1410 *Chem. Mater.* **2010,** *22,* 1410–1419
DOI:10.1021/cm902254f

CHEMISTRY OF MATERIALS
Article

# Three Color Random Fluorene-Based Oligomers for Fast Micrometer-Scale Photopatterning

Esther Scheler and Peter Strohriegl*

*Macromolecular Chemistry 1, University of Bayreuth, Universitätsstr. 30, 95440 Bayreuth, Germany*

*Received July 23, 2009. Revised Manuscript Received December 7, 2009*

In this contribution we show that random fluorene cooligomers with photo reactive acrylate units can be prepared in a simple 1-step Yamamoto synthesis. The acrylate functionalities are preserved quantitatively under Yamamoto conditions. NMR and Maldi-ToF measurements point to an almost statistical incorporation of the comonomers into the oligomer chain. Maldi-ToF analyses give a further insight into the chain compositions, and we found fluorene-only oligomers to be present in low quantities. Thin films of the aromatic amine containing cooligomer show a blue fluorescence, the benzothiadiazole oligomer shows yellow photoluminescence, and the bithiophene oligomer emits orange-red light upon excitation. Compared to pure fluorene oligomers with a HOMO of 5.7 eV the HOMO levels of the TPD and bithiophene derivatives are increased to 5.25 and 5.31 eV, respectively, whereas the HOMO level of the benzothiadiazole oligomer is decrased to 5.85 eV. Photolithography experiments reveal that a careful optimization of the conditions, for example, the choice of the photoinitiator, temperature, and irradiation wavelength, leads to well-resolved micrometer sized patterns. A minimum feature size of 1 $\mu$m was obtained. Thus we showed that with a simple 1-step Yamamoto coupling oligomers with photo-cross-linkable acrylate groups are accessible. UV irradiation leads to densely cross-linked, insoluble networks. Thus these materials are ideal candidates for multilayer as well as patterned semiconducting devices.

## Introduction

Conjugated organic materials have been in the focus of research for more than 20 years due to their various applications in organic light emitting devices (OLEDs) or organic field effect transistors (OFETs). The first commercially available products based on semiconducting organic molecules were launched in the late 1990s, and since then constant research and development has opened up many more applications. A critical feature in the manufacturing of such devices often is the spatial patterning of the organic material.[1] Furthermore in view of the ongoing miniaturization in the electronic world it can be expected that the feature sizes of patterns from organic semiconductors will become smaller in the future.

In general, there are two different approaches for lateral patterning: additive and subtractive techniques. Additive methods include vacuum deposition using shadow masks and printing techniques. The vacuum deposition technique is only suitable for small molecules, needs expensive equipment, and the scalability to larger substrate sizes is difficult. In contrast, printing techniques allow a roll-to-roll production process and are therefore most suitable for the production of low cost and large area devices. A critical feature in the printing process is the spatial resolution. The single droplets must not mix on the substrate, which is difficult to achieve when it comes to very small pattern sizes. Thus to obtain a reasonable separation in the range of $\leq 10$ $\mu$m prepatterned substrates are often used.[2] This adds considerable complexity and costs to the production process.

Subtractive techniques include lithographic methods, like photolithography or electron beam lithography. Here, a chemical modification of the organic material is induced by light or an electron beam, which leads to different solubilities of the exposed and nonexposed areas. With lithographic techniques, very small feature sizes of less than 100 nm are attainable. To realize these small feature sizes ultra precise equipment and cleanroom conditions are necessary, which makes the process expensive. For feature sizes in the range of $1-10$ $\mu$m the cost argument is less pronounced. However conventional photolithography is not well suited to pattern conjugated organic semiconductors.[3] A very promising approach is the use of conjugated organic polymers with pendant photo-cross-linkable groups. Such materials can be processed exactly like negative photoresists. Thus the direct formation of single pixels or patterns of arbitrary size and shape becomes possible. A second advantage of such compounds is their multilayer capability. Upon cross-linking the organic

---

*Author to whom correspondence should be addressed. Phone: +49/921/553296. Fax +49/921/553206. E-mail peter.strohriegl@uni-bayreuth.de.

(1) Holdcroft, S. *Adv. Mater.* **2001**, *13*, 1753.

(2) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. *Science* **2000**, *290*, 2123.

(3) Huang, J.; Xia, R.; Kim, Y.; Wang, X.; Dane, J.; Hofmann, O.; Mosley, A.; de Mello, A. J.; de Mello, J. C.; Bradley, D. D. C. *J. Mater. Chem.* **2007**, *17*, 1043.

semiconductor becomes insoluble and allows the successive spincoating of a second layer.

It was shown that oxetane-substituted light-emitting polymers can be directly patterned with lithographic techniques under mild conditions, and resolutions of 2 $\mu$m were obtained.[4,5] Photo-cross-linkable acrylates for example for passive optical elements like polarizers are also described in the literature.[6−11] Further on fluorene based polymers were intensively studied due to their strong blue fluorescence properties and are frequently used as emitting materials in OLEDs.[12,13]

In recent papers we have described the synthesis and photopatterning of acrylate functionalized oligofluorenes.[14,15] Fluorene copolymers with electron donating or withdrawing comonomers have become increasingly important in organic electronics. Copolymers incorporating aromatic amines like TPD (*N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-bis(phenyl)-benzidine) are used as hole conductors[16] and bithiophene copolymers such as F8T2 (poly(9,9̀-dioctylfluorene-co-bithiophene)) are known to exhibit high mobilities in organic field effect transistors.[17]

We have now extended our studies on photopatternable fluorene acrylates to cooligomers with TPD, benzothiadiazole, and bithiophene units. In this paper we describe the synthesis, photophysical characterization, and photopatterning of three novel cross-linkable fluorene cooligomers.

## Experimental Section

**Measurements.** The molecular weights were determined by a Waters gel permeation chromatography system (GPC) for polymers (2 analytical columns: cross-linked polystyrene gel, length 2 × 30 cm, width 0.8 cm, particle size 5 $\mu$m, eluent THF (0.5 mL/min), oligofluorene calibration). The Maldi-ToF spectra were recorded with a Bruker Reflex III with a high-mass detector in the linear mode using POPOP (1,4-Bis(5-phenyl-2-oxazolyl)benzene) as matrix. The differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer DSC7 at a heating rate of 40 K/min. The thermogravimetric analyses (TGA) were performed on a Netsch Simultane Thermoanalysis apparatus STR 409 C with a heating rate of 10 K/min under $N_2$. The abosrption spectra were recorded with a Hitachi U-3000 spectrophotometer and the photoluminescence spectra were measured with a Shimadzu RF-5301 PC spectrofluorometer. For the solution measurements distilled chloroform was used. The HOMO energy values were measured using a Riken Keiki AC-2 apparatus. For scanning electron microscopy (SEM) a Phenom from Fei Company was used. For the AFM experiments a commercial AFM (Dimension 3100 equipped with a Nano-Scope IV SPM controller and a XY closed-loop scanner, all from Veeco) was used. The $^1$H NMR spectra were obtained in $CDCl_3$ with a Bruker AC 250. A Finnigan Mat 8500 Mat 112 S Varian with EI iniziation was used for the mass spectra. The fluorescence microscope used was a Leica DMR-SP with selective filter systems (here: dichromatic mirror 400 nm, suppression filter LP 420 nm).

**Film Preparation and Irradiation.** For the formation of thin films, the oligomers and 1 wt % of photoinitiator Irgacure 784 (Ciba Geigy) were mixed. From this mixture 4 wt % solutions in toluene were prepared and spin coated onto cleaned silicon wafers at 1000 rpm for 60 s. For the spin coating and development procedure purified solvents were used. The film thicknesses were approximately 100 nm. The irradiation was performed with a Hg/Xe lamp Ushio UXM 200H with an intensity of 70mW/cm$^2$ and a selective filter UG5 (Schott).

**Materials.** The Yamamoto and Suzuki reagents $Ni(COD)_2$, COD, bipyridyl, $Pd(OAc)_2$, $P(o\text{-tol})_3$, and Aliquat were used as received from Aldrich. $CCl_4$, dry DMF and dry toluene were used as received from Fluka. Na-*tert*-butylat, *N*-Bromosuccinimide (NBS), 5,5′-dibromo-2,2′-bithiophene, and tri*tert*-butylphosphin were used as obtained from Aldrich. $CuBr_2-Al_2O_3$,[18] 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dihexylfluorene[19], and 4,7-dibromo-2,1,3-benzothiadiazole[20] were prepared according to literature methods. The acrylate monomers **F** and **E** were synthesized as described elsewhere.[15]

***N*,*N*′-bis(4-methylphenyl)-*N*,*N*′-diphenyl-benzidine (1).** A Schlenk flask was charged with 4 g (12 mmol) *N*,*N*′-diphenylbenzidine, 6.1 g (36 mmol) 4-bromotoluene, 0.08 g (0.34 mmol) $Pd(OAc)_2$ and 3.05 g (31 mmol) sodium-*tert*-butylat under argon. 75 mL dry freshly distilled THF were added. 7.8 g (1 mmol) tri*tert*-butylphosphin were added and the solution was heated to 80 °C upon stirring. After 3 h the solution was filtered over neutral alumina and washed with THF. The solvent was removed and compound **1** precipitated into MeOH. After drying 4.6 g (75%) of **1** were obtained as light brown powder. $^1$H NMR ($CDCl_3$): $\delta$ 7.4 (s, 5H), 7.07 (s, 21 H), 2.32 (s, 6H). *m*/*z* 515 (M+, 100%), 258 (M2+, 80%)

***N*,*N*′-bis(4-methylphenyl)-*N*,*N*′-bis(4-bromophenyl)-benzidine (C1).** We weighed 2.5 g (5 mmol) of compound **1** and 1.72 g (10 mmol) NBS into a flask. Twenty-five mL of chloroform were added, and the solution was stirred at room temperature (RT) for 1 h. We added 12.5 mL of acetic acid, and the solution was stirred for further 6.5 h at RT. The product was extracted with diethyl ether and the solvent was removed. The crude product was purified by column chromatography using hexane/toluene

---

(4) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nyken, O.; Becker, H.; Meerholz, K. *Nature* **2003**, *421*, 829.

(5) Gather, M. C.; Köhnen, A.; Falcou, A.; Becker, H.; Meerholz, K. *Adv. Func. Mater.* **2007**, *17*, 191.

(6) Wu, G.; Yang, C.; Fan, B.; Zang, B.; Chen, X.; Li, Y. *J. Appl. Polym. Sci.* **2006**, *100*, 2336.

(7) Yao, Y.-H.; Kung, L.-R.; Chang, S.-W.; Hsu, C.-S. *Liq. Cryst.* **2006**, *33*, 33.

(8) Jandke, M.; Hanft, D.; Strohriegl, P.; Whitehead, K.; Grell, M.; Bradley, D. D. C. *Proc. SPIE* **2001**, *4105*, 338.

(9) O'Neill, M; Kelly, S. M. *Adv. Mater.* **2003**, *15*, 1135.

(10) Broer, D. J.; Boven, J.; Mol, G. N.; Challa, G. *Makromol. Chem.* **1989**, *190*, 2255.

(11) Broer, D. J.; Lub, J.; Mol, G. N. *Nature* **1995**, *378*, 467.

(12) Grell, M.; Knoll, W.; Lupo, D.; Meisel, A.; Miteva, T.; Neher, D.; Nothofer, H.-G.; Scherf, U.; Yasuda, A. *Adv. Mater.* **1999**, *11*, 671.

(13) Whitehead, K. S.; Grell, M.; Bradley, D. D. C.; Jandke, M.; Strohriegl, P. *Appl. Phys. Lett.* **2000**, *76*, 2946.

(14) Scheler, E.; Bauer, I.; Strohriegl, P. *Macromol. Symp.* **2007**, *254*, 203.

(15) Scheler, E.; Strohriegl, P. *J. Mater. Chem.* **2009**, *19*, 3207.

(16) Redecker, M.; Bradley, D. D. C.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. *Adv. Mater.* **1999**, *11*, 241.

(17) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. *Appl. Phys. Lett.* **2000**, *77*, 406.

(18) Kodomari, M.; Satoh, H.; Yshitomi, S. *J. Org. Chem.* **1988**, *53*, 2093.

(19) Thiem, H.; Jandke, M.; Hanft, D.; Strohriegl, P. *Macromol. Chem. Phys.* **2006**, *207*, 370.

(20) Mancilha, F. S.; Da Silveira Neto, B. A.; Lopes, A. S.; Moreira, P. F., Jr.; Quina, F. H.; Goncalves, R. S.; Dupont, J. *Eur. J. Org. Chem.* **2006**, *21*, 4924.

5:1 as eluent. After drying 2.35 g (75%) of **C2** were obtained as pale yellow needles. $^1$H NMR ($CDCl_3$): $\delta$ 7.36 (m, 8H), 7.23 (m, 2H), 7.11 (m, 14H), 2.34 (s, 6H). *m*/*z* 672 (M+, 100%), 336 (25%).

**4,7-bis(9,9′-dihexylfluorene-2-yl)-2,1,3-benzothiadiazole (2).** We weighed 0.22 g (0.75 mmol) 4,7-dibromo-2,1,3-benzothiadiazole and 0.69 g (1.5 mmol) 2−4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dihexylfluorene into a Schlenk flask under argon. Thirty mL of toluene, 15 mL of 2 M $K_2CO_3$, and one drop of Aliquat were added. The mixture was degassed by three freeze−thaw cycles before it was heated to 65 °C for 12 h. The product was extracted with diethyl ether and the solvent was removed. The crude product was purified by column chromatography using hexane/toluene 2:1 as eluent. 0.416 g (70%) of **2** were obtained as yellow crystalline material. $^1$H NMR ($CDCl_3$): $\delta$ 8.1 (m, 2H), 7.95 (s, 2H), 7.88 (m, 4H), 7.77 (m, 2H), 7.36 (d, 6H), 2.03 (m, 8H), 1.08 (s, 24H), 0.77 (t, 20H). *m*/*z* 800 (M+, 100%).

**4,7-bis[2,7-dibromo-(9,9′-dihexylfluorene-2-yl)]-2,1,3-benzothiadiazole (C2).** A flask was charged with 0.219 g (0.27 mmol) **2** and 0.91 g $CuBr_2-Al_2O_3$. Thirty mL $CCl_4$ were added and the suspension was stirred at 70 °C for two weeks. The $CuBr_2-Al_2O_3$ was filtered off and washed with $CH_2Cl_2$. The crude product was purified by recrystallization from hexane. 70 mg (30%) of **C2** as yellow crystals were obtained. $^1$H NMR ($CDCl_3$): $\delta$ 8.1 (m, 2H), 7.95 (s, 2H), 7.88 (m, 4H), 7.64 (m, 2H), 7.50 (d, 4H), 2.00 (m, 8H), 1.10 (s, 24H), 0.77 (t, 20H). *m*/*z* 958 (M+, 100%).

**Oligo[(9-(2-ethylhexyl)-9-((6-acryloyloxy)-hexyl)-fluorene-2,7-diyl)-*co*-2,2′-bithiophene] (O3).** A Schlenk flask was charged with nickeldicyclooctadiene (Ni(COD)$_2$, 0.45 g, 1.64 mmol), cyclooctadiene (COD, 0.17 g, 1.64 mmol), 2,2′-bipyridyl (0.25 g, 1.64 mmol), and 20 mL dry DMF under argon. The mixture was degassed by three freeze−thaw cycles before it was heated to 80 °C for 30 min while stirring. Appropriate amounts of monomer **F** (0.203 g, 0.34 mmol), the end-capper **E** (0.04 g, 0.08 mmol) and **C3** (0.048 g, 0.147 mmol) were weighed into a separate flask under argon. A trace of BHT (2,6-ditert-butyl-p-cresol) and 40 mL of dry toluene were added and the mixture was degassed by three freeze−thaw cycles. Subsequently the monomer mixture was added to the catalyst mixture using a cannula. The reaction mixture was stirred at 80 °C for five days in the dark. Afterward it was poured into methanol/HCl(conc.) 1:1 and stirred at room temperature for two hours. The organic layer was separated from the HCl layer which was then washed with $Et_2O$. The combined organic layers were washed with water and the solvent was evaporated. The crude product was washed with alkaline EDTA solution (5%) then filtered over a short neutral alumina column using toluene as eluent. It was reprecipitated twice from THF into methanol and dried under vacuum, yielding 0.130 g (50%) of **O3** as a red powder. $^1$H NMR ($CDCl_3$): $\delta$ 7.72 (m, 7.9H), 6.3 (d, 1H), 6.06 (m, 1H), 5.74 (d, 1H), 4.01 (s, 2.6H), 2.05 (s, 5.6H), 0.887 (m, 36.7H). $M_n$ (GPC, oligofluorene calibration) 5500 g/mol.

The oligomers **O1** and **O2** were prepared in an analogous manner, but the workup of **O1** was slightly changed. The crude product mixture of **O1** was directly extracted with $Et_2O$ without pouring it into MeOH/HCl(conc.) before.

Data for **O1**: $^1$H NMR ($CDCl_3$): $\delta$ 7.63 (m, 10.9H), 7.14 (m, 8.9H), 6.28 (d, 1H), 6.04 (m, 1H), 5.73 (d, 1H), 4.00 (s, 2.1H), 2.35 (s, 2.6H), 2.05 (s, 4.7H), 0.887 (m, 27.8H). $M_n$ (GPC, polyfluorene calibration) 5200 g/mol, yield 84%.

Data for **O2**: $^1$H NMR ($CDCl_3$): $\delta$ 7.72 (m, 9.7H), 7.34 (m, 1.2H), 6.33 (d, 1H), 6.04 (m, 1H), 5.74 (d, 1H), 4.01 (m, 2.6H), 2.08 (s, 6.7H), 0.887 (m, 42.6H). $M_n$ (GPC, polyfluorene calibration) 5800 g/mol, yield 30%.

## Results and Discussion

**Oligomer Synthesis.** Scheme 1 shows the overall reaction pathway to the acrylate functionalized fluorene cooligomers **O1−3**. The preparation of the comonomers **C1** and **C2** is described in Scheme 2. The TPD-comonomer **C1** was prepared in a two-step synthesis. In the first step diphenylbenzidine and p-bromo-toluene were coupled using palladium acetate as catalyst. The resulting TPD derivative **1** was brominated in its two vacant para-positions using NBS. The overall yield was 56%. The benzothiadiazole trimer **C2** had to be designed because we found that the strong electron withdrawing 4,7-dibromo-2,1,3-benzothiadiazole was not incorporated into the polyfluorene chains in the Yamamoto polymerization. The trimer **2** was prepared from a fluorene borolane and 4,7-dibromo-2,1,3-benzothiadiazole in a Suzuki coupling with 70% yield (Scheme 2 *right*). Compound **2** was then selectively brominated in the two terminal positions of the fluorene rings using activated $CuBr_2$ on alumina to yield in 30% **C2**.[21] The bithiophene comonomer **C3** is commercially available.

The Yamamoto condensation was chosen as aryl−aryl coupling method, because acrylates are tolerated and the coupling reaction can be carried out without any protecting groups.[14,15] Conjugated polymers often suffer from their low solubility. In the fluorene cooligomers described here the comonomers do not contain any solubilizing substituents. To ensure a good solubility and processability of the cooligomers we have limited the molecular weights by the addition of a monofunctional end-capper **E** during the polymerization. The end-capper terminates the chain growth in a controlled way and residual bromine end groups are avoided.[15] Further on, decreased molecular weights also led to lower glass transition temperatures as we have shown previously.[22] Low glass transition temperatures allow low processing temperatures during photolithography and photodegradation upon UV illumination is prevented. From our experience on fluorene oligomers we chose a ratio of 6:1 of dibromo monomers (**F+C**) to the monobrominated end-capper **E** for oligomers **O1** and **O3**. In the case of the comonomer **C2** with higher molecular weight a ratio **(F+C2)/E** of 4:1 was applied. For the cooligomerization ~70 mol % of the fluorene compound **F** and ~30 mol % of the comonomers **C1−3** were used to ensure a good solubility of the oligomers and to introduce enough acrylate functionalities for a fast photo-cross-linking reaction.

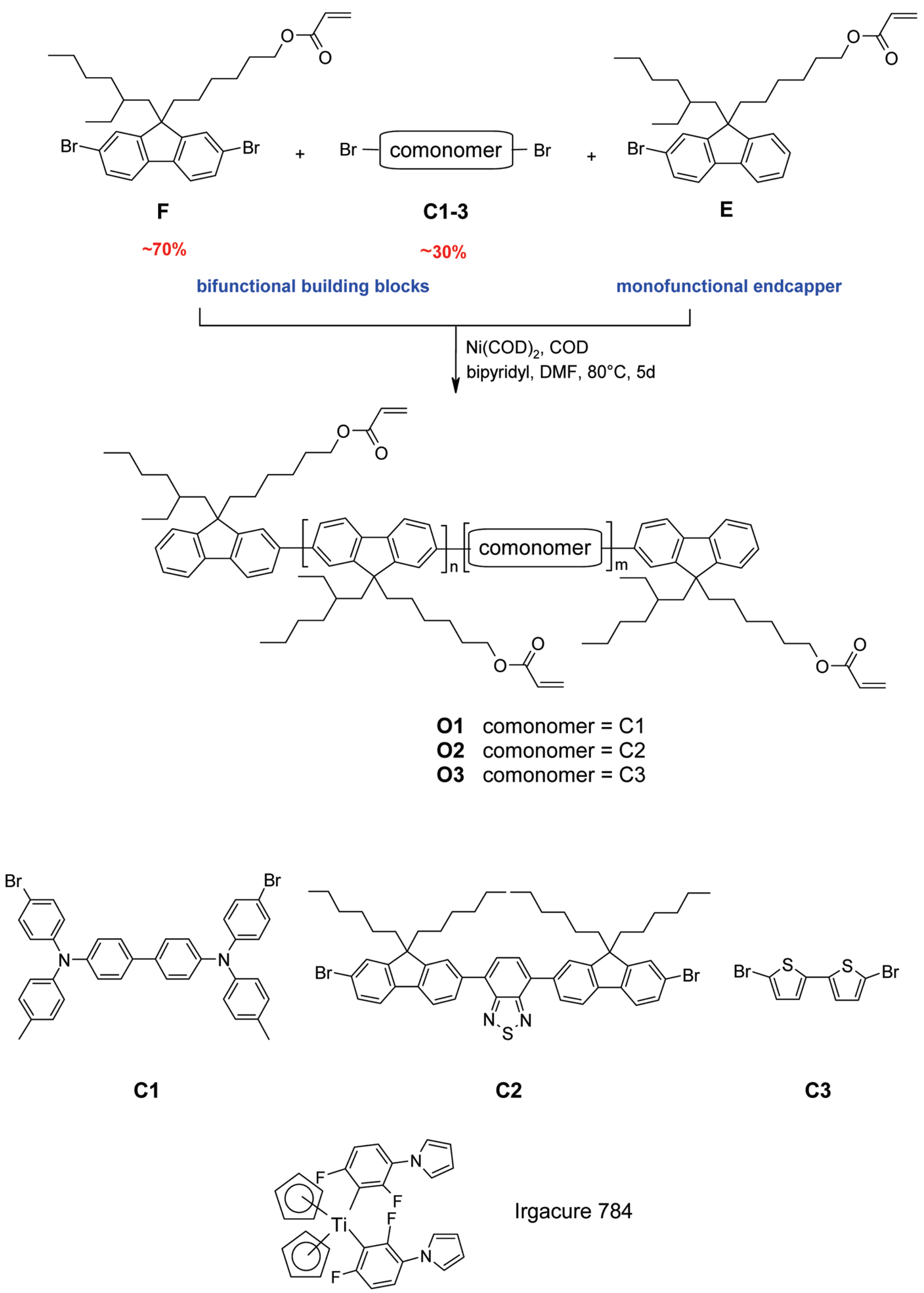
The molecular weights of **O1−3** were determined by gel permeation chromatography (GPC) and were in the range of 5200−5800 g/mol (oligofluorene calibration, see Table 1). The molecular weight distributions are monomodal and are shown in Supporting Information (SI) Figure S1. Details about the generation of the oligofluorene GPC calibration are also given in the SI (Figures S2 and S3). The ratio of fluorene acrylate to comonomers **C1−3** incorporated into the oligomer chains were determined with NMR analyses (Table 1). We found that the

---

(21) Kodomari, M.; Satoh, H.; Yoshitomi, S. *J. Org. Chem.* **1988**, *53*, 2093.

(22) Scheler, E.; Strohriegl, P. *Liq. Cryst.* **2007**, *34*, 667.

**Scheme 1. Synthetic Route for the Preparation of the Acrylate Containing Fluorene Cooligomers O1-3. the Photoinitiator Irgacure 784 Is Displayed below**



comonomer feeds correlate well with the contents in the oligomers. Hence all monomers seem to have similar reactivities in the Yamamoto coupling and a statistical linkage is most probable. However a statement about the monomer sequence in the chains is not possible, but the probability for the formation of block sequences is very low. The NMR spectra of **O1**−**3** are given in the SI (Figures S4−S6).

**Thermal Properties.** All oligomers were characterized by both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are summarized in Table 1. The decomposition temperatures are all in the range of 350 °C. The DSC scans of the oligomers showed no signs of melting or recrystallization. The glass transition temperatures ($T_g$s) were 50 and 58 °C °C for **O2** and **O3**, respectively, and 119 °C for

**Scheme 2. Synthesis of the Comonomers C1 and C2**

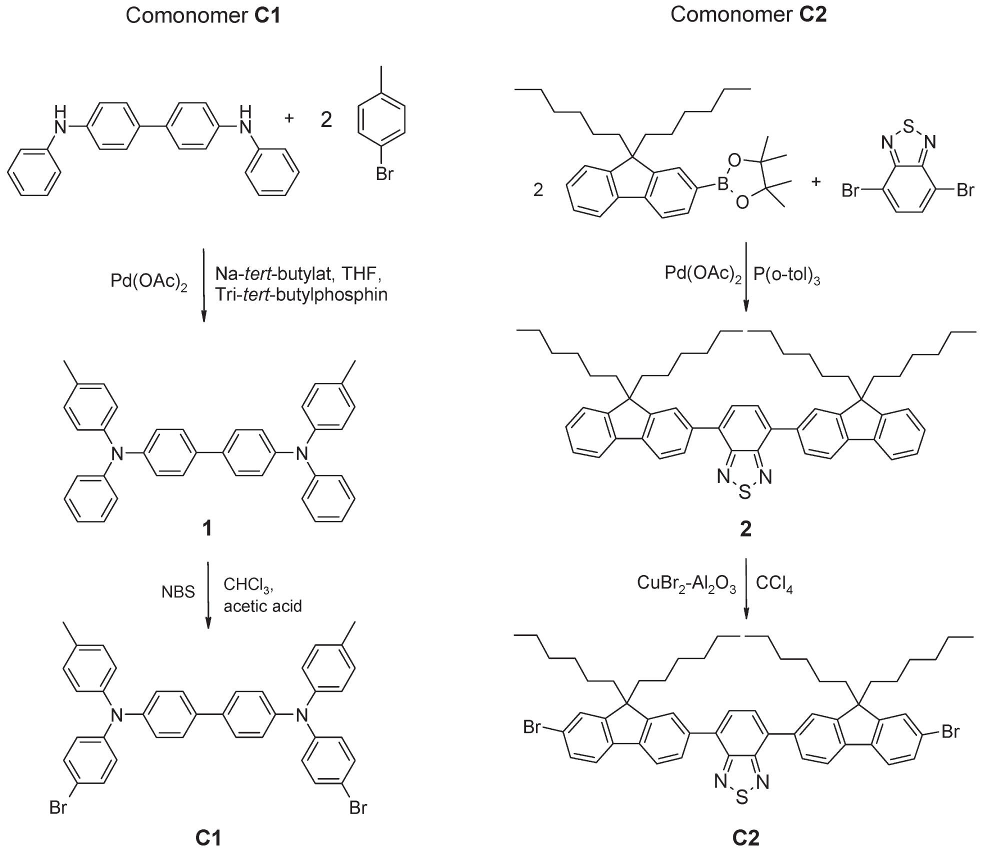


**Table 1. Composition, Molecular Weights, And Thermal Analyses of O1-3**

| oligomer | comonomer | ratio (F+C):E | feed **C1−3** [mol %] | found **C1−3** [mol %][a] | $M_n$ [g/mol][b] | $M_w$ [g/mol][b] | $T_g$ [°C][c] | $T_{d,onset}$ [°C][d] |
|---|---|---|---|---|---|---|---|---|
| **O1** | **C1** | **6:1** | 30 | 30 | 5200 | 7900 | 119 | 340 |
| **O2** | **C2** | **4:1** | 20 | 25 | 5800 | 7400 | 50 | 355 |
| **O3** | **C3** | **6:1** | 30 | 33 | 5500 | 6100 | 58 | 350 |

[a] Comonomer content determined by NMR. [b] Values determined by GPC, oligofluorene calibration. [c] Measured with DSC upon heating with a rate of 40 K/min. [d] Onset of decomposition determined by thermogravimetry with a heating rate of 10 K/min under N$_2$.

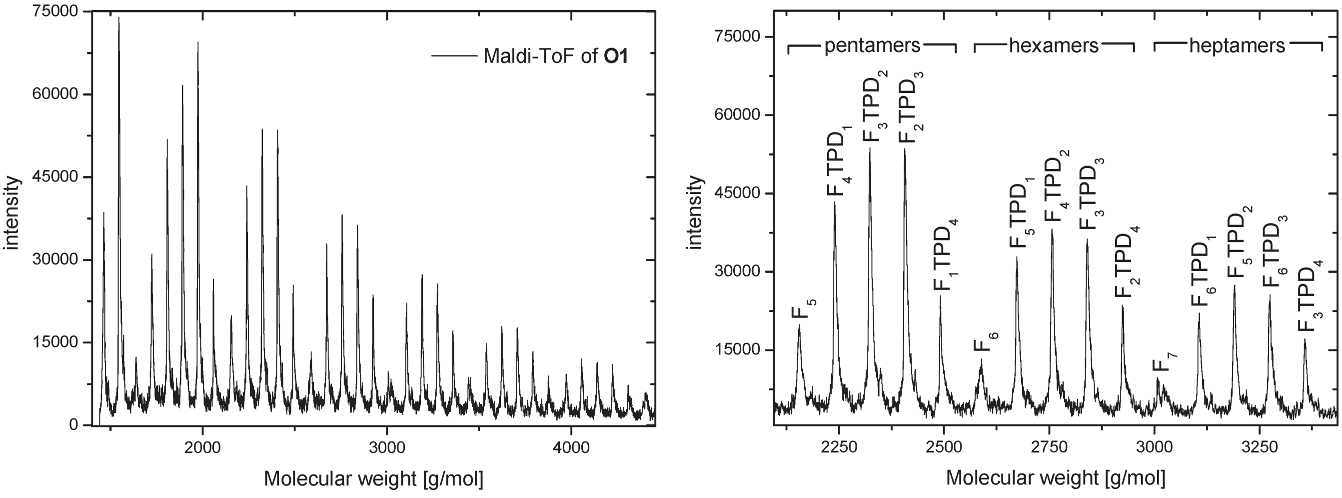


**Figure 1.** *Left:* Maldi-ToF spectrum of **O1**. *Right:* Magnification and assignment of the signals between 2100 and 3400 g/mol. The spectrum was recorded in the linear mode using POPOP as matrix. **F** corresponds to a fluorene and **TPD** to a **C1** unit according to Scheme 1. **F$_4$TPD$_2$**, for example, is an oligomer consisting of four fluorene and two **TPD** repeat units.

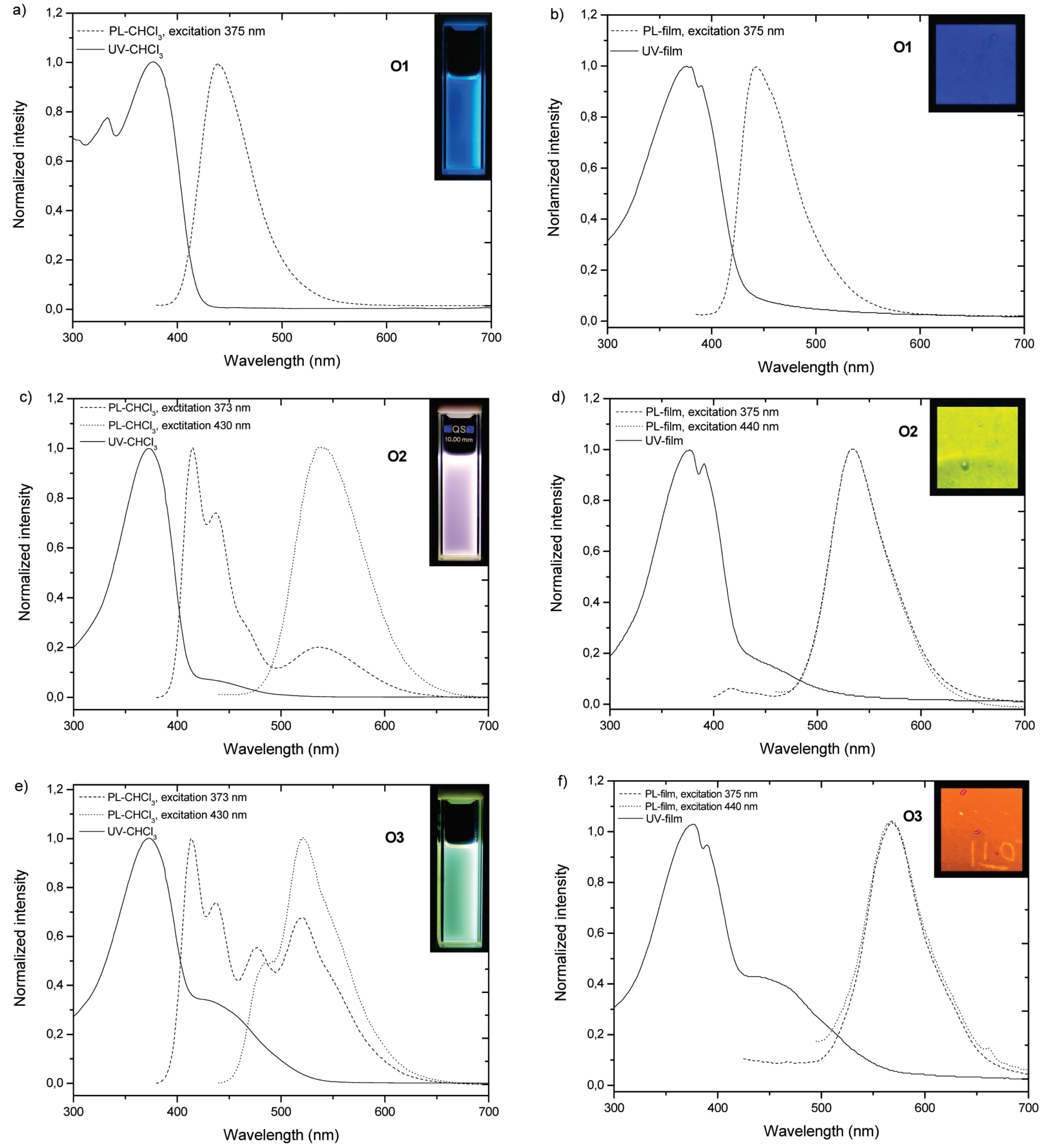


**Figure 2.** Normalized absorption and emission spectra of **O1**−**3** (a−f) in chloroform solutions and as thin films. The photographical insets show the chloroform solutions and thin films upon excitation at 366 nm.

**O1**. The transition enthalpies were very small and only detectable using a heating rate of 40 K/min. They were determined upon heating and due to the high heating rate the values are expected to be slightly overestimated. The value of 119 °C measured for **O1** is in the range of the reported value for TPD containing polyfluorenes.[16,23] For an efficient photopolymerization the acrylate units have to be mobile. Thus photo-cross-linking experiments with organic semiconductors are usually carried out at elevated temperatures to provide an appropriate mobility of the reactive groups. Here the low $T_g$s of **O2** and **O3** allow low processing temperatures, which helps to avoid photodegradation during UV exposure.

Due to the limited molecular weights of the oligomers Maldi-ToF measurements could be performed and the Maldi-ToF spectrum of **O1** is shown in Figure 1. Oligomer **O1** is well suited for Maldi-ToF investigations since aromatic amines are known to form stable molecular

---

(23) Sato, H.; Ogino, K.; Hirai, H. *Macromol. Symp.* **2001**, *175*, 159.

**Table 2. Optical Properties of Chloroform Solutions and Thin Films of O1-3**

| | solution | | films | |
|---|---|---|---|---|
| | UV $\lambda_{max}$ (nm) | PL $\lambda_{em.}$ (nm) | UV $\lambda_{max}$ (nm) | PL $\lambda_{em.}$ (nm) |
| **O1** | 375 | 439 (375)[a] | 375 | 442 (375)[a] |
| **O2** | 373, 430 | 415, 437, 537 (373)[a] 540 (430)[a] | 375, 440 | 534 (375, 440)[a] |
| **O3** | 373, 430 | 413, 438, 477, 520 (373)[a] 521 (430)[a] | 375, 440 | 568 (375, 440)[a] |

[a] The values in brackets give the corresponding excitation wavelength in nm.

ions. The spectrum was recorded in the linear mode with POPOP (1,4-Bis(5-phenyl-2-oxazolyl)benzene) as matrix. The signals are well resolved in the range of 1000−4500 g/mol. A magnification of the spectrum between 2100 and 3400 g/mol is also shown in Figure 1 *right*. Every single peak can be assigned to an oligomer with a distinct composition of **TPD** and **F** (=fluorene) units and a detailed assignment is included in Figure 1. In general all expected products are found and different "series" can be observed. Consequently the reactivities of fluorene monomers **F** and **E** in the Yamamoto condensation seem to be similar to those of **C1−3**. In the range of 2100−2500 g/mol all pentamers, between 2600 and 2900 g/mol all hexamers, and from 3000 to 3400 g/mol all heptamers are found. In the case of the hexamers, five different signals are observed. The signal at lowest molecular weight corresponds to a pure fluorene hexamer named $\mathbf{F_6}$ and with increasing molecular weight the number of incorporated **TPD** units increases. The highest molecular weight hexamer consists of two fluorene units **F** and four **TPD** units (named $\mathbf{F_2TPD_4}$). The occurrence of fluorene-only oligomers is not unexpected if mathematical probability considerations are performed. The probability of adding a fluorene monomer **F** to a growing chain end is 70% according to the monomer feed. If now the two end-capping molecules **E** are fixed at both ends of the chain, the probability of a (hexamer)-chain consisting of six fluorene units is 24%, assuming an equal reactivity of **F** and **TPD**.

Within the pentamers and heptamers pure fluorene oligomers, named $\mathbf{F_5}$ and $\mathbf{F_7}$, respectively, are also found. However the probability for the formation of fluorene-only compounds decreases with increasing chain lengths according to reaction statistics.

The existence of these pure fluorene oligomers has major consequences on the spectroscopic properties in solution as described later on. In the case of the pentamers in addition to the expected oligomers a peak corresponding to a monoend-capped pentamer ($\mathbf{F_1TPD_4}$) is observed. For higher molecular weight oligomers monoend-capped species are not found. Oligomers with bromine end groups are not present.

**Optical Properties.** The absorption and emission spectra of **O1−3** were measured in chloroform solution and thin film and are shown in Figure 2. The solution spectra are displayed left and the film spectra right. The results are summarized in Table 2. In solution the TPD containing oligomer **O1** exhibits one absorption maximum at 375 nm. Upon excitation at 375 nm one photoluminescence maximum at 439 nm is observed. The film spectra of **O1** are similar to the solution spectra, an absorption maximum at 375 nm and an emission maximum at 442 nm are found. In the case of **O2** the solution absorption spectrum shows two maxima, a dominant maximum at 373 nm and a small maximum at 430 nm (Figure 2c). Upon excitation at 373 nm a PL spectrum with three maxima is obtained. The first two maxima at 415 and 437 nm correspond to the typical oligfluorene emission pattern and result from the fluorene-only oligomers present in the mixture. The third maximum at 537 nm originates from the benzothiadiazole containing cooligomers. If the excitation wavelength is 430 nm the fluorene-only emission is suppressed and only the benzothiadiazole oligomers emit light with a maximum at 540 nm.[24] The film spectra of **O2** are displayed in Figure 2d. Here the absorption also shows two maxima, one dominant maximum at 375 nm and a weak one at 440 nm. An excitation at 375 and 440 nm lead to the same PL maxima at 534 nm. This demonstrates that in thin films an intermolecular energy transfer between different oligomer chains becomes possible. The energy is transferred from the fluorene-only compounds to the benzothiadiazole oligomers and a pure yellow emission color independent from excitation is obtained. The solution absorption spectrum of **O3** (Figure 2e) also exhibits two maxima, one at 373 nm and one at 430 nm. An excitation at 373 nm leads to a complex PL spectrum with four maxima. The first two maxima at 413 and 438 nm display the emission pattern of the pure oligofluorenes present in the mixture. The other maxima at 477 and 520 nm originate from the bithiophene cooligomers. However an excitation at 430 nm leads to a simpler PL spectrum with one dominant maximum at 521 nm. Here only the bithiophene cooligomers are excited and emit light, the fluorene-only emission is suppressed. The thin film spectra of **O3** are shown in Figure 2f. The absorption spectrum again exhibits two maxima, a dominant one at 375 nm and a weak one

**Table 3. Energy Levels and Optical Bandgaps of O1-3**

| | HOMO [eV][a] | LUMO [eV][b] | optical bandgap [eV][c] |
|---|---|---|---|
| **O1** | 5.25 | 2.30 | 2.95 |
| **O2** | 5.85 | 3.29 | 2.56 |
| **O3** | 5.31 | 2.91 | 2.40 |
| **Oligofluorene**[d] | 5.70 | 2.73 | 2.97 |

[a] Measured with photoelectron spectrometry. [b] Calculated from the HOMO and optical bandgap values. [c] Determined as intersection of absorption and emission spectra (film spectra). [d] Oligofluorene with an average degree of polymerization of 13 from ref 15.

---

(24) Chuang, C.-Y.; Shih, P.-I.; Chien, C.-H.; Wu, F.-I.; Shu, C.-F. *Macromolecules* **2007**, *40*, 247.

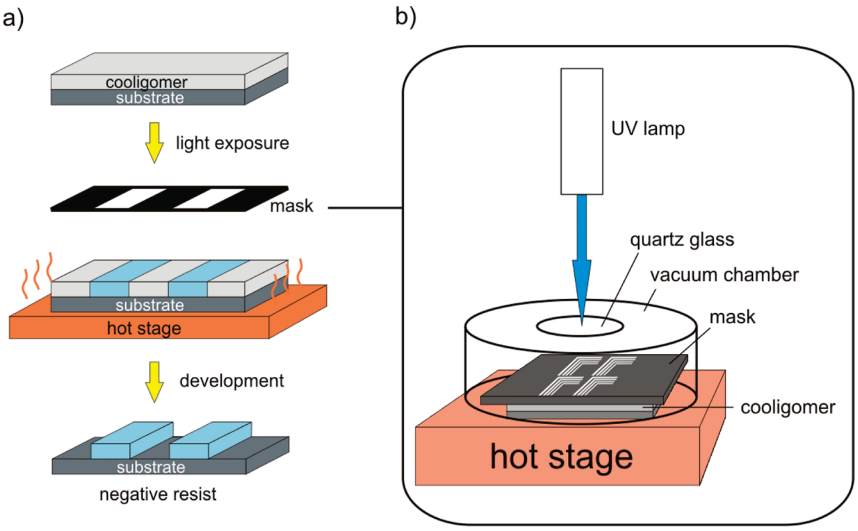


**Figure 3.** (a) Photolithographic process for a (negative) fluorene resist system. The first step is the spin coating of the oligofluorene followed by the irradiation with light through a mask (shown in detail in (b)). The exposure is carried out on a hot stage. In the last step the lithographic pattern is developed by dissolving the nonexposed parts in THF. (b) Experimental setup of the exposure step. The film is irradiated in a closed chamber in vacuum to avoid degradation processes.

at 440 nm. Upon excitation at both wavelengths (375 and 440 nm) the same PL spectrum with a maximum at 568 nm is obtained. Thus an intermolecular energy transfer from the fluorene-only oligomers to the bithiophene oligomers takes place and pure emission colors independent from the excitation wavelength are obtained. Here we note that for **O3** the PL maximum in solution is blue-shifted (47 nm) compared to the film spectrum. This may be due to well-known packing phenomena described for thiophene compounds.[25]

In general the typical fluorene emission pattern found for solutions of **O2** and **O3** also indicate that pure-fluorene compounds are present in the mixtures, which confirms the Maldi-ToF results. However for practical applications as emitters in yellow and red OLEDs, the oligomers are well suited since the blue oligofluorene fluorescence is not present in thin films.

The HOMO levels were measured by photoelectron spectrometry (Riken Keiki AC-2) from thin films. From the optical bandgaps, determined as intersection of the UV/vis and photoluminescence spectra, the LUMO values were calculated. All data are listed in Table 3. The oligomers **O1** and **O3** with electron donating units have HOMO energies of 5.25 and 5.31 eV respectively. In comparison to a fluorene-only oligomer, whose data are also displayed in Table 3, the HOMO values are increased. For the oligomer **O2** with an electron withdrawing comonomer we find a slight decrease of the HOMO level from 5.70 to 5.85 eV and a LUMO energy level of 3.29 eV, which is 0.59 eV lower than for a fluorene-only oligomer. Both **O2** and **O3** have smaller bandgaps (2.56 and 2.40 eV, respectively) and decreased LUMO energy values compared to a pure fluorene oligomer.

**Photolithography.** With regard to the use of **O1−3** as photopatternable materials the photo-cross-linking conditions were thoroughly investigated. Concerning the use of the patterned oligomers as semiconductors it is very important that, during the cross-linking procedure, the chemical structure of the material is not altered.[26] However, photo-cross-linking often causes a substantial degree of photochemical degradation. To avoid this, the processing conditions have to be very mild in terms of temperature and exposure time. The new materials **O1−3** are well suited due to their large number of acrylate functionalities and their low glass transition temperatures. To exclude any oxygen we put the samples into a vacuum chamber during the exposure procedure (Figure 3b).

The first processing step is the spin coating of the oligomer onto cleaned silicon wafers (see Figure 3). After that the films were dried at 115 °C for one minute under inert atmosphere. The thickness of all films was about 100 nm. The second step is the UV-exposure. The samples were put in a vacuum chamber as shown in Figure 3b, annealed at a certain temperature for several minutes in the chamber and then irradiated using a Hg−Xe lamp while keeping the temperature. The heating during irradiation is essential because the chains have to be mobile to polymerize. The last lithographic step is the development of the patterns, which is achieved by dissolving the nonirradiated areas in THF for 30 s.

Our previous experiments with photopolymerizable oligofluorenes showed that the use of an additional filter during exposure is helpful.[15] In that case we used the long pass filter GG400 (Schott) to cut off wavelengths below 400 nm, which avoids the excitation of the fluorene backbone. Thus most of the energy is absorbed by the initiator Irgacure 784 and a very fast cross-linking can be achieved. Here we note that the initiator Irgacure 784 shows absorption below 360 nm and above 400 nm.

---

(25) Yasuda, T.; Namekawa, K.; Iijima, T.; Yamamoto, T. *Polymer* **2007**, *48*, 4375.

(26) Qiang, L.; Ma, Z.; Zeng, Z.; Yin, R.; Huang, W. *Macromol. Rapid Commun.* **2006**, *27*, 1779.

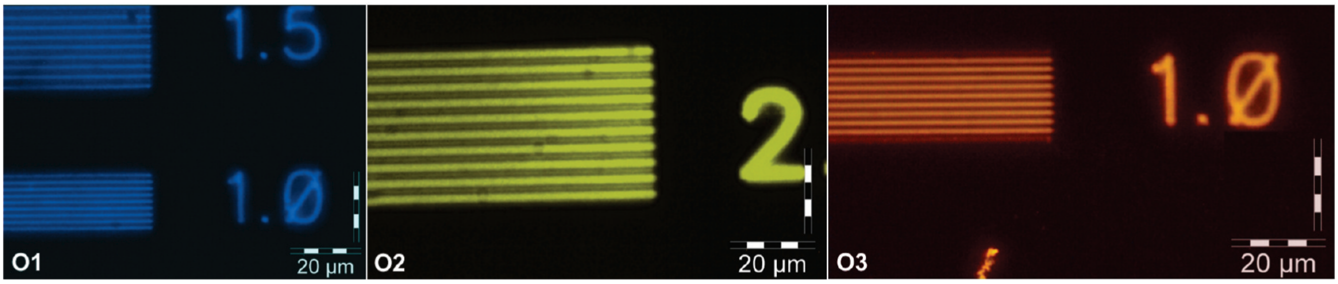


**Figure 4.** Fluorescent microstructures of **O1**−**3** observed under a fluorescence microscope with an excitation wavelength of 340−380 nm. Upon cross-linking the filter UG5 was used and the detailed conditions were: **O1**: exposure at 40 °C for 2 min; **O2**: exposure at 50 °C for 6 min; **O3**: exposure at 50 °C for 4.5 min. The corresponding SEM images are found in Figure 5. The numbers next to the stripes represent their width in $\mu$m.

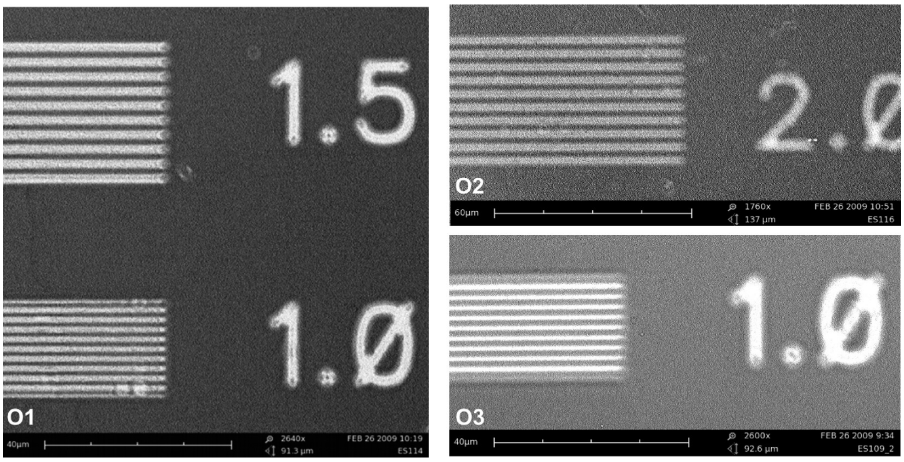


**Figure 5.** SEM images of microstructured oligomers **O1**−**3**. White corresponds to the cross-linked material, black and dark gray represent the wafer. For the SEM pictures the same samples were used as for the fluorescence microscopy images from Figure 4. The numbers next to the stripes represent their width in $\mu$m.

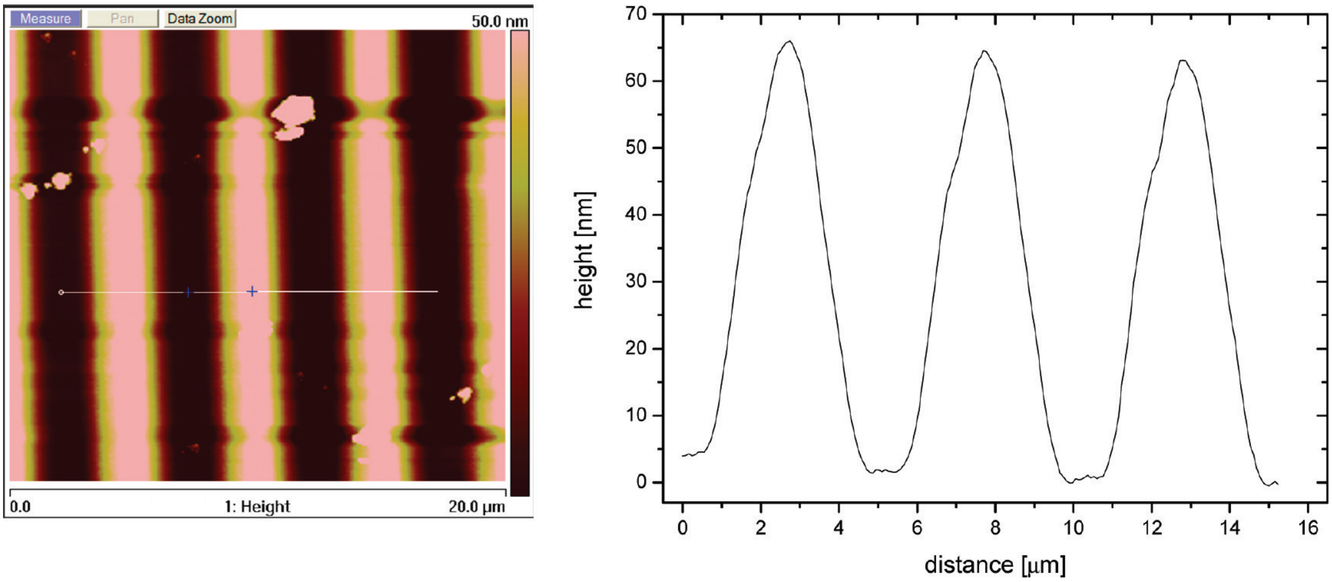


**Figure 6.** *Left*: AFM height image of the 2.5 $\mu$m-lines of oligomer **O3**. *Right:* Cross section of the stripes as indicated in the height image.

Its chemical structure is presented in Scheme 1. For **O1**−**3** we also tested the filter GG400, but the irradiation times needed appeared to be very long (up to 15 min). We attribute that to the absorption of **O1**−**3** above 400 nm. Irgacure 784 is not able to decompose into radicals, because most of the light energy is absorbed by the oligomers. Therefore we decided to irradiate using wavelengths below 300 nm. We utilized the Schott filter UG5, which transmits light between 230 and 400 nm and blocks shorter and longer wavelengths. Here we find much faster photo-cross-linking. For **O1** an exposure of 2 min at 40 °C was sufficient enough for the formation of well resolved patterns. In the case of **O2** the films had to be exposed for 6 min at 50 °C and for **O3** an irradiation at

50 °C for 4.5 min were found to be most suitable. In each case minimum resolutions of 1−2 μm were achieved.

Photooxidation was not observed, during the whole process the fluorescence colors of the oligomers were preserved, which was checked by fluorescence spectroscopy and microscopy.

The quality of the patterns was investigated with fluorescence microscopy and scanning electron microscopy (SEM). In the fluorescence microscope the excitation wavelength was 340−380 nm. Strong blue, yellow-green, and red fluorescent micrometer-sized stripes are observed (see Figure 4). A comparison of the fluorescence colors of irradiated and nonirradiated films using the fluorescence microscope showed that both films yielded identical fluorescence colors. That points to the preservation of the chemical structure and thus the opto-electronic properties of the oligomers during irradiation. The silicon wafers appear black, which indicates a complete removal of the polyfluorene in the nonexposed areas. The resolution goes down to 1 μm for **O1** and **O3** and 2 μm for **O2**. From the same samples SEM images were taken and are displayed in Figure 5. Here the same resolutions are found as observed with fluorescence microscopy. For **O1** and **O2** a slight overexposure is observed because the micrometer sized lines are slightly broader than given by the mask. To examine the slope and quality of the patterns we performed AFM experiments. Figure 6 shows an AFM height image and the corresponding cross-section of the 2.5 μm lines of **O3**. The desired rectangular line shape can not be observed, which points to nonideal patterning conditions.

## Conclusion

In this publication we show that random fluorene cooligomers with photo reactive acrylate units can be prepared in a simple 1-step Yamamoto synthesis. The acrylate functionalities are preserved quantitatively under Yamamoto conditions. NMR and Maldi-ToF measurements point to an almost statistical incorporation of the comonomers into the oligomer chain. Maldi-ToF analyses give a further insight into the chain compositions and we found fluorene-only oligomers to be present in low quantities. Thin films of the aromatic amine containing cooligomer show a blue fluorescence, the benzothiadiazole oligomer shows yellow photoluminescence and the bithiophene oligomer emits orange-red light upon excitation. Compared to pure fluorene oligomers with a HOMO of 5.7 eV the HOMO levels of the TPD and bithiophene derivatives are increased to 5.25 and 5.31 eV, respectively, whereas the HOMO level of the benzothiadiazole oligomer is decrased to 5.85 eV. Photolithography experiments reveal that a careful optimization of the conditions, for example, the choice of the photoinitiator, temperature, and irradiation wavelength, leads to well resolved micrometer sized patterns. A minimum feature size of 1 μm was obtained. Thus we showed that with a simple 1-step Yamamoto coupling oligomers with photo-cross-linkable acrylate groups are accessible. UV irradiation leads to densely cross-linked, insoluble networks. Thus these materials are ideal candidates for multilayer as well as patterned semiconducting devices.

**Acknowledgment.** We thank Evonik Degussa GmbH and especially Dr. Heiko Thiem for the Riken Keiki AC-2 and SEM measurements. We thank Markus Hund, Irene Bauer, Dr. Klaus Kreger for their help and the Bavarian Elite study program Macromolecular Science for the financial support.

**Supporting Information Available:** Additional information including Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.