °C by ring opening and subsequent cycloaddition<sup>28</sup> as well as trifluorovinyl ethers that undergo a thermal [2+2] cycloaddition at 230 °C.<sup>29-31</sup> Another method is the oxidative crosslinking of carbazole units of the hole transporting material poly(vinylcarbazole) at rather low temperatures of 110 °C.<sup>32</sup>

A powerful ligation to generate three-dimensional networks under mild conditions is the ambient-temperature activated Diels-Alder reaction between a conjugated diene and a suitable dieneophile.<sup>33</sup> When using photo-caged dienes such as *ortho*-methylbenzaldehydes the Diels-Alder cycloaddition can be triggered in a controlled way by targeted UV irradiation.<sup>34-36</sup> Recently, our group has demonstrated another facile way to photo-crosslink such *o*-methylbenzaldehydes by exploiting their self-dimerization.<sup>37,38</sup>

Herein, we introduce the design of precision tailored copolymer structures suitable for inkjet printing of multilayer OLED devices (Figure 1). The bespoke structures incorporate the TADF emitter 4-(9H-carbazol-9-yl)-2-(3'-hydroxy-[1,1'-biphenyl]-3-yl)isoindoline-1,3-dione as well as photocrosslinkable groups as side group functionalities. The crosslinking of the emissive layer instead of only the hole transporting layer paves the way for fully solution-processed OLED devices. To the best of our knowledge, no TADF materials have been used in a crosslinkable emissive layer ink so far.



**Figure 1.** Photochemically induced crosslinking of polymer precursors by means of a [4+2] Diels-Alder cycloaddition between maleimide and *o*-methylbenzaldehyde as photocaged diene, while maintaining the TADF emitter functionality (blue spheres, structure shown on the right) in the final network.

## EXPERIMENTAL SECTION

**Monomer Synthesis.** To a solution of 4-(9H-carbazol-9-yl)-2-(3'-hydroxy-[1,1'-biphenyl]-3-yl)isoindoline-1,3-dione (5.25 g, 10.2 mmol, 1 eq.) and triethylamine (0.14 mL, 0.10 g, 1.0 mmol, 0.1 eq.) in dry DMF (76.5 mL) a solution of 2-isocyanatoethyl methacrylate (1.44 mL, 1.58 g, 10.1 mmol, 1.0 eq.) in DMF (20 mL) was added dropwise and stirred at room temperature for 22 h. The reaction mixture was extracted with ethyl acetate, washed with water and dried over MgSO<sub>4</sub> before the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, eluent: cyclohexane:ethyl acetate 3:1) and dried in vacuo (yield: 92%).

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ [ppm]= 8.17 – 8.11 (m, 3H, Ar-H), 8.02 (dd, *J*=8.0, 7.3 Hz, 1H, Ar-H), 7.96 (dd, *J*=8.0, 1.0 Hz, 1H, Ar-H), 7.58 (t, *J*=1.9 Hz, 1H, Ar-H), 7.54 (dt, *J*=7.8, 1.5 Hz, 1H, Ar-H), 7.48 (t, *J*=7.9 Hz, 1H, Ar-H), 7.42 – 7.36 (m, 5H, Ar-H), 7.33 – 7.29 (m, 3H, Ar-H),

7.21 (dt,  $J=8.2, 0.8$  Hz, 2H, Ar-H), 7.11 (dtd,  $J=6.9, 4.3, 2.0$  Hz, 1H, Ar-H), 6.15 (q,  $J=1.2$  Hz, 1H, CH<sub>2</sub>=CH), 5.61 (p,  $J=1.6$  Hz, 1H, CH<sub>2</sub>=CH), 5.30 (t,  $J=5.9$  Hz, 1H, NH), 4.30 (t,  $J=5.3$  Hz, 2H, CH<sub>2</sub>-O), 3.59 (q,  $J=5.6$  Hz, 2H, CH<sub>2</sub>-N), 1.96 (t,  $J=1.3$  Hz, 3H, CH<sub>3</sub>).

**Example of a Polymerization Procedure (PC2).** Methyl methacrylate and THF were passed over basic alumina prior to utilization. The emitter carbamate methacrylate **M1** (48.4 mg, 0.08 mmol, 5 eq.), furan protected maleimide methacrylate **M2** (21.1 mg, 0.08 mmol, 5 eq.), 2-(methacryloyloxy)ethyl 4-((2-formyl-3-methyl-phenoxy)-methyl)-benzoate **M3** (29.1 mg, 0.08 mmol, 5 eq.) and AIBN (10.0mg, 0.06 mmol, 2 eq.) were carefully weighed in a dry headspace vial. Methyl methacrylate (0.14 mL, 0.13 g, 1.30 mmol, 85 eq.) and THF (2.4 mL) were added, the vial sealed airtight and degassed by bubbling argon for 5 min. The polymerization mixture was then placed in a preheated oil bath and stirred at 65 °C for 20 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 polymer was dried in vacuo (yield: 82%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]= 10.75 (s, 1H, C=O-H), 8.19 – 7.89 (m, 7H, Ar-H), 7.63 – 7.43 (m, 5H, Ar-H), 7.43 – 7.27 (m, 8H, Ar-H), 7.21 (m, 2H, Ar-H), 7.11 (s, 1H, Ar-H), 6.93 – 6.78 (m, 2H, Ar-H), 6.55 (s, 2H, CH=CH), 5.26 (s, 4H, CH-O-CH, Ar-CH<sub>2</sub>-O), 4.52 (s, 2H, CH<sub>2</sub>-O), 4.30 (s, 2H, CH<sub>2</sub>-O), 4.09 (m, 4H, CH<sub>2</sub>-O), 3.76 (s, 3H, CH<sub>2</sub>-O), 3.58 (m, 57H, CH<sub>3</sub>-O PMMA), 2.97 (s, 2H, O=C-CH-CH-C=O), 2.59 (s, 3H, Ar-CH<sub>3</sub>), 1.84 (m, 38H, CH<sub>3</sub> PMMA), 1.39 (m, 5H, PMMA), 1.01 (s, 22H, PMMA), 0.92 – 0.64 (m, 40H, PMMA).

**Example of a Maleimide Deprotection Procedure.** The polymer was dissolved in toluene ( $c=1$  mgmL<sup>-1</sup>) and heated to 100 °C for 24 h. The solvent was removed under reduced pressure and the polymer precipitated in ice-cold methanol (10% water) and subsequently dried in vacuo.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm]= 10.75 (s, 1H, C=O-H), 8.19 – 7.87 (m, 6H, Ar-H), 7.63 - 7.43 (m, 4H, Ar-H), 7.42 - 7.33 (m, 7H, Ar-H), 7.33 -7.28 (m, 2H, Ar-H), 7.11 (s, 1H, Ar-H), 6.93 – 6.68 (m, 4H, Ar-H, CH=CH), 5.26 (s, 2H, Ar-CH<sub>2</sub>-O), 4.53 (s, 2H, CH<sub>2</sub>-O), 4.30 (s, 2H, CH<sub>2</sub>-O), 4.20 – 3.95 (m, 4H, CH<sub>2</sub>-O), 3.85 – 3.75 (m, 3H, CH<sub>2</sub>-O), 3.59 (s, 48H, CH<sub>3</sub>-O PMMA), 2.59 (s, 3H, Ar-CH<sub>3</sub>), 1.84 (s, 32H, CH<sub>3</sub> PMMA), 1.49 - 1.32 (m, 5H, PMMA), 1.25 (s, 7H, PMMA), 1.15 – 0.92 (m, 20H, PMMA), 0.93 – 0.59 (m, 36H, PMMA).

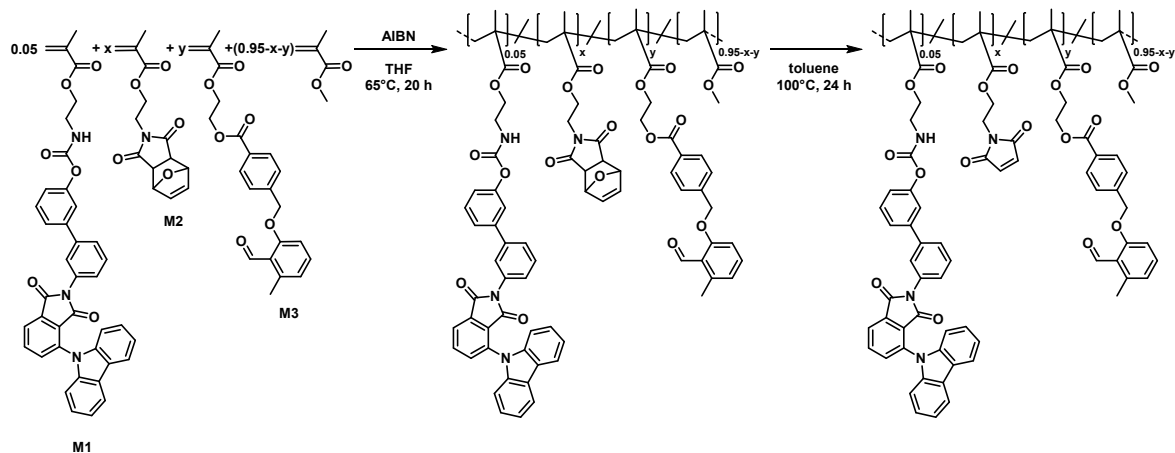
**Photocrosslinking: Sample Preparation.** The polymers were dissolved in anisole (10 wt%) and spin-coated (3400 rpm, 1 min) on a plasma cleaned cover glass (20 × 20 mm<sup>2</sup>). The polymer films were irradiated with a LED ( $\lambda_{\text{max}} = 365$  nm, 1.45 W) for 2, 5 or 15 minutes. For the solubility tests the polymer films were partially covered with aluminum foil as photomask and dipped several times in a beaker with anisole or acetone. Details are provided in the supporting Information.

## RESULTS AND DISCUSSION

**Polymer Precursor Design.** The methacrylate based polymer precursors were obtained by free radical polymerization utilizing methyl methacrylate as the major component as well co-monomers equipped with the TADF emitter functionality and the photoreactive crosslinking groups (Scheme 1). The polymers were synthesized with variable monomer feed ratios in a free radical polymerization reaction at 65 °C in THF and 2,2-azobis(2-methylpropionitrile) (AIBN) as thermal initiator. The use of a thiol as a chain transfer agent/retarder to reduce the typically rather high dispersity was avoided as the thiol was shown to react with the maleimide protection group in a thiol-ene reaction. The number average molecular weight ( $M_n$ ) of the synthesized polymers was targeted between 10k and 20k g mol<sup>-1</sup> to ensure sufficient solubility. All obtained polymers were characterized by  $^1\text{H-NMR}$  spectroscopy, size exclusion chromatography (SEC) and **PC3** was



further characterized by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) (refer to Figures S15 and S16).



**Scheme 1.** Free radical polymerization conditions for polymer precursor synthesis and subsequent maleimide deprotection conditions with a fixed emitter monomer **M1** content of 5% and variable contents of crosslinker monomers **M2** and **M3**.

The emitter content was kept constant for all synthesized polymers in order to ensure comparability in the later performed crosslinking study and the resulting properties. The TADF emitter **M1** and the *o*-methylbenzaldehyde methacrylate **M3** exhibits strong overlap in their absorbance profile in the UV range (refer to Figure S4). Small molecule TADF emitters tend to exhibit exciton concentration quenching leading to a red shift of the emission if the molecules aggregate.<sup>39</sup> Interestingly, diluting the emitter by placing it in a host matrix such as poly(methyl methacrylate) (PMMA) or incorporating it as a dopant in a suitable host molecule for the emissive layer shifts the maximum emission to shorter wavelengths. The same effect is observed for phthalimide carbazole that emits around 550 nm in bulk but can be shifted to around 490 nm as a 5 mol% mixture in PMMA (Figure S3). As a result, a constant TADF emitter **M1** content of 5 mol% was chosen for the polymer synthesis. **M1** was prepared by an addition reaction of the TADF

with 2-isocyanatoethyl methacrylate assisted by catalytic amounts of triethylamine affording a carbamate species in high yield (92%) and can be purified by column chromatography. The simple addition reaction is a very versatile monomer synthesis and allows to expand the method not only to the TADF emitter used in this study but also to a variety of emitter materials in a one-step preparation if a nucleophilic group such as an alcohol, thiol or amine is present. The furan protected maleimide methacrylate (**M2**) as well as *o*-methylbenzaldehyde methacrylate (**M3**) as the photoreactive crosslinking moieties, were synthesized according to literature procedures.<sup>40,41</sup>

A library of polymers with the set amount of TADF emitter functionality (5%) and varying ratios of the crosslinking groups was synthesized in order to evaluate their suitability for inkjet printing (Table 1). The targeted crosslinker contents span from 2.5 to 12.5% (**PC1-PC5**) for each of the components, *o*-methylbenzaldehyde and maleimide, respectively. As a reference **P0** was prepared without the addition of crosslinkable functional groups.

**Table 1.** Building block composition and molecular weight distribution of synthesized polymers for photochemical crosslinking with *o*-methylbenzaldehyde (oMBA) and/or furan protected maleimide (fpMI).

#	%MMA <sup>a</sup>	%emitter <sup>a</sup>	%oMBA <sup>a</sup>	%fpMI <sup>a</sup>	$M_n$ [g mol <sup>-1</sup> ] <sup>b</sup>	$D$ <sup>b</sup>
<b>P0</b>	94.9	5.1	-	-	10 300	2.2
<b>PC1</b>	89.1	5.7	2.9	2.7	9 400	2.2
<b>PC2</b>	86.3	4.7	4.3	4.7	22 400	2.3
<b>PC3</b>	80.6	4.8	7.2	7.4	14 000	1.9
<b>PC4</b>	74.4	5.5	10.0	10.1	17 800	2.6
<b>PC5</b>	71.0	5.1	12.0	11.9	18 500	2.4
<b>PC6</b>	85.5	4.7	9.8	-	8 800	1.6

<b>PC7</b>	78.0	4.9	17.1	-	8 000	1.9
<b>PC8</b>	84.5	6.0	-	9.5	13 400	2.4

<sup>a</sup> calculated from <sup>1</sup>H-NMR spectrum.

<sup>b</sup> determined by SEC in THF.

The compositions of the synthesized polymers were determined by <sup>1</sup>H-NMR-spectroscopy on the basis of characteristic building block resonances prior to maleimide deprotection as the resonances overlap in the spectrum of the deprotected polymers. A typical example is shown in Figure S1. The <sup>1</sup>H-NMR spectra of all synthesized polymers clearly indicate the presence of *o*-methylbenzaldehyde with characteristic aldehyde resonances at  $\delta = 10.74$  ppm and the methyl group at  $\delta = 2.58$  ppm as well as the methoxy protons of methyl methacrylate at  $\delta = 3.58$  ppm. The resonance of the maleimide alkene protons overlaps with the signals of the aromatic protons from the TADF emitter at  $\delta = 6.80$  ppm. The emitter as well as the crosslinker monomers were statistically incorporated into the polymer backbone according to the intended monomer ratios as calculated from the <sup>1</sup>H-NMR spectrum (Table 1).

After the polymerization, the maleimide protection group was removed in a retro-Diels-Alder reaction at 100 °C for 24 h at low concentrations to prevent uncontrolled crosslinking. The deprotection was considered successful when the broad singlet resonance of the furan protection group in the <sup>1</sup>H-NMR spectrum at  $\delta = 2.94$  ppm had vanished. Importantly, no high molecular shoulders appeared in the SEC trace (Figure S2).

To investigate whether the electronic properties of the emitter in the polymer changed compared to the small molecule the frontier orbital energy levels were determined by cyclic voltammetry. Table 2 shows the calculated energy levels of the pure TADF emitter as well as the emitter PMMA polymer without (**P0**) and with the crosslinker pair (**PC3**, 7.5%).

**Table 2.** HOMO and LUMO energy levels of the emitter as a PMMA polymer with (**PC3**) and without crosslinker (**P0**) determined by cyclic voltammetry (1 mM in THF or DCM (Bu<sub>4</sub>NPF<sub>6</sub> 0.1M) scan rate 100 mVs<sup>-1</sup>).

	HOMO	LUMO
TADF emitter	-6.00 eV	-3.14 eV
TADF emitter polymer without crosslinker ( <b>P0</b> )	-6.13 eV	-3.29 eV
TADF emitter polymer with crosslinker ( <b>PC3</b> )	-6.14 eV	-3.22 eV

The Highest Occupied Molecular Orbital (HOMO) of the small molecule was determined to be -6.00 eV. In the PMMA based polymer **P0** the HOMO level is slightly reduced to -6.13 and -6.14 eV for the crosslinkable polymer **PC3**. However, the energy shift of ~0.1 eV is still within the experimental error range of the method used for the determination of the energy levels. Similarly, the Lowest Unoccupied Molecular Orbital (LUMO) of the small molecule was measured to be -3.14 eV, whereas the polymer is at -3.29 eV and the polymer with the crosslinker pair at -3.22 eV. Hence, the energy levels are only minimally affected by the addition of the TADF emitter species to the polymer backbone and therefore, the small molecule properties are maintained. As the small molecule properties are in general often tested in PMMA as a host matrix to prevent self-quenching effects,<sup>39</sup> the chemical environment of the emissive species in the polymer is almost identical and therefore the electronic properties would be expected to be similar.

**Photocrosslinking.** Subsequent to the synthesis of suitable polymer precursors, their photochemical crosslinking was studied. In order to validate the retained functionality of the TADF emitter after irradiation with UV light, **P0** was irradiated in film as well as in a solution in anisole and the absorbance in the UV/vis region was recorded (refer to Figures S6 and S7). The samples were irradiated for preselected time intervals, i.e. 2, 5, 15, 30, 45 and 60 minutes. The corresponding absorbance spectra remain unchanged compared to  $t=0$ , indicating the photostability of the emitter species upon crosslinking.

The crosslinking of the polymer precursors was studied in thin films with an approximate thickness of close to 220 nm. The films were irradiated with a 1.4 W LED with a peak emission at 365 nm. In a first approach, the network formation of the polymer films was evaluated in a solvent resistance test. As a reference, a part of the polymer film was covered with a photomask (Figure S21) during the UV irradiation and the films were subsequently washed with acetone and anisole. The crosslinking was successful, when the irradiated films did not dissolve whereas the film under the photomask remained soluble in anisole and acetone. For every synthesized polymer three thin films were prepared and irradiated at 365 nm for 2, 5 or 15 minutes. The results of the subsequent solvent resistance tests are shown in Table S1.

The defined lower limit for efficient network formation is reached with a crosslinker content of 2.5 % *o*-methylbenzaldehyde and 2.5 % maleimide **PC1**. A corresponding film exhibits solvent resistance after 15 min irradiation. All polymers with a crosslink content higher than 5% show complete solvent resistance after 2 minutes of irradiation, even though the UV absorption of the *o*-methylbenzaldehyde and the TADF emitter strongly overlap (Figure S4).

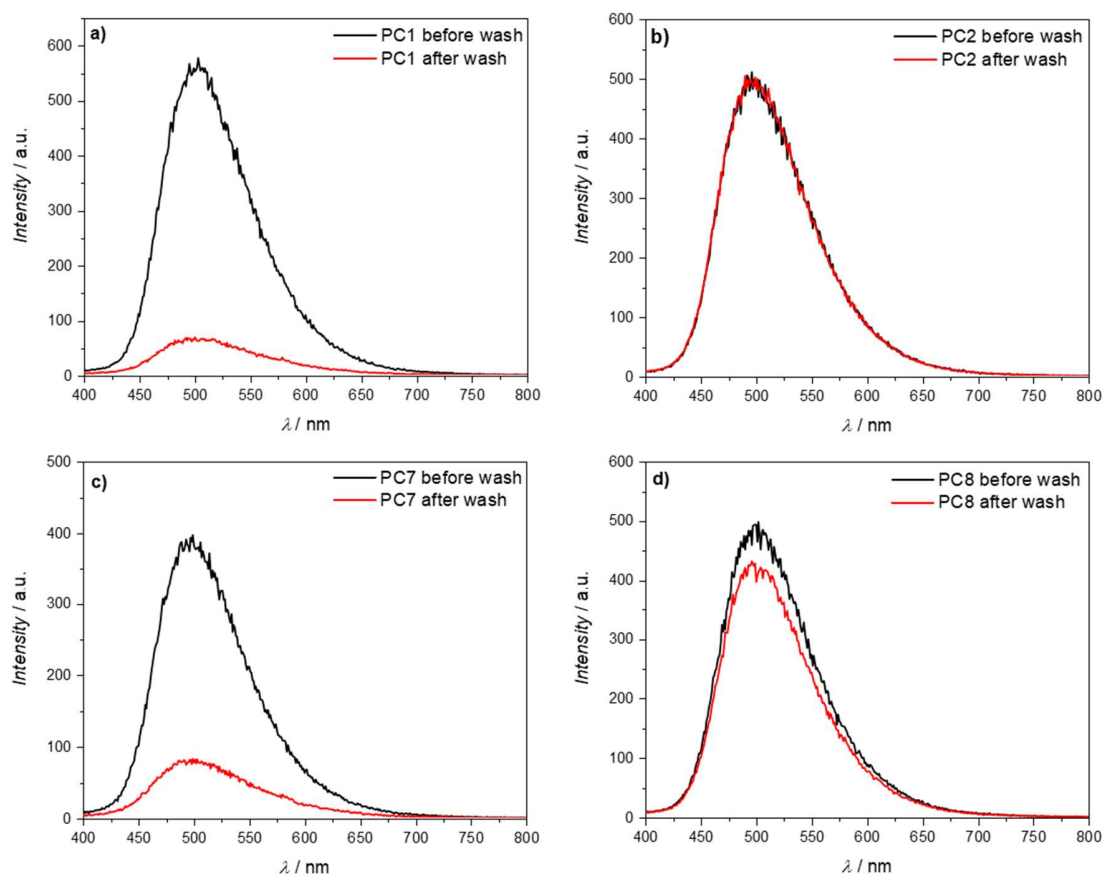
In addition, alternative crosslinking mechanisms such as the dimerization of the crosslinker moieties were investigated as a comparison to the bimolecular Diels-Alder cycloaddition. Krappitz

et al.<sup>37</sup> showed successful crosslinking of *o*-methylbenzaldehyde containing polymers in bulk utilizing the dimerization of *o*-methylbenzaldehyde. **PC6** with 10% *o*-methylbenzaldehyde and no maleimide functionality, however, remained soluble after extended irradiation times of up to 2 hours. As the crosslinker content in the previous study was higher than 20 mol%, the crosslinking via dimerization for polymer **PC7** containing 17% *o*-methylbenzaldehyde was attempted. After 15 minutes of irradiation a complete solvent resistance was observed. In comparison, a polymer with only 10% maleimide content and no *o*-methylbenzaldehyde functional groups was already insoluble after 2 min UV exposure forming a network based on a [2+2] cycloaddition.<sup>42</sup>

To quantify the efficiency of the crosslinking, the photoluminescence of the irradiated films was measured before and after a washing step with anisole. The results (Figure 2 and Figure S5) confirm the initial solubility tests. Limited solvent resistance is observed in the case of low crosslinker content of the polymers, e.g. after 2 minutes irradiation of **PC1** containing solely 2.5% crosslinker, the photoluminescence of **PC1** decreases significantly after washing procedure (Figure 2a). An increased crosslinker content of 5% (**PC2**) is, however, sufficient to yield complete solvent resistance after 2 minutes. The photoluminescence of **PC2** remains unchanged by the washing procedure (Figure 2b). Similarly, **PC3-5** (Figure S5) are resistant to the anisole treatment with quasi identical photoluminescence spectra before and after the solvent wash. Hence, a crosslinker content of 5% *o*-methylbenzaldehyde and 5% maleimide results in sufficient crosslinking points to maintain the polymer film structure after 2 minutes irradiation at 365 nm.

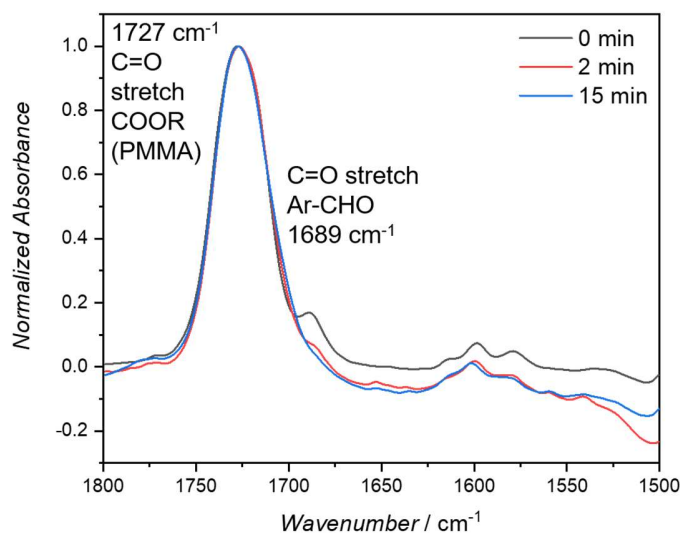
Furthermore, solvent resistance of alternative crosslinking mechanisms such as the dimerization of *o*-quinodimethane were investigated in a similar manner. **PC7** with 17% *o*-methylbenzaldehyde still showed extensive resolubilisation (Figure 2c) upon treatment with anisole demonstrated by the photoluminescence intensity decrease. Moreover, the crosslinking of the maleimide groups of

polymer **PC8** (Figure 2d) also shows a decrease in fluorescence intensity even though it is less pronounced than in **PC7**. Overall, this demonstrates clearly that the combination of the crosslinker pair maleimide and *o*-methylbenzaldehyde, that crosslinks in a Diels-Alder reaction, yields the most efficient network formation leading to a solvent resistant polymer film.



**Figure 2.** Fluorescence spectra of the photocrosslinked polymer films (2 minutes at 365 nm) before and after washing step with anisole (a) **PC1** 2.5% *o*-methylbenzaldehyde and 2.5% maleimide, b) **PC2** 5% *o*-methylbenzaldehyde and 5% maleimide, c) **PC7** 17% *o*-methylbenzaldehyde, d) **PC8** 10% maleimide).

The Diels-Alder crosslinking process of the polymer films was also monitored via ATR-IR spectroscopy (Figure 3). Without irradiation, the C=O stretch vibration band from the *o*-methylbenzaldehyde gives a distinct signal at 1689 cm<sup>-1</sup> typical for aryl substituted aldehydes next to the ester band of the PMMA backbone at 1727 cm<sup>-1</sup>. The band decreases with increasing irradiation time although there are still aldehyde groups left after 2 minutes irradiation despite the insolubility of the films. Moreover, the disappearance of the aldehyde supports the Diels-Alder mechanism of the crosslinking process.



**Figure 3.** ATR-IR spectra of polymer **PC3** before UV exposure and after 2 and 15 minutes irradiation at 365 nm showing the consumption of the aldehyde functionality of *o*-methylbenzaldehyde (aromatic aldehyde band at 1689 cm<sup>-1</sup>).

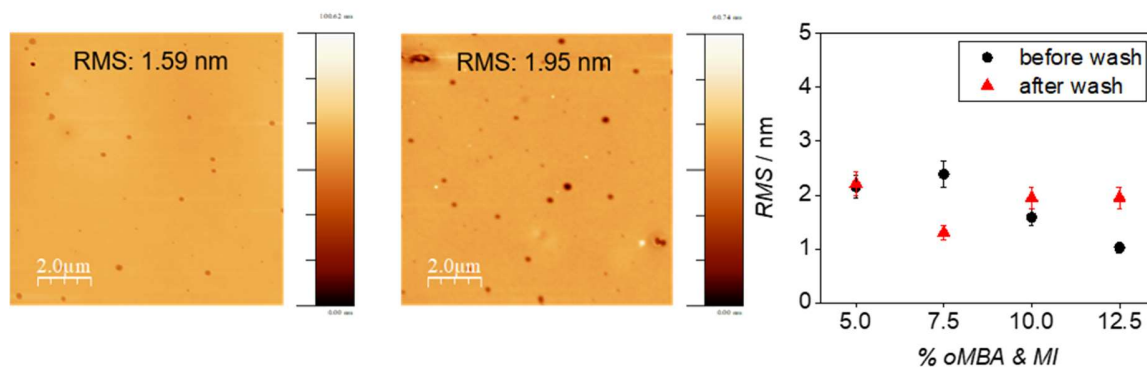
Further evidence that the Diels-Alder reaction is the main mechanism in the network formation was gathered in a ToF-SIMS measurement. A series of polymer films with 7.5% *o*-methylbenzaldehyde and 7.5 % maleimide and different curing states (no irradiation, 1 minutes, 2 minutes, 15 minutes) was investigated and compared. The abundance of fragments with mass to



charge ratios corresponding to the terminal maleimide (96.01 u) and the *o*-methylbenzaldehyde (135.05 u) decreases with increasing irradiation time, thus clearly indicating the consumption of the crosslinker groups. Principal component analysis (PCA) was performed to identify fragments resulting from a competing crosslinking mechanism via *o*-methylbenzaldehyde dimerization. However, no fragments with dimerization structures identified by Krappitz et al.<sup>37</sup> could be detected. This clearly shows that even though competing crosslinking mechanisms are possible the Diels-Alder cycloaddition of *o*-methylbenzaldehyde and maleimide is the most kinetically favored reaction.

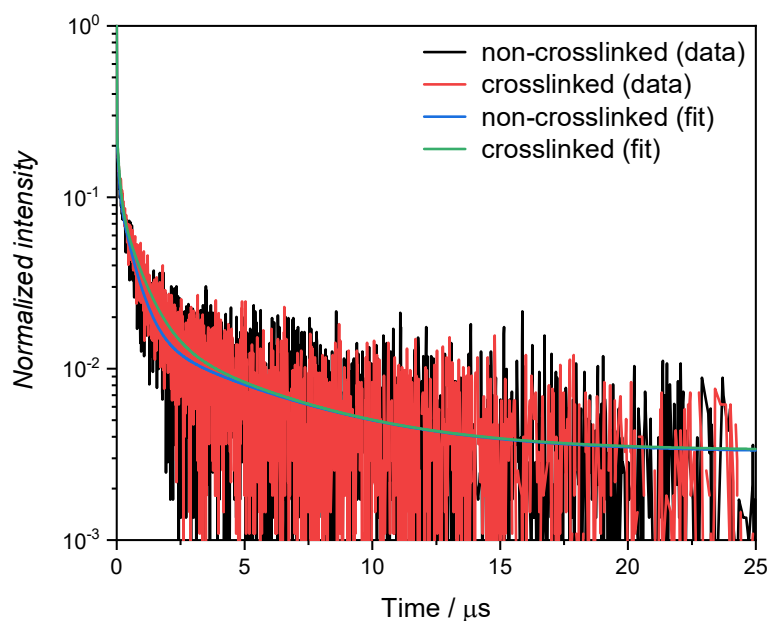
The lateral distribution of the polymer films measured by ToF-SIMS shows chemically homogeneous films before UV irradiation (Figure S9 top). After short UV exposures of 1 min ring patterns in the size range of about 50  $\mu\text{m}$  of the emitter fragments as well as the maleimide and *o*-methylbenzaldehyde (Figure S9 bottom) can be observed, which is likely to be caused by phase separation. Since the penetration depth of ToF-SIMS is typically below 5 nm this seems to be a surface effect as the irradiated polymer films give homogeneously fluorescent images on the same scale under a Laser Scanning Microscope (Figure S10).

Another parameter that should not be affected upon contact with an organic solvent, particularly for applications in OLEDs, is the surface roughness of the polymer films. Figure 4 shows the Atomic Force Microscopy (AFM) images of sample surface of **PC4** with a crosslinker content of 10% *o*-methylbenzaldehyde and maleimide before and after washing of the crosslinked polymer film. In general, the surface of the 220 nm thick film is rather homogeneous with some holes that might be solvent artefacts from the spin-coating process. Figure 4 (right) shows the surface roughness (root mean square) values of **PC2-5** on a 10 x 10 mm<sup>2</sup> area. The surface roughness (root mean square) is quite low for all samples (1-2 nm) and is constant after the solvent treatment.



**Figure 4.** AFM images and surface roughness values (RMS) of **PC4** before (left) and after solvent wash (middle) and surface roughness (root mean square RMS, determined on area  $10 \times 10 \mu\text{m}^2$ ) of crosslinked films of **PC2-5** before and after anisole wash (right).

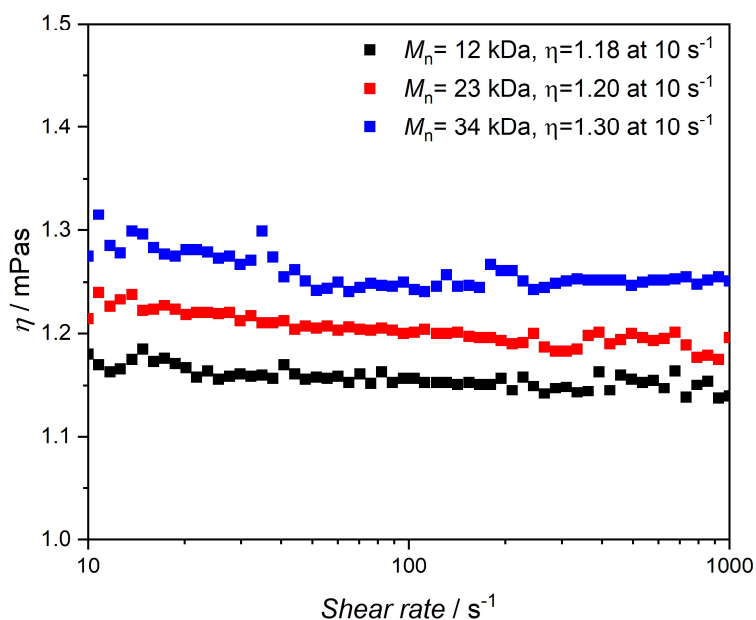
In order to verify that the emitter species still has TADF properties in the crosslinked polymer network, time resolved photoluminescence measurements of thin films of **PC3** were recorded (Figure 5). The measurement was achieved through time-correlated single photon counting (TCSPC) at the peak emission of the photoluminescence of 495 nm under vacuum to prevent the quenching of triplet excitons by oxygen.<sup>43</sup> Figure 5 was fitted using a sum of four exponentials. The multiple exponential fit is most likely due to the intrinsic disorder within the material. It is common for TADF materials to show complex decays that cannot be fitted by bi-exponential or tri-exponential fits.<sup>44</sup> Figure 5 reveals that both the crosslinked polymer and the uncrosslinked polymer displayed prompt and delayed fluorescence. Additionally, it is evident that the uncrosslinked and crosslinked polymers both share near identical prompt and delayed fluorescence lifetimes. Thus, the crosslinking of the polymer precursors does not affect the TADF properties of the emissive species.



**Figure 5:** Time resolved photoluminescence non-crosslinked and crosslinked films of polymer **PC3** showing continued delayed fluorescence of the emitter in the polymer network (data and fit).

**Inkjet Printing.** To demonstrate that the polymer ink can be not only processed by spin-coating but also by inkjet-printing which allows precise depositions and high materials yield increasingly relevant for industrial applications we processed **PC3** with an inkjet printer. Anisole was chosen as the solvent for the ink formulation due to its high boiling point and low toxicity. For smooth printing results, the polymer ink should have a viscosity below 20mPas as recommended by the instrument manufacturer.<sup>45</sup> A crucial influence on rheological properties such as the viscosity of a polymer solution is the molecular weight. Therefore, a series of polymers with 7.5% crosslinker and molecular weight of 12 (**PC3i**), 23 (**PC3ii**) and 34 kDa (**PC3iii**) was synthesized and their viscosity measured as a 15 mg mL<sup>-1</sup> anisole solution at 25 °C. The viscosity was first measured at a constant shear rate of 10 s<sup>-1</sup> and the average calculated from three measurements with 20 data

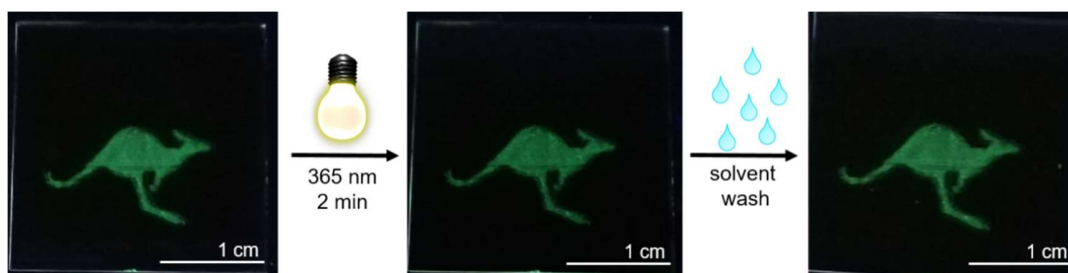
points each (Figure 6 legend). **PC3i** with a molecular weight of 12 kDa showed a viscosity of 1.18 mPas, for **PC3ii** with a molecular weight of 24 kDa the viscosity was determined to be 1.20 mPas and **PC3iii** with the highest molecular weight of 34 kDa only increased the viscosity to 1.30 mPas. Thus, the influence of the molecular weight of the polymer seems to be negligible in such dilute solutions that are required for the fabrication of thin films for OLED multilayer devices. Furthermore, the viscosity was measured with increasing shear rate and all three polymer solutions show Newtonian behavior with a constant viscosity of about 1.2 mPas.



**Figure 6.** Measured viscosity with increasing shear rate for polymer solutions (**PC3i**, **PC3ii**, **PC3iii**) with different molecular weights (15 mgmL<sup>-1</sup> in anisole) and the viscosity measured at a constant shear rate of 10 s<sup>-1</sup> (average over 20 data points, 3 measurements each).

The printer was subsequently loaded with a filtered solution of 15 mg mL<sup>-1</sup> **PC3** in anisole and the polymer was printed on an ITO coated substrate in the shape of a kangaroo demonstrating the printability of the polymer ink (Figure 7). After 2 minutes UV treatment at 365 nm the printed

polymer film was resistant to a solvent wash in anisole. For multilayer OLED device fabrication, this concept would enable the implementation of a solution processed electron transporting layer on top of the crosslinked emissive layer and therefore enabling fully solution processed OLED devices.



**Figure 7.** Image of inkjet printed polymer PC3 before (left) and after photocrosslinking (middle, 2 minutes at 365 nm) and solvent wash in anisole (right) showing the solvent resistance of the printed ink after UV curing (images taken under UV lamp  $\lambda = 254$  nm).

## CONCLUSIONS

We introduce several poly(methyl methacrylate) based polymers with a phthalimide carbazole TADF small molecule emitter and an *o*-methylbenzaldehyde maleimide crosslinker pair for photoinduced Diels-Alder network formation. Time resolved photoluminescence and cyclic voltammetry indicate that the characteristics of the small molecule TADF emitter remain unchanged upon incorporation into a polymer network. Studies of the photocrosslinking behavior show that 5% of *o*-methylbenzaldehyde and maleimide are sufficient to generate a polymer film that is resistant to solvent treatment after 2 minutes irradiation at 365 nm. Alternative crosslinking mechanisms such as the dimerization of *o*-methylbenzaldehyde and maleimide proved to be less efficient leading to films that are washed away by the solvent. ToF-SIMS and ATR-FT-IR analysis clearly show the consumption of the crosslinker moieties with increasing irradiation time. The

photocrosslinked films are resistant towards a washing step and the roughness of the polymer films remains unchanged. Furthermore, we demonstrated the processability of the polymer inks with a commercial inkjet printer leading to precise deposition of the emissive material suitable for further solution processed multilayer OLED device fabrication after photocrosslinking.

## ASSOCIATED CONTENT

**Supporting Information** Additional figures, synthetic procedures, instrumentation, experimental procedures and analysis of the compounds is available in the Supporting Information free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Tang, C. W.; VanSlyke, S. A. Organic Electroluminescent Diodes. *Appl. Phys. Lett.* **1987**, *51* (12), 913–915.
- (2) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly Efficient Organic Light-Emitting Diodes from Delayed Fluorescence. *Nature* **2012**, *492* (7428), 234–238.
- (3) Bui, T.-T.; Goubard, F.; Ibrahim-Ouali, M.; Gigmes, D.; Dumur, F. Thermally Activated Delayed Fluorescence Emitters for Deep Blue Organic Light Emitting Diodes: A Review of Recent Advances. *Appl. Sci.* **2018**, *8* (4), 494.

- (4) Nuyken, O.; Jungermann, S.; Wiederhirn, V.; Bacher, E.; Meerholz, K. Modern Trends in Organic Light-Emitting Devices (OLEDs). *Monatshefte für Chemie - Chem. Mon.* **2006**, *137* (7), 811–824.
- (5) Germino, J. C.; de Freitas, J. N.; Domingues, R. A.; Quites, F. J.; Faleiros, M. M.; Atvars, T. D. Z. Organic Light-Emitting Diodes Based on PVK and Zn(II) Salicylidene Composites. *Synth. Met.* **2018**, *241*, 7–16.
- (6) Zuniga, C. A.; Barlow, S.; Marder, S. R. Approaches to Solution-Processed Multilayer Organic Light-Emitting Diodes Based on Cross-Linking. *Chem. Mater* **2011**, *23*, 658–681.
- (7) Sax, S.; Rugen-Penkalla, N.; Neuhold, A.; Schuh, S.; Zojer, E.; List, E. J. W.; Müllen, K. Efficient Blue-Light-Emitting Polymer Heterostructure Devices: The Fabrication of Multilayer Structures from Orthogonal Solvents. *Adv. Mater.* **2010**, *22* (18), 2087–2091.
- (8) Ma, W.; Iyer, P. K.; Gong, X.; Liu, B.; Moses, D.; Bazan, G. C.; Heeger, A. J. Water/Methanol-Soluble Conjugated Copolymer as an Electron-Transport Layer in Polymer Light-Emitting Diodes. *Adv. Mater.* **2005**, *17* (3), 274–277.
- (9) Kim, W. H.; Mäkinen, A. J.; Nikolov, N.; Shashidhar, R.; Kim, H.; Kafafi, Z. H. Molecular Organic Light-Emitting Diodes Using Highly Conducting Polymers as Anodes. *Appl. Phys. Lett.* **2002**, *80* (20), 3844–3846.
- (10) Wei, Q.; Ge, Z.; Voit, B. Thermally Activated Delayed Fluorescent Polymers: Structures, Properties, and Applications in OLED Devices. *Macromol. Rapid Commun.* **2019**, *40* (1), 1800570.
- (11) Albrecht, K.; Matsuoka, K.; Fujita, K.; Yamamoto, K. Carbazole Dendrimers as Solution-



- Processable Thermally Activated Delayed-Fluorescence Materials. *Angew. Chemie Int. Ed.* **2015**, *54* (19), 5677–5682.
- (12) Liao, X.; Yang, X.; Zhang, R.; Cheng, J.; Li, J.; Chen, S.; Zhu, J.; Li, L. Solution-Processed Small-Molecular White Organic Light-Emitting Diodes Based on a Thermally Activated Delayed Fluorescence Dendrimer. *J. Mater. Chem. C* **2017**, *5* (38), 10001–10006.
- (13) Sun, K.; Sun, Y.; Liu, D.; Feng, Y.; Zhang, X.; Sun, Y.; Jiang, W. CBP Derivatives Dendronized Self-Host TADF Dendrimer: Achieving Efficient Non-Doped near-Infrared Organic Light-Emitting Diodes. *Dye. Pigment.* **2017**, *147*, 436–443.
- (14) Xie, G.; Luo, J.; Huang, M.; Chen, T.; Wu, K.; Gong, S.; Yang, C. Inheriting the Characteristics of TADF Small Molecule by Side-Chain Engineering Strategy to Enable Bluish-Green Polymers with High PLQYs up to 74% and External Quantum Efficiency over 16% in Light-Emitting Diodes. *Adv. Mater.* **2017**, *29* (11), 1604223.
- (15) Wei, Q.; Kleine, P.; Karpov, Y.; Qiu, X.; Komber, H.; Sahre, K.; Kiriya, A.; Lygaitis, R.; Lenk, S.; Reineke, S.; et al. Conjugation-Induced Thermally Activated Delayed Fluorescence (TADF): From Conventional Non-TADF Units to TADF-Active Polymers. *Adv. Funct. Mater.* **2017**, *27* (7), 1605051.
- (16) Nikolaenko, A. E.; Cass, M.; Bourcet, F.; Mohamad, D.; Roberts, M. Thermally Activated Delayed Fluorescence in Polymers: A New Route toward Highly Efficient Solution Processable OLEDs. *Adv. Mater.* **2015**, *27* (44), 7236–7240.
- (17) Ren, Z.; Nobuyasu, R. S.; Dias, F. B.; Monkman, A. P.; Yan, S.; Bryce, M. R. Pendant Homopolymer and Copolymers as Solution-Processable Thermally Activated Delayed

- Fluorescence Materials for Organic Light-Emitting Diodes. *Macromolecules* **2016**, *49* (15), 5452–5460.
- (18) Li, C.; Nobuyasu, R. S.; Wang, Y.; Dias, F. B.; Ren, Z.; Bryce, M. R.; Yan, S. Solution-Processable Thermally Activated Delayed Fluorescence White OLEDs Based on Dual-Emission Polymers with Tunable Emission Colors and Aggregation-Enhanced Emission Properties. *Adv. Opt. Mater.* **2017**, *5* (20), 1700435.
- (19) Shao, S.; Hu, J.; Wang, X.; Wang, L.; Jing, X.; Wang, F. Blue Thermally Activated Delayed Fluorescence Polymers with Nonconjugated Backbone and Through-Space Charge Transfer Effect. *J. Am. Chem. Soc.* **2017**, *139* (49), 17739–17742.
- (20) Zuniga, C. A.; Barlow, S.; Marder, S. R. Approaches to Solution-Processed Multilayer Organic Light-Emitting Diodes Based on Cross-Linking. *Chem. Mater.* **2011**, *23* (3), 658–681.
- (21) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. Multi-Colour Organic Light-Emitting Displays by Solution Processing. *Nature* **2003**, *421* (6925), 829–833.
- (22) Grigalevicius, S.; Zhang, B.; Xie, Z.; Forster, M.; Scherf, U. Polycarbazole-Based Networks Made by Photo-Crosslinking for Hole Transporting Layers of OLED Devices. *Org. Electron.* **2011**, *12* (12), 2253–2257.
- (23) Braig, T.; Müller, D. C.; Groß, M.; Meerholz, K.; Nuyken, O. Crosslinkable Hole-Transporting Polymers by Palladium-Catalyzed C—N-Coupling Reaction. *Macromol. Rapid Commun.* **2000**, *21* (9), 583–589.

- (24) Li, X.-C.; Yong, T.-M.; Grüner, J.; Holmes, A. B.; Moratti, S. C.; Cacialli, F.; Friend, R. H. A Blue Light Emitting Copolymer with Charge Transporting and Photo-Crosslinkable Functional Units. *Synth. Met.* **1997**, *84* (1), 437–438.
- (25) Bender, M.; Schelkle, K. M.; Jürgensen, N.; Schmid, S.; Hernandez-Sosa, G.; Bunz, U. H. F. Photo-Cross-Linkable Polyfluorene–Triarylamine (PF–PTAA) Copolymer Based on the [2 + 2] Cycloaddition Reaction and Its Use as Hole-Transport Layer in OLEDs. *Macromolecules* **2016**, *49* (8), 2957–2961.
- (26) Sun, H.; Liu, Z.; Hu, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. Crosslinkable Poly(p-Phenylenevinylene) Derivative. *J. Polym. Sci. Part A Polym. Chem.* **2004**, *42* (9), 2124–2129.
- (27) Chen, J. .; Klaerner, G.; Lee, J.-I.; Markiewicz, D.; Lee, V. .; Miller, R. .; Scott, J. . Efficient, Blue Light-Emitting Diodes Using Cross-Linked Layers of Polymeric Arylamine and Fluorene. *Synth. Met.* **1999**, *107* (2), 129–135.
- (28) Ma, B.; Lauterwasser, F.; Deng, L.; Zonte, C. S.; Kim, B. J.; Fréchet, J. M. J.; Carsten, B.; Thompson, M. E. New Thermally Cross-Linkable Polymer and Its Application as a Hole-Transporting Layer for Solution Processed Multilayer Organic Light Emitting Diodes. *Chem. Mater.* **2007**, *19* (19), 4827–4832.
- (29) Lim, B.; Hwang, J.-T.; Kim, J. Y.; Ghim, J.; Vak, D.; Noh, Y.-Y.; Lee, S.-H.; Lee, K.; Heeger, A. J.; Kim, D.-Y. Synthesis of a New Cross-Linkable Perfluorocyclobutane-Based Hole-Transport Material. *Org. Lett.* **2006**, *8* (21), 4703–4706.
- (30) Huang, F.; Cheng, Y.-J.; Zhang, Y.; Liu, M. S.; Jen, A. K.-Y. Crosslinkable Hole-

- Transporting Materials for Solution Processed Polymer Light-Emitting Diodes. *J. Mater. Chem.* **2008**, *18* (38), 4495–4509.
- (31) Zhao, J.; Bardecker, J. A.; Munro, A. M.; Liu, M. S.; Niu, Y.; Ding, I.-K.; Luo, J.; Chen, B.; Jen, A. K.-Y.; Ginger, D. S. Efficient CdSe/CdS Quantum Dot Light-Emitting Diodes Using a Thermally Polymerized Hole Transport Layer. *Nano Lett.* **2006**, *6* (3), 463–467.
- (32) Aizawa, N.; Pu, Y.-J.; Chiba, T.; Kawata, S.; Sasabe, H.; Kido, J. Instant Low-Temperature Cross-Linking of Poly(*N*-Vinylcarbazole) for Solution-Processed Multilayer Blue Phosphorescent Organic Light-Emitting Devices. *Adv. Mater.* **2014**, *26* (45), 7543–7546.
- (33) Adzima, B. J.; Kloxin, C. J.; DeForest, C. A.; Anseth, K. S.; Bowman, C. N. 3D Photofixation Lithography in Diels–Alder Networks. *Macromol. Rapid Commun.* **2012**, *33* (24), 2092–2096.
- (34) Gruending, T.; Oehlenschlaeger, K. K.; Frick, E.; Glassner, M.; Schmid, C.; Barner-Kowollik, C. Rapid UV Light-Triggered Macromolecular Click Conjugations via the Use of *o*-Quinodimethanes. *Macromol. Rapid Commun.* **2011**, *32* (11), 807–812.
- (35) Hildebrandt, K.; Pauloehrl, T.; Blinco, J. P.; Linkert, K.; Börner, H. G.; Barner-Kowollik, C.  $\lambda$ -Orthogonal Pericyclic Macromolecular Photoligation. *Angew. Chemie Int. Ed.* **2015**, *54* (9), 2838–2843.
- (36) Pauloehrl, T.; Delaittre, G.; Winkler, V.; Welle, A.; Bruns, M.; Börner, H. G.; Greiner, A. M.; Bastmeyer, M.; Barner-Kowollik, C. Adding Spatial Control to Click Chemistry: Phototriggered Diels-Alder Surface (Bio)Functionalization at Ambient Temperature. *Angew. Chemie Int. Ed.* **2012**, *51* (4), 1071–1074.

- (37) Krappitz, T.; Feist, F.; Lamparth, I.; Moszner, N.; John, H.; Blinco, J. P.; Dargaville, T. R.; Barner-Kowollik, C. Polymer Networks Based on Photo-Caged Diene Dimerization. *Mater. Horizons* **2019**, *6* (1), 81–89.
- (38) Bialas, S.; Michalek, L.; Marschner, D. E.; Krappitz, T.; Wegener, M.; Blinco, J.; Blasco, E.; Frisch, H.; Barner-Kowollik, C. Access to Disparate Soft Matter Materials by Curing with Two Colors of Light. *Adv. Mater.* **2019**, *31* (8), 1807288.
- (39) Kim, H. S.; Park, S.-R.; Suh, M. C. Concentration Quenching Behavior of Thermally Activated Delayed Fluorescence in a Solid Film. *J. Phys. Chem. C* **2017**, *121* (26), 13986–13997.
- (40) Fuhrmann, A.; Göstl, R.; Wendt, R.; Kötteritzsch, J.; Hager, M. D.; Schubert, U. S.; Brademann-Jock, K.; Thünemann, A. F.; Nöchel, U.; Behl, M.; et al. Conditional Repair by Locally Switching the Thermal Healing Capability of Dynamic Covalent Polymers with Light. *Nat. Commun.* **2016**, *7*, 13623.
- (41) Claus, T. K.; Richter, B.; Hahn, V.; Welle, A.; Kayser, S.; Wegener, M.; Bastmeyer, M.; Delaitre, G.; Barner-Kowollik, C. Simultaneous Dual Encoding of Three-Dimensional Structures by Light-Induced Modular Ligation. *Angew. Chemie Int. Ed.* **2016**, *55* (11), 3817–3822.
- (42) Decker, C.; Bianchi, C. Photocrosslinking of a Maleimide Functionalized Polymethacrylate. *Polym. Int.* **2003**, *52* (5), 722–732.
- (43) Endo, A.; Sato, K.; Yoshimura, K.; Kai, T.; Kawada, A.; Miyazaki, H.; Adachi, C. Efficient Up-Conversion of Triplet Excitons into a Singlet State and Its Application for Organic Light

Emitting Diodes. *Appl. Phys. Lett.* **2011**, 98.

(44) Dias, F. B.; Penfold, T. J.; Monkman, A. P. Photophysics of Thermally Activated Delayed Fluorescence Molecules. *Methods Appl. Fluoresc.* **2017**, 5 (1), 012001.

(45) Technologies, M. Inkjet printer MicroFab MJ-AT manual  
[http://www.microfab.com/images/pdfs/manuals/MJ-AT\\_Manual.pdf](http://www.microfab.com/images/pdfs/manuals/MJ-AT_Manual.pdf).

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