6440 *Macromolecules* **2009**, *42*, 6440–6447
DOI: 10.1021/ma9008862

Macromolecules
ARTICLE

Synthesis and Spectroscopy of Poly(9,9-dihexylfluorene-2,7-diyl-*co*-9,9-dihexylfluorene-3,6-diyl)s and Their Model Oligomers

Nadezda Fomina, Stephen E. Bradforth,* and Thieo E. Hogen-Esch*

Department of Chemistry and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089

Received April 22, 2009; Revised Manuscript Received July 28, 2009

ABSTRACT: A series of poly(9,9-dihexylfluorene-2,7-diyl-*co*-9,9-dihexylfluorene-3,6-diyl) copolymers of varying composition were synthesized by Suzuki polymerization. Their composition and properties were determined by NMR, UV−vis, and fluorescence spectroscopy and cyclic voltammetry. The incorporation of 3,6-fluorene units gives distinct blue emissions and near-UV absorptions that are blue-shifted in a nonlinear fashion as the fraction of 3,6-units increases. Sequences of 2,7-fluorene units with different lengths punctuated by 3,6-units indicate the presence of distinct chromophores. In order to better understand these changes, dimer and trimer model co-oligomers of the 2,7- and 3,6-fluorene monomers were synthesized, and their spectral properties were compared with those of the copolymers. ZINDO calculations on the models showed excellent agreement of experimental and calculated absorption spectra.

Introduction

Poly(9,9-dialkylfluorene-2,7-diyl)s (27PDAF) and their copolymers have attracted much attention in the past decade as efficient blue light-emitting materials.[1−7] Recently, the synthesis of a poly(9,9-dialkylfluorene-3,6-diyl) has been reported.[8,9] This polymer showed a significantly blue-shifted absorption and steady-state emission spectra compared to 27PDAFs.[10,11] A similar blue shift was observed for poly(9,9-bisoctylsilafluorene-3,6-diyl) and poly(9,9-bisoctylsilafluorene-3,6-diyl)-*co*-(9,9-dioctlylfluorene-2,7-diyl)s.[12] In the latter case the blue shift was attributed to the mixing of the electronic states of 2,7- and 3,6-fluorene units. However, no detailed studies were done to clarify the role of the 3,6-linkages in the copolymer spectra.

Here we report the synthesis and photophysical properties of poly(9,9-dihexylfluorene-2,7-diyl-*co*-9,9-dihexylfluorene-3,6-diyl)s (27*co*36's). In order to better understand the spectroscopy of the copolymers and explain the origin of the blue shift, we synthesized and studied several model oligomers of the 2,7- and 3,6-fluorene (Scheme 1). DFT calculations on the model oligomers were used in order to obtain optimized geometries, and the ZINDO was employed to compare calculated and observed absorption spectra.

Experimental Section

Materials. 2-Bromofluorene, 2,7-dibromo-9,9-dihexylfluorene, 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-proanediol) ester, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, *n*-BuLi, $Pd(OAc)_2$, $P(Ph)_3$, iodohexane, diethyldithiocarbamic acid sodium salt, and all the solvents were purchased from commercial sources and used without further purification.

Measurements. SEC and LS measurements were carried out in THF at room temperature on a Waters 510 HPLC equipped with a Beckman 156 refractive index detector and a Wyatt Dawn light scattering detector. A flow of 1 mL/min was maintained through three columns (Waters PLgel 5 μL 50A, PLgel 5 μL 10^3A, and PLgel 5 μL 10^4A). The data were analyzed using Wyatt Astra 4.90.07 software. Absorption spectra were recorded on CARY-14 spectrophotometer (Online Instrument Systems) in 10^{-9} g/L chloroform solutions. Integrated absorption coefficients were obtained as products of the linear absorption coefficients and band widths at half-height. For copolymers 27*co*36(50), 27*co*36(67), and 36PDHF having two bands in their absorption spectra, integrated absorption coefficients were calculated only for the lower energy transitions. Emission spectra were recorded on a Fluorolog Tau-3 luminescence spectrometer (Joblin Yvou Horiba). Photoluminescence quantum yields were measured in chloroform solutions by using the C9920-03 absolute quantum yield measurement system (Hamamatsu Photonics) consisting of an excitation xenon light source, monochromator, an integrating sphere, and a multichannel CCD spectrometer. Excitation wavelengths were set at the lowest energy transition. For this measurement 9,10-diphenylanthracene solution in chloroform was used as a reference, and a fluorescence quantum efficiency of 92% was recorded. Polymer films were spin-coated from 10^{-6} g/mL toluene solutions and annealed at 150 °C under high vacuum. NMR spectra were recorded on a Varian Mercury-400 NMR spectrometer. Cyclic voltammograms were recorded on potentiostat/galvanostat model 283 (EG&G Princeston Applied Research) in acetonitrile solutions with carbon fiber as the working electrode and Pt wire as counter electrode, Ag wire as pseudoreference electrode, and Bu_4NPF_6 as electrolyte. Only oxidation potentials of the copolymers could be recorded. For this arrangement ferrocene half-wave potential was observed at 0.468 eV. The HRMS and MALDI-TOF experiments were carried out by independent commercial entities. DFT and related calculations were performed using the Gaussian 03 program package with the GaussView 3.0 interface program. The geometries of the model oligomers were optimized by DFT (B3LYP/6-31G*). The optimized structures were used in further HF/STO-3G and HF/6-31G* calculations to obtain the shapes of HOMO and LUMO orbitals and in ZINDO calculations in order to obtain the excitation maxima.

Bis(4,4,5,5-tetramethyl[1.3.2]dioxoborolan-3,6-diyl)-9,9-bis(hexyl)fluorene (***1***). 1.276 g (2.59 mmol) of **4** was dissolved in dry THF under argon and cooled to −78 °C. *n*-BuLi (6.48 mL, 10.37 mmol) was added dropwise; the solution was stirred for

---

*Corresponding authors. E-mail: hogenesc@usc.edu, bradfort@usc.edu.

1 h at −78 °C and quenched with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.11 mL, 15.54 mmol). The reaction mixture was allowed to warm up overnight and was worked up with a saturated solution of $NaHCO_3$. The aqueous fraction was extracted with diethyl ether and organic solution was dried over $MgSO_4$, and solvents were removed under vacuum. Purification by chromatography with chloroform as eluent yielded the product as pale yellow oil that slowly crystallized at room temperature (35%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.24$ (s, 2H), 7.76 (d, $J = 7.2$ Hz, 2H), 7.34 (d, $J = 7.6$ Hz, 2H), 1.97−1.93 (m, 4H), 1.38 (s, 24H), 1.11−0.96 (m, 12H), 0.75 (t, $J = 7.2$ Hz, 6H), 0.59−0.52 ppm (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.92$, 140.61, 133.53, 126.31, 122.19, 83.69, 55.53, 40.34, 31.43, 29.68, 24.94, 23.66, 22.55, 13.99 ppm. HRMS: *m*/*z*: 609.4263 [$M+Na^+$] (calcd: 609.4257).

9,9,9′,9′-Tetrakis(*hexyl*)*-2,2′-bifluorene* (*2,2′-BF*). Ni(COD)$_2$ (0.1511 g, 0.55 mmol), BiPy (0.086 g, 0.55 mmol), and COD (0.07 mL, 0.55 mmol) were dissolved in DMF (8 mL) under N_2 and stirred at 75 °C for 30 min to allow the formation of reactive complex. After that 2-bromo-9,9-dihexylfluorene (0.3 g, 0.726 mmol) in DMF (2 mL) was added to the reaction flask under N_2, and the solution was stirred at 75 °C for 2 h. After cooling to room temperature, the reaction mixture was poured into concentrated HCl (30 mL) and stirred for 30 min. The product was extracted with $CHCl_3$, washed with H_2O, and dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by column chromatography over silica gel with hexane yielding white solid product (75%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.78$ (d, $J = 8$ Hz, 2H), 7.74 (d, $J = 7.6$ Hz, 2H), 7.65 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, 2H), 7.62 (s, 2H), 7.35 (m, 3H), 2.04 (m, 8H), 1.00 (m, 24H), 0.74 (m, 20H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.40$, 150.95, 140.76, 140.46, 140.24, 126.94, 126.74, 125.98, 122.88, 121.37, 119.83, 119.67, 55.12, 40.35, 31.45, 29.67, 23.74, 22.55, 14.00 ppm. HRMS: *m*/*z*: 666.5163 [M^+] (calcd: 666.5165).

9,9,9′,9′-Tetrakis(*hexyl*)*-2,3′-bifluorene* (*2,3′-BF*). 3-Bromo-9,9-dihexylfluorene (0.1 g, 0.24 mmol), (4,4,5,5-tetramethyl [1.3.2] dioxoborolan-2-yl)-9,9-bis(hexyl)fluorene (0.112 g, 0.24 mmol), and $K_3PO_4 \cdot H_2O$ (0.253 g, 1.098 mmol) were dissolved in a mixture of dioxane, toluene, and H_2O (1.25 mL of each) and purged with N_2 for 1 h. After that Pd(OAc)$_2$ (0.001 g, 0.005 mmol) and PPh$_3$ (0.008 g, 0.025 mmol) in 0.25 mL of dioxane were added to the reaction flask under N_2. The flask was shielded from light with aluminum foil, and the reaction mixture was heated to reflux with vigorous stirring for 5 h under protection of N_2. After the reaction mixture was cooled to 60 °C, 10 mL of 10% diethyldithiocarbamic acid sodium salt solution in water was added, and the mixture was stirred for 3 h. The organic layer was extracted with diethyl ether, washed with water, and dried over $MgSO_4$. The residue was purified by column chromatography over silica gel with hexane as eluent and solidified from MeOH at −10 °C to yield the product as a white solid (75%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (d, $J = 1.2$ Hz, 1H), 7.82 (m, 2H), 7.75 (d, $J = 7.6$ Hz, 1H), 7.69 (m, 2H), 7.63 (dd, $J_1 = 8$ Hz, $J_2 = 1.6$ Hz, 1H), 7.44 (d, $J = 8$ Hz, 1H), 7.40−7.31 (m, 6H), 2.08−2.00 (m, 8H), 1.17−1.06 (m, 24H), 0.81−0.69 ppm (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 151.32, 151.09, 150.94, 149.69, 141.68, 140.92, 140.85, 140.37, 140.21, 129.68, 127.13, 126.91, 126.73, 126.23, 126.00, 125.51, 123.07, 122.84, 121.42, 119.85, 119.67, 119.59, 118.27, 55.15, 54.85, 40.48, 40.42, 31.50, 29.73, 23.83, 23.76, 22.60, 14.01 ppm. HRMS: *m*/*z*: 666.5158 [M^+] (calcd: 666.5165).

9,9,9′,9′-Tetrakis(*hexyl*)*-3,3′-bifluorene* (*3,3′-BF*). The compound was prepared from 3-bromo-9,9-dihexylfluorene according to the method used for 2,2′-BF. Purification by column chromatography with hexane/ethyl acetate (9/1) yielded an opaque oily product (75%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.02$ (d, $J = 1.6$ Hz, 2H), 7.79 (d, $J = 8$ Hz, 2H), 7.64 (dd, $J_1 = 8$ Hz, $J_2 = 1.6$ Hz, 2H), 7.42 (d, $J = 7.6$ Hz, 2H), 7.38−7.31 (m, 6H), 2.02−1.98 (m, 8H), 1.15−1.03 (m, 24H), 0.78 (t, $J = 7$ Hz, 12H), 0.72−0.63 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.12$, 149.66, 141.71, 141.08, 140.35, 127.12, 126.33, 123.07, 122.89, 119.71, 118.50, 54.90, 40.49, 31.56, 29.79, 23.83, 22.63, 14.05 ppm. HRMS: *m*/*z*: 666.5159 [M^+] (calcd: 666.5165).

9,9,9′,9′,9″,9″-Hexakis(*hexyl*)*-3,2′,7′,3″-terfluorene* (*3,2′,7′,3″-TF*). The compound was prepared according to the method used for 2,3′-BF by using 3-bromo-9,9-dihexylfluorene (0.113 g, 0.273 mmol) and 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**2**) (0.055 g, 0.109 mmol), $K_3PO_4 \cdot H_2O$ (0.506 g, 2.2 mmol), in 4.5 mL of a mixture of dioxane, toluene, and H_2O (1.5 mL of each) and Pd(OAc)$_2$ (0.001 g, 0.005 mmol) and PPh$_3$ (0.008 g, 0.025 mmol) in 0.25 mL of dioxane. Purification by column chromatography with hexane/chloroform (9/1) yielded white solid product (64%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (s, 2H), 7.82 (d, $J = 7.6$ Hz, 4H), 7.69 (d, $J = 8.4$ Hz, 4H), 7.63 (d, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 8$ Hz, 2H), 7.38−7.31 (m, 6H), 2.11 (m, 4H), 2.00 (m, 8H), 1.1 (m, 36H), 0.77 (m, 30H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.62$, 151.09, 149.70, 141.70, 140.92, 140.36, 139.99, 127.14, 126.73, 126.24, 126.10, 123.09, 122.86, 121.44, 119.92, 119.70, 118.67, 55.32, 54.86, 40.58, 40.43, 31.53, 29.77, 23.83, 22.62, 14.02 ppm. HRMS: *m*/*z*: 998.7663 [M^+] (calcd: 998.7669).

9,9,9′,9′,9″,9″-Hexakis(*hexyl*)*-2,3′,6′,2″-terfluorene* (*2,3′,6′,2″-TF*). The compound was prepared according to the method used for 2,3′-BF by using (4,4,5,5-tetramethyl [1.3.2] dioxoborolan-2-yl)-9,9-bis(hexyl)fluorene **7** (0.206 g, 0.45 mmol), **4** (0.099 g, 0.202 mmol), and $K_3PO_4 \cdot H_2O$ (1.012 g, 4.4 mmol) in 9 mL of a mixture of dioxane, toluene, and H_2O (3 mL of each) and Pd(OAc)$_2$ (0.0022 g, 0.01 mmol) and PPh$_3$ (0.016 g, 0.05 mmol) in 0.5 mL of dioxane. Purification by column chromatography with hexane/chloroform (9/1) yielded white solid product melting at RT (79%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.09$ (s, 2H), 7.8−7.61 (m, 10H), 7.45 (d, $J = 8$ Hz, 2H), 7.37−7.29 (m, 6H), 2.06−2.02 (m, 12H), 1.16−1.07 (m, 36H), 0.8−0.68 (m, 30H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.36$, 150.92, 150.15, 141.53, 140.86, 140.48, 140.38, 140.25, 126.93, 126.74, 126.45, 126.04, 123.14, 122.85, 121.42, 119.86, 119.67, 118.33, 55.17, 54.70, 40.49, 31.55, 31.49, 29.83, 29.71, 23.96, 23.74, 22.64, 22.57, 14.03 ppm. HRMS: *m*/*z*: 998.7659 [M^+] (calcd: 998.7669).

General Procedure for Synthesis of 27co36 Copolymers by Suzuki Copolymerization. The appropriate amounts of 3,6-dibromo-9,9-dihexylfluorene, 2,7-dibromo-9,9-dihexylfluorene, and 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (total 1 mmol, bromide:boronic acid ester = 1:1) and $K_3PO_4 \cdot H_2O$ (0.506 g, 2.2 mmol) were dissolved in a mixture of dioxane, toluene, and H_2O (2.5 mL of each) and purged with N_2 for 1 h. After that, Pd(OAc)$_2$ (0.001 g, 0.005 mmol) and PPh$_3$ (0.008 g, 0.025 mmol) in 0.25 mL of dioxane were added to the reaction flask under N_2. The flask was shielded from light with aluminum foil, and the reaction mixture was heated to reflux with vigorous stirring for 2 h under purified nitrogen. After cooling to 60 °C, 10 mL of 10 wt % diethyldithiocarbamic acid sodium salt solution in water was added, and the mixture was stirred for 3 h. After cooling to RT the reaction mixture was washed with water three times in a separatory flask and precipitated in 50 mL of MeOH. The polymers were obtained as white to light yellow solids.

Yamamoto Polymerization of 4. All manipulations were carried out in the dark under an argon atmosphere. Ni(COD)$_2$ (0.44 g, 1.6 mmol), bipyridine (0.249 g, 01.6 mmol), and 1,5-cyclooctadiene (0.2 m,l 1.6 mmol) were stirred in 8 mL of DMF for 30 min at 90 °C. Then **4** (0.32 g, 0.65 mmol) in 2 mL of DMF was added to the reaction mixture, and polymerization was allowed to proceed for 5 days. The reaction mixture was worked up with concentrated HCl (40 mL), the organic layer was separated, and the aqueous layer was extracted with two portions of DCM. The organic fractions were combined and washed with water. The solvents were removed under vacuum; the resulting crude yellow oily solid product was stirred with 10 mL of MeOH at RT for 30 min, filtered, and air-dried to give white solid product (76%). ^1H NMR

(400 MHz, $CDCl_3$): $\delta = 0.76$ (m), 1.75 (m), 2.03 (m), 7.51 (d), 7.70 (d), 8.12 (s), 8.30 (s) ppm. ^{13}C (100 MHz, $CDCl_3$): $\delta = 14.18$, 22.74, 23.98, 29.92, 31.69, 40.65, 54.88, 118.68, 123.24, 126.57, 140.49, 141.81, 150.19 ppm. Calculated: C, 90.36%, H, 9.64%. Found: C, 90.34%, H, 9.57%.

Results

Copolymers. The synthesis of 3,6-dibromo-9,9-dihexylfluorene (**4**) was published earlier.[9] Monomer **1** was obtained by treating **4** with *n*-BuLi at −78 °C followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,2,3-dioxaborolane. The poly(9,9-dihexylfluorene-2,7-diyl-*co*-9,9-dihexylfluorene-3,6-diyl)s (27*co*36's) and poly(9,9-dihexylfluorene-2,7-diyl) (27PDHF) were synthesized by Suzuki coupling (Scheme 1, Table 1). The copolymerization of monomers **2** and **4** gave the alternating 27*co*36(50). As indicated in Scheme 1, monomers **2**, **3**, and **4** were used to synthesize the copolymers with less than 50 mol % of 3,6-fluorene units with the 3,6-units occurring *singly*. For the 27*co*36(67) monomers **1**, **2**, and **4** were copolymerized so that in this case the 2,7-fluorene units occurred singly. Thus, with the exception of the 27*co*36(50) the other copolymers represent statistical distributions of the prevailing comonomer. Interestingly, the homopolymerization of **4** by Yamamoto coupling[9,13] proceeded much slower (at least 10 times) compared to that of **3** and yielded lower molecular weights (MW's) under otherwise identical conditions.

The 3,6-content in the copolymers was determined by integration of the 4-protons of 3,6-fluorene units relative to the other aromatic protons and is in good agreement with the calculated values (Table 1). However, in line with the above, the polymerization yields and degree of incorporation of the 3,6-fluorene units decrease slightly with increasing 3,6-comonomer feed (Table 1), confirming the lower polymerization rates of **4** compared with the 2,7-comonomers.

Table 1. Synthesis of 27,36 Copolymers

name	3,6-content, mol % feed[a]	3,6-content, mol % NMR[b]	M_w(LS)[c]	M_w(PS)[d]	PDI	yield, %
27PDHF	0	0	42 400	121 700	1.45	99.5
27*co*36(5)	5	7	45 000	120 300	2.08	98.7
27*co*36(20)	20	21	13 000	24 400	1.61	94.6
27*co*36(33)	33	31.5	14 000	26 100	1.27	91
27*co*36(50)	50	50	28 500	33 800	1.82	90
27*co*36(67)	67	62	12 000	11 200	1.6	85
36PDHF	100	100	27 000	26 500	3.37	76[e]

[a] mol % of monomers **2** and **4** in the monomer mixture. [b] Copolymer mol % of 3,6-fluorene units determined by ^1H NMR. [c] Weight-average molecular weight determined with light scattering detector. [d] Weight-average molecular weight determined by polystyrene standards. [e] Yield of crude product including a low molecular weight fraction of cyclic oligomers.

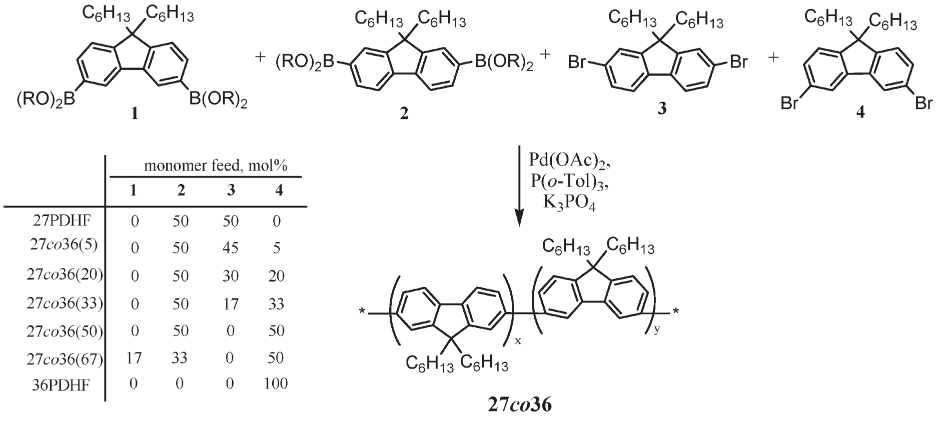
For 27PDHF the ratio of the light scattering MW relative to that determined by SEC with polystyrene standards is close to 3 (Table 1).[14−16] However, this ratio decreases with increasing 3,6-content and is close to 1 for 36PDHF, indicating a significantly decreased size of the copolymers consistent with the presence of strongly bent (90°) 3,6-fluorene units linked through rotationally labile carbon−carbon bonds. This shape is also reflected in the formation of appreciable quantities of homopolymerization cyclic products with the predominant formation of the cyclic tetramer.[9]

The absorption and emission spectra of the 27,36 copolymers are blue-shifted with increasing 3,6-content (Figure 1, Table 2). Thus, the 27*co*36(5) copolymer shows an absorption maximum at 392 nm that is only slightly blue-shifted compared to that of 27PDHF (394 nm) and consistent with the reported conjugation length of 27PDAF's of about 12 fluorene units.[17,18] As the 3,6-content increases to 20%, the absorption spectrum is blue-shifted by 14 nm (from 394 to about 380 nm) and the band is broadened, suggesting the presence of different distinct chromophores (see below) corresponding to shorter sequences of 2,7-fluorene units. For 27*co*36(33) the absorption maximum is further blue-shifted to 354 nm and is even broader with a distinct shoulder around 380 nm that seems to correspond to the main transition of the 27*co*36(20) copolymer. Hence, the bands at 354 and 380 nm appear to represent distinct sequences of 2,7-fluorenes separated by isolated 3,6-fluorene units (see below).

For the strictly alternating 27*co*36(50) copolymer the absorption spectrum shows a further blue shift to 339 nm, but the main band is more narrow and there is no shoulder around 380 nm, consistent with the absence of longer 2,7-fluorene sequences. At 67 mol % of the 3,6-units the lowest energy transition is slightly blue-shifted (333 nm) compared to the 27*co*36(50) copolymer, and a new intense transition appears at 267 nm (Table 2). This higher energy transition is also present in 36PDHF (262 nm) along with the lower energy transition at 325 nm and may be attributed presumably to very short sequences of 3,6-fluorene units (see below).

The introduction of 3,6-fluorene units also has a strong effect on the copolymers absorption coefficients, calculated per fluorene unit (Table 2). Thus, at 5 and 50 mol % of 3,6-units the linear absorptivities are significantly higher (ε = 38 300 and 32 700 L mol^{-1} cm^{-1}) compared to 27PDHF (ε = 27 200 L mol^{-1} cm^{-1}) as well as the integrated absorptivities (ε_{int} = 1.558 × 10^6 and 1.423 × 10^6 L mol^{-1} cm^{-1} compared to 0.896 × 10^6 L mol^{-1} cm^{-1}). The integrated absorptivity of the

Scheme 1. Synthesis of 27,36 Copolymers by Suzuki Reaction



	monomer feed, mol% 1	2	3	4
27PDHF	0	50	50	0
27*co*36(5)	0	50	45	5
27*co*36(20)	0	50	30	20
27*co*36(33)	0	50	17	33
27*co*36(50)	0	50	0	50
27*co*36(67)	17	33	0	50
36PDHF	0	0	0	100

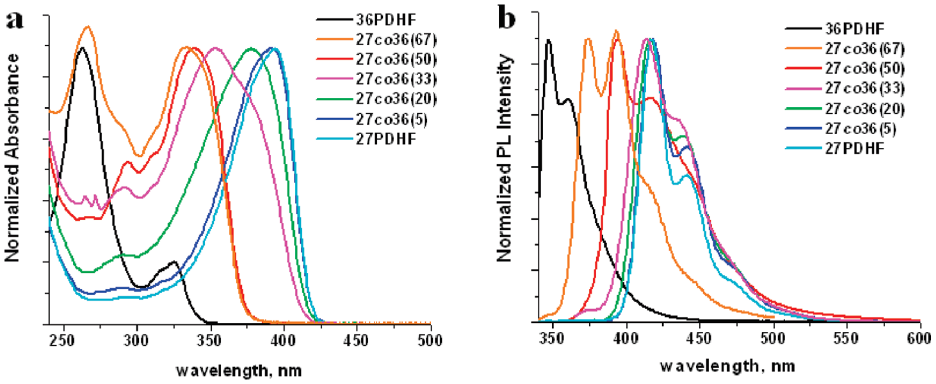


Figure 1. Absorption (a) and emission (b) spectra of 27PDHF, 36PDHF, and 27*co*36's in $CHCl_3$. The λ_{exc} were chosen at the lower energy absorption bands maxima.

Table 2. Absorption and Emission of 27,36 Copolymers

name	λ_{max}(abs)[a]	ε,[b] L mol^{-1} cm^{-1}	ε_{int},[c] L mol^{-1} cm^{-1} ($\times 10^6$)	λ_{max}(em)[a]	Φ,[a] %	λ_{max}(em) film	E_{ox}
27PDHF	394	27 200	0.896	420, (441)	99	430, (453)	0.06
27*co*36(5)	392	38 300	1.558	417, (441)	97	421, (447)	1
27*co*36(20)	378	26 000	1.333	415, (439)	98	420, (445)	1.03
27*co*36(33)	354	20 800	1.410	413, (434)	99	418, (442)	1.09
27*co*36(50)	339	32 700	1.430	395, (416)	97	396, (417)	1.18
27*co*36(67)	333, (267)	19 100, (20 600)	0.988	374, (394)	90	(377, 396), 415	1.28
36PDHF	325, (262)	8 800, (43 400)	0.262	347, (361)	23	(347), 369	1.47

[a] Experimental values determined in $CHCl_3$ solution at 25 °C. [b] Absorption coefficients calculated per fluorene unit. [c] Integrated absorption coefficients obtained as a product of linear absorption coefficient and bandwidth at half-height (for the lower energy transitions only).

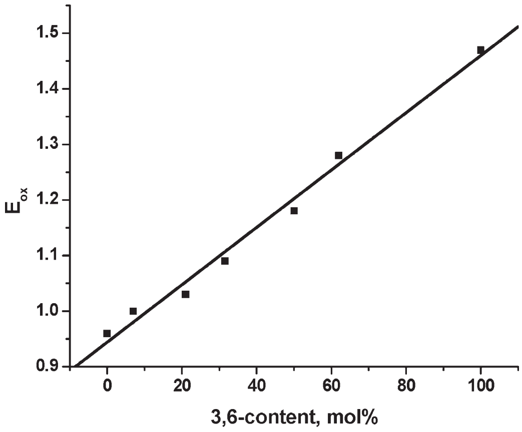


Figure 2. Dependence of E_{ox} on the composition of 27,36 copolymers in acetonitrile at 25 °C.

lower energy band of 27*co*36(67) (0.988 × 10^6 L mol^{-1} cm^{-1}) is lower than that of 27*co*36(50) with the integrated absorptivity of the 325 nm band of 36PDHF being the lowest (0.262 × 10^6 L mol^{-1} cm^{-1}). These changes appear to indicate the occurrence of additional accessible transitions of the copolymers in the 250−350 nm region.

Like the absorption spectra, the emission bands of the 27*co*36 copolymers compared with the 27PDHF are blue-shifted as 3,6-fluorene content increases (Table 2, Figure 1). However, this shift is not pronounced for the copolymers with low 3,6-content (≤33%), but a sizable blue shift (35 nm) is seen for the alternating copolymer, 27*co*36(50). For the 27*co*36(67) copolymer the emission is further blue-shifted by 21 nm and for 36PDHF by another 27 nm (Table 2). The reason for the small changes in the emissions of the copolymers with low 3,6-content may be energy transfer from higher energy chromophores (see above). This is also consistent with the values of quantum efficiencies being high for the copolymers with up to 67% of 3,6-fluorene units.

The thin films of the copolymers were spin-coated from toluene solutions and annealed in vacuum for 2 h at 150 °C. As shown in Table 2 and Figure S18, the emission of 27PDHF film shows a well-documented red-shifted emission at 430 nm and a more pronounced vibronic structure (453, 480 nm) compared to the solution data with the shoulders extending well into the 500−600 nm range and may be attributable to excimer formation.[19] Like their solutions, the copolymer films with less than 50% 3,6-content show small blue shifts (429−419 nm) with increasing 3,6-content. The blue shifts are, again, consistent with the presence of shorter 2,7-fluorene sequences. The 27*co*36(50) and 27*co*36(67) copolymer films, unlike their solutions, are nearly identical and are blue-shifted further with the main emission at 414 and 416 nm and show a different vibronic structure compared to the other copolymers with shoulders at 396/440 and 397/440 nm (Figure 3, Table 2). Given the well-defined structure of the strictly alternating 27*co*36(50) copolymer, this abrupt change in film emission may be linked to either a 3,6−2,7−3,6 or a 2,7−3,6−2,7 "triad" (see below). Finally, the emission of 36PDHF shows new vibronic structure that is different from that in solution. As the emission of 36PDHF (10 wt %) in PMMA matrix is identical to the solution (Figure S19), this may be attributed to intermolecular interactions and/or to reabsorption.

The oxidation potentials of the copolymers were measured by cyclic voltammetry in acetonitrile (Table 2). It was found that the oxidation potentials (E_{ox}) increased linearly with 3,6-content, indicating decreasing HOMO levels as the fraction of 3,6-fluorene units increases (Figure 2). This is consistent with lower conjugation lengths for the polymers having higher 3,6-content.

Oligomers. In order to clarify the above spectral data, model oligomers were synthesized (Scheme 2). 3-Bromo-9,9-dihexylfluorene was synthesized by the same protocol as **4**. Oligomers 2,2′-BF and 3,3′-BF were synthesized by Yamamoto coupling of the corresponding monobromofluorenes.

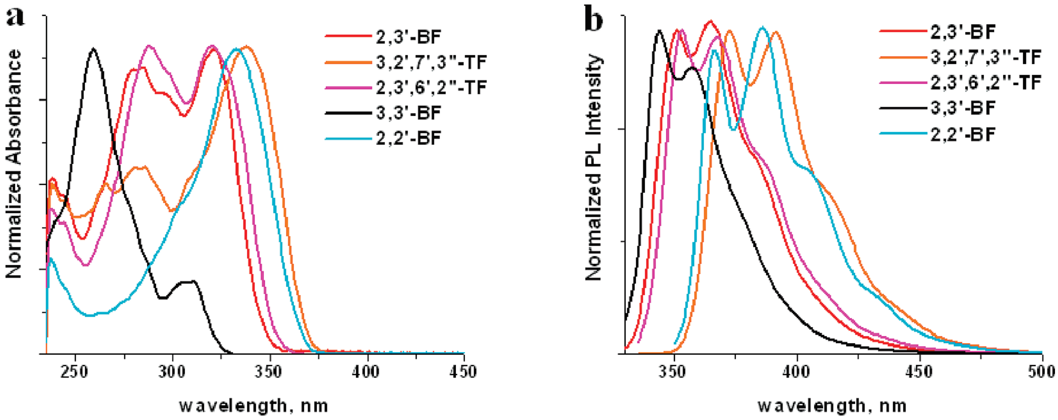


Figure 3. Absorption (a) and emission (b) spectra of model oligomers in $CHCl_3$. The λ_{exc} were chosen at the lower energy absorption bands maxima.

Scheme 2. Structures of the Model Oligomers

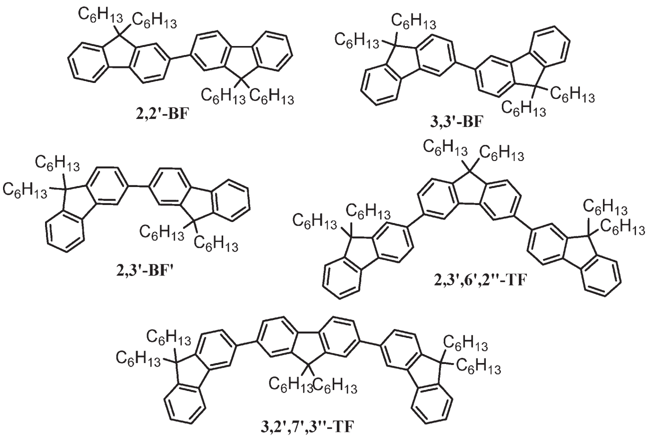


Table 3. Experimental and Calculated Properties of Model Oligomers

name	$\lambda_{max}^{(abs)a}$	ε,[b] L mol^{-1} cm^{-1}	$\lambda_{max}^{(em)a}$	Φ,[c] %	θ^d	$\lambda_{max}^{(exc)d}$
3,3′-BF	259 310	80 900 19 700	344, 357	19	39.4	306
2,3′-BF	284 321	32 200 34 300	351, 365	47	38.2	320
2,2′-BF	332	49 900	366, 385	99	38.0	335
2,3′,6′,2″-TF	288 320	61 800 60 500	353, 368	55	38.5	324
3,2′,7′,3″-TF	285 338	42 000 55 500	372, 391	99	38.1	337
3,(2′,7′)$_2$,3″-TF					38.4, 37.6	354

[a] Experimental values in $CHCl_3$ at room temperature. [b] Linear molar absorption coefficients. [c] Absolute fluorescence quantum yields measured in $CHCl_3$ at room temperature. [d] Calculated values: dihedral angles calculated by DFT (B3LYP/6-31G*) on oligomers containing 9-methyl groups to reduce computational times; $\lambda_{max}^{(exc)}$ were obtained by the ZINDO method.

Conversion of 2-bromo-9,9-dihexylfluorene into (4,4,5,5-tetramethyl[1.3.2]dioxoborolan-2-yl)-9,9-bis(hexyl)fluorene and reaction with 3-bromo-9,9-dihexylfluorene under Suzuki reaction conditions afforded 2,3′-BF. Similarly, the trimers, 2,3′,6′,2″-TF and 3,2′,7′,3″-TF, were synthesized by Suzuki coupling of the corresponding bromides and boronic esters.

The oligomers absorption and emission spectra are shown in Figure 3 and summarized in Table 3. The absorption spectrum of 2,2′-BF shows a single strong transition with a maximum at 332 nm with molar absorption coefficient of 49 900 L mol cm^{-1}. All other oligomers have two absorption maxima (Figure 3). Thus, the 2,3′-BF has transitions at 321 and 284 nm (34 300 and 32 200 L mol^{-1} cm^{-1}, respectively). Interestingly, the absorption of the trimer, 2,3′,6′,2″-TF (320 and 288 nm), is almost identical to that of 2,3′-BF, but the molar absorption coefficients are higher, as expected (ε = 60 500 and 61 800 L mol^{-1} cm^{-1}). The 3,2′,7′,3″-TF trimer shows a transition at 338 nm (ε = 55 500 L mol^{-1} cm^{-1}) that is similar and slightly red-shifted compared with the 2,2′-dimer band at 332 nm and a lower intensity transition at 285 nm that is very similar in shape to the higher energy band of the 2,3′-BF. Compared with the 3,2′,7′,3″-TF trimer, the 2,3′,6′,2″-TF trimer shows a blue-shifted main absorption at 320 nm.

Compared with 2,2′-BF (332 nm) and 2,3′-BF (321, 285 nm), the absorption of 3,3′-BF (310, 262 nm) shows a strong blue shift but weaker transition at 310 nm (ε = 19 700 L mol^{-1} cm^{-1}) and an intense higher energy transition (ε = 80 900 L mol^{-1} cm^{-1}) at 259 nm. In fact, the decreasing intensity of the lower energy absorption of the dimers with increasing 3,6-content is consistent with strongly decreased conjugation.

The oligomers emissions generally follow the same pattern as their absorption spectra (Figure 3b). Thus, the emissions of 2,2′-BF and 3,2′,7′,3″-TF show maxima at 385 (365) nm and 395 (370) nm and shoulders at 405 and 415 nm. The emissions of 2,3′-BF and 2,3′,6′,2″-TF, like their absorptions, are nearly identical with maxima at 365 (351) and 368 (353) nm, respectively. The 3,3′-BF has the most blue-shifted emission at 344 nm with a shoulder at 357 nm. The fluorescence quantum efficiencies decrease strongly with increasing 3,6-content. This may be due, in part, to intersystem crossing as phosphorescence is observed for both 3,3′- and 2,3′-dimers and 2,3′,6′,2″-trimer.[20]

Calculations. The major factors that are known to affect the band gap in conjugated systems without electron-donating or electron-withdrawing groups are (a) the dihedral angles between the consecutive units and/or (b) resonance energy stabilization.[21] In order to probe these effects, the geometries including the "syn" and "anti" conformations of the dimers were optimized with DFT calculations using a B3LYP method with a 6-31G* basis set as shown in Table 3. In order to reduce the computation times, the 9-hexyl groups were substituted by methyl groups. The effect of this substitution is expected to be minor and may slightly increase the torsion angles but should be similar for all oligomers.[16]

The dihedral angles between the successive fluorene units were found to be between 38.0° and 39.4° for "syn" conformations (143° and 140.5° for "anti" conformations) for all types of dimers (Table 3), and the energies of formation of the "syn" and "anti" dimers conformers were found to be

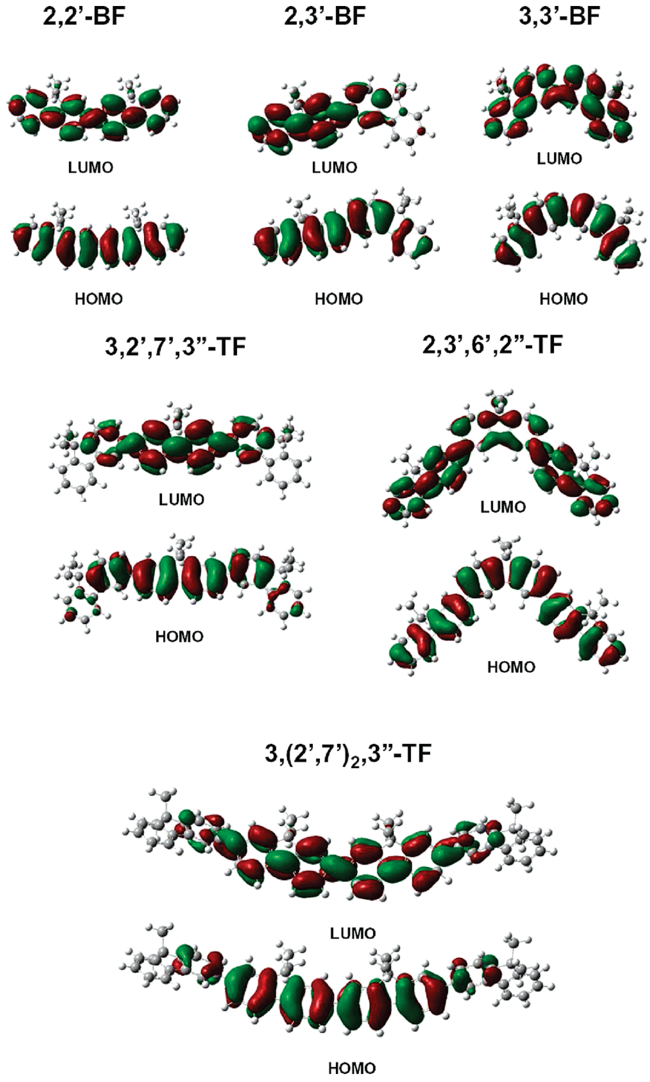


Figure 4. Ground-state HOMO and LUMO orbitals of the model oligomers ("syn"-conformations) obtained by the HF/STO-3G method.

nearly identical.[16] The dihedral angles of the trimers (calculated for "syn−syn" conformations) were close to those of the dimers, indicating that the dihedral angles do not play a major role in the shift of the absorption spectra. Hence, the effects of resonance should be considered in more detail.

The shapes of the HOMO and LUMO orbitals of the model oligomers were obtained from Hartree−Fock calculations. Density functional theory calculations (DFT (B3LYP/6-31G*)) were also employed to derive the occupied orbitals giving very similar results. For the LUMOs a minimal basis, STO-3G, was used. However, the shapes of both the HOMO and LUMO orbitals looked very similar when using the larger 6-31G* basis set. As shown in Figure 4, in 2,2′-BF the electron density is delocalized through four benzene rings, while in 2,3′-BF it is distributed mainly between 2-fluorene unit and one benzene ring of the 3-fluorene unit. This is consistent with shorter conjugation length and the observed absorption and emission blue shifts. In the 3,3′-dimer the conjugation is interrupted at the C1 and C4 atoms in the middle benzene rings, accounting for an even greater blue shift. These results are also consistent with the experimental values of absorption coefficients (Table 3) increasing from 3,3′-BF through 2,3′-BF to 2,2′-BF. In 3,2′,7′,3″-TF the electron density is located predominantly on the central fluorene unit and the inner benzene rings of the 3,6-fluorene fragments. The shape of HOMO and LUMO of 2,3′,6′,2″-TF is similar to that of 3,3′-BF with conjugation being interrupted on the C1 and C4 atoms of the central 3,6-fluorene unit. This should result in a blue shift of absorption and emission compared to the 3,2′,7′,3″-trimer. The above observations are consistent with previously observed interruption in the degree of delocalization by the meta-linkages in phenylenevinylene oligomers.[22,23]

The excited-state energies and absorption maxima of the oligomers were calculated using the ZINDO[24] method. This method has been successfully used to account for the optical properties of conjugated polyphenylenevinylene-type systems.[25−27] The ZINDO orbitals were visually identical to those obtained by Hartree−Fock calculations. The progressive red shifts in the 3,3′-BF < 2,3′-BF < 3,2,3′,6′,2″-TF < 2,2′-BF < 3,2′,7′,3″-TF series appear to correlate with electron density being delocalized over a larger number of benzene rings. The calculated and the experimental values of the absorption maxima of the oligomers are in very good agreement (Table 3).

Discussion

The spectra of the model oligomers show interesting correlations with that of the copolymers (Figures 1 and 4). For instance, the 36PDHF shows absorption and emission bands (262, 325 nm) that look similar to those of 3,3′-BF (259, 310 nm). Both show high absorption coefficient transitions at around 260 nm, indicating that this transition originates from a 3,6-sequence. The emission maxima and quantum efficiencies of the 3,3′-dimer and 36PDHF are also similar. The 3,6-trimer was also synthesized and showed lower energy absorption maximum at 317 nm,[20] which suggests a 36PDHF conjugation length of at least four fluorene units.

The absorption of 27*co*36(67) at 267 nm looks similar to that of the 3,3′-dimer at 262 nm, and both have high absorption coefficients and thus appear to originate from the 3,6-sequence. However, the transition of the 27*co*36(67) copolymer at 333 nm is close to that of the 3,2′,7′,3″-TF (338 nm). The copolymer also has a shoulder at about 285 nm that appears to correspond to that of the 3,2′,7′,3″-TF. The emissions of the 3,2′,7′,3″-TF and the 27*co*36(67) copolymer are also remarkably similar to two main emission bands at 372/391 and 374/394 nm, respectively. Thus, the 3,2′,7′,3″-trimer appears to represent the lowest energy segment of the 27*co*36(67) copolymer, suggesting a conjugation length of three units. Significantly, the emission from 3,6-sequences in this copolymer is not observed, consistent with energy transfer from the higher energy sequences to the lower energy 3,2′,7′,3″-triad.

The absorption bands of the 27*co*36(50) copolymer resemble those of the 27*co*36(67), also suggesting a conjugation length of about three fluorene units, but lack the 267 nm absorption corresponding to the 3,6-sequence that is missing in this strictly alternating copolymer. With increasing 3,6-content absorptivities in the 250−325 nm region increase, including a shoulder at 285 nm that is also observed in the 3,2′,7′,3″-TF and the 2,3′-BF and hence may be attributable to 2,3′ polymer dyads. However, the emission of the 27*co*36(50) copolymer is complex with bands at 395 nm and a distinct shoulder at 415 nm. The 395 nm band is also seen in the 3,2′,7′,3″-TF, but a band at 374 nm is lacking in the copolymer, indicating that this emission may have a different origin and is probably not due to the 3,2′,7′,3″-triad. Like the copolymers with a higher 2,7-content, its emission extends well into the visible spectrum with pronounced shoulders at 415 and 432 nm that may be due in part to longer 3,6−2,7 sequences for which we do not have absorption evidence. This may be due to longer conjugation lengths in the excited state. In all of these cases the absorption maxima of the oligomers correspond very well (within 1−4 nm) with the calculated values using the ZINDO method, thus providing solid support for the assignments (Table 3). The presence of the $3,2',7',3''$-triads in both 27*co*36(50) and 27*co*36(67) copolymers may account for the similarity in their film emissions (Figure 3). Thus, energy transfer to these lower energy sequences may occur more effectively in the solid state.

Comparison with the published data on the absorption and emission maxima of the 2,7-fluorene oligomers[18] shows that the absorption/emission spectra of the 27*co*36 copolymers cannot be simply correlated with the 2,7-fluorene oligomers of the same average lengths. Thus, for the 27*co*36(33) copolymer the most probable 2,7-sequence should correspond to a dyad. However, the absorption maximum of the copolymer is significantly red-shifted compared to the 2,7-dimer (354 nm vs 327 nm[18]). The same holds for the 27*co*36(20) and the corresponding 2,7-tetramer (378 nm vs 358 nm[18]). The 27*co*36(33) copolymer, having 3,6-units occurring singly, shows a very broad absorption at 354 nm with an additional band at about 380 nm. The 354 nm band is red-shifted by 20 nm compared to the $2,3',6',2''$-TF that does seem to be a good model for this copolymer. A better model could be the $3,(2',7')_n,3''$-tetramer containing two 2,7-units flanked on each side by 3,6-units that was not synthesized (Figure 4). Using ZINDO calculations for the $3,(2',7')_2 3''$-TF gives a predicted maximum at 354 nm that agrees very well with that of the 27*co*36(33) copolymer (Table 2). The HF/STO-3G method for this oligomer predicts that the electron density is delocalized predominantly on the two central 2,7-units and on the inner benzene rings of the 3,6-fluorenes (Figure 4). Thus, the corresponding $3,(2',7')_2 3''$-tetrad appears to represent the lowest energy chromophore for this copolymer.[4,5,18] The 27*co*36(20) copolymer, likewise, has a 24 nm red-shifted and also very broad absorption with a maximum at 378 nm, indicating the presence of a sequence(s) denoted as $3,(2',7')_n,3''$ where $n \geq 3$. This absorption corresponds closely with the 27*co*36(33) copolymer shoulder at 380 nm, the origin of which may represent a particular longer $3,(2',7')_n,3$ sequence. It is interesting that there is no continuous wavelength shift as the 2,7-sequence length increases, but the persistence of the 380 nm absorption is intriguing.

The emissions of copolymers having less than 50 mol % 3,6-content show slight red shifts as 2,7-contents increase (Table 2), consistent with the presence of $3,(2',7')_n,3''$ sequences and energy transfer to these lower energy chromophores from the shorter sequences. Compared with the 27*co*36(33) and 27*co*36(20) copolymers, the absorption maximum of the 27*co*36(5) copolymer (392 nm) is red-shifted about 12 nm and is virtually identical to that of 27PDHF (394 nm), suggesting similar conjugation length of about 12 units.[17,18]

The linear absorption coefficients of the oligomers and (co)polymers are virtually identical (when both calculated per fluorene unit), for instance, for 36PDHF and 3,3′-BF as well as 2,2′-BF and 27PDHF. However, in other cases, for example the 27*co*36(50) and especially the 27*co*36(5) copolymers, both the linear and integrated absorptivities are remarkably high. The reason for this behavior is unclear at present.

Conclusions

Novel 27,36-fluorene copolymers and the matching dimers and trimers were synthesized. The introduction of 3,6-fluorene units leads to the copolymers with shorter conjugation lengths (3−4 units for 33−67 mol % 3,6-content). A new band structure is formed involving both 2,7- and 3,6-fluorene units, as shown by absorption and emission spectroscopy and supported by HF/STO-3G and ZINDO calculations. In most cases the spectra of the model mixed 27,36-fluorene oligomers correlate well with the corresponding copolymers.

Acknowledgment. HRMS analyses were carried out by the Department of Chemistry at the University of Arizona, Tucson. We acknowledge support by the Loker Hydrocarbon Research Institute. We also thank Prof. Mark Thompson and Dr. Peter Djurovich for the use of the absolute quantum yield measurement system and Prof. Anna Krylov and Dr. Vadim Mozhayskiy for their help with calculations of HOMO and LUMO orbitals.

Supporting Information Available: Synthesis of 3-bromo-9,9-dihexylfluorene, ^{1}H and ^{13}C spectra of compounds **1** and **4**, the model oligomers, 36PDHF, and 27*co*36(50), thin film emission spectra of the homo- and copolymers, and emission spectrum of 36PDHF in PMMA matrix. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Jacob, J.; Zhang, J.; Grimsdale, A. C.; Mullen, K.; Gaal, M.; List, E. J. W. *Macromolecules* **2003**, *36*, 8240–8245. (b) Cho, H. J.; Jung, B. J.; Cho, N. S.; Lee, J.; Shim, H. K. *Macromolecules* **2003**, *36*, 6704–6710. (c) Beauprè, S.; Leclerc, M. *Adv. Funct. Mater.* **2002**, *12*, 192–196. (d) Shu, C. F.; Dodda, R.; Wu, F. I.; Liu, M. S.; Jen, A. K. Y. *Macromolecules* **2003**, *36*, 6698–6703.

(2) (a) Klarner, G.; Davey, M. H.; Chen, W. D.; Miller, R. D. *Adv. Mater.* **1998**, *10*, 993–997. (b) Miteva, T.; Meisel, A.; Knoll, W.; Nothofer, H. G.; Scherf, U.; Muller, D. C.; Meerholz, K.; Yasuda, A.; Neher, D. *Adv. Mater.* **2001**, *13*, 565–570. (c) Kong, X.; Kulkarni, A. P.; Jenekhe, S. A. *Macromolecules* **2003**, *36*, 8992–8999.

(3) (a) Yang, W.; Hou, Q.; Liu, C.; Niu, Y.; Huang, J.; Yang, R.; Cao, Y. *J. Mater. Chem.* **2003**, *13*, 1351–1356. (b) Yang, W.; Huang, J.; Liu, C.; Niu, Y.; Hou, Q.; Yang, R.; Cao, Y. *Polymer* **2004**, *45*, 865–872. (c) Ritchie, J.; Crayston, J.; Markhamb, J. P. J.; Samuel, I. D. W. *J. Mater. Chem.* **2006**, *16*, 1651–1656. (d) Taranekar, P.; Abdulbaki, M.; Krishnamoorti, R.; Phanichphant, S.; Waenkaew, P.; Patton, D.; Fulghum, T.; Advincula, R. *Macromolecules* **2006**, *39*, 3848–3854.

(4) (a) Yang, Y.; Pei, Q. *J. Appl. Phys.* **1997**, *81*, 3294–3298. (b) Gross, M.; Muller, D. D.; Nothofer, H. G.; Scherf, U.; Neher, D.; Brauchle, C.; Meerholz, K. *Nature* (*London*) **2000**, *405*, 661–665. (c) Leclerc, M. *J. Polym. Sci., Polym. Chem.* **2001**, *39*, 2867–2873. (d) Huang, F.; Zhang, Y.; Liu, M. S.; Cheng, Y. J.; Jen, A. K.-Y. *Adv. Funct. Mater.* **2007**, *17*, 3808–3815. (e) Zhou, X. H.; Niu, Y. H.; Huang, F.; Liu, M. S.; Jen, A. K.-Y. *Macromolecules* **2007**, *40*, 3015–3020.

(5) (a) Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T.; Ashenhyrst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099–1103. (b) Zhao, X.; Pinto, M. R.; Hardison, L. M.; Mwaura, J.; Muller, J.; Jiang, H.; Witker, D.; Kleiman, V. D.; Reynolds, J. R.; Schanze, K. S. *Macromolecules* **2006**, *39*, 6355–6366. (c) Xia, C.; Advincula, R. *Macromolecules* **2001**, *34*, 5854–5859. (d) Copenhafer, J.; Walters, R. W.; Meyer, T. Y. *Macromolecules* **2008**, *41*, 31–35. (e) Zeng, G.; Yu, W.-L.; Chua, S.-J.; Huang, W. *Macromolecules* **2002**, *35*, 6907–6914.

(6) (a) Charas, A.; Morgado, J.; Martinho, J. M. G.; Alcacer, L.; Lim, S. F.; Friend, R. H.; Cacialli, F. *Polymer* **2003**, *44*, 1843–1850. (b) Charas, A.; Morgado, J.; Martinho, J. M. G.; Alcacer, L.; Cacialli, F. *Synth. Met.* **2003**, *135*, 387–388. (c) Lim, S.-F.; Friend, R. H.; Rees, I. D.; Li, J.; Ma, Y.; Robinson, K.; Holmes, A. B.; Hennebicq, E.; Beljonne, D.; Cacialli, F. *Adv. Funct. Mater.* **2005**, *15*, 981–988. (d) Morgado, J.; Charas, A.; Martinho, J. M. G.; Alcacer, L. *Synth. Met.* **2005**, *154*, 81–84.

(7) (a) Pei, Q. B.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416–7417. (b) Schefr, U.; List, I. G. *Adv. Mater.* **2002**, *14*, 477–487. (c) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1366. (d) Klaerner, G.; Lee, J. I.; Davey, M. H.; Miller, R. D. *Adv. Mater.* **1999**, *11*, 115–119. (e) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686–7691.

(8) Mo, Y.; Jiang, X.; Cao, D. *Org. Lett.* **2007**, *9*, 4371–4373.

(9) Fomina, N.; Hogen-Esch, T. E. *Macromolecules* **2008**, *41*, 3765–3768.

(10) Liu, B.; Yu, W.-L.; Lai, Y.-H.; Huang, W. *Macromolecules* **2002**, *35*, 4975–4982.

(11) Sainova, D.; Miteva, T.; Nothofer, H. G.; Scherf, U.; Glowacki, I.; Fujikawa, H.; Neher, D. *Appl. Phys. Lett.* **2000**, *76*, 1810–1812.

(12) Wang, E.; Li, C.; Mo, Y.; Zhang, Y.; Ma, G.; Shi, W.; Peng, J.; Yang, W.; Cao, Y. *J. Mater. Chem.* **2006**, *16*, 4133–4140.

(13) Yamamoto, T. *Prog. Polym. Sci.* **1992**, *17*, 1153–1205.

(14) Grell, M.; Bradley, D. D. C.; Long, X.; Chamberlain, T.; Inbasekaran, M.; Woo, E. P.; Soliman, M. *Acta Polym.* **1998**, *49*, 439–444.

(15) Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798–802.

(16) Ling, J.; Fomina, N.; Rasul, G.; Hogen-Esch, T. E. *J. Phys. Chem. B* **2008**, *112*, 10116–10122.

(17) Klaerner, G.; Mullen, R. D. *Macromolecules* **1998**, *31*, 2007–2009.

(18) Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. Y. *Chem.—Eur. J.* **2004**, *10*, 2681–2688.

(19) (a) Liu, B.; Yu, W.-L.; Lai, Y.-H.; Huang, W. *Chem. Mater.* **2001**, *13*, 1984–1991. (b) Cho, N. S.; Hwang, D.-H.; Lee, J.-I.; Jung, B.-J.; Shim, H.-K. *Macromolecules* **2002**, *35*, 1224–1228.

(20) Fomina, N.; Hogen-Esch, T. E. unpublished data.

(21) Martin, R.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350–1377.

(22) Pascal, L.; Vanden Eynde, J. J.; Van Haverbeke, Y.; Dubois, P.; Michel, A.; Rant, U.; Zojer, E.; Leising, G.; Van Dorn, L. O.; Gruhn, N. E.; Cornil, J.; Bredas, J. L. *J. Phys. Chem. B* **2002**, *106*, 6442–6450.

(23) Pogantsch, A.; Kai Mahler, A.; Hayn, G.; Saf, R.; Stelzer, F.; List, E. J. W.; Bredas, J. L.; Zojer, E. *Chem. Phys.* **2004**, *297*, 143–151.

(24) (a) Zojer, E.; Buchacher, P.; Wudl, P.; Cornil, J.; Calbert, J.; Bredas, J.; Leising, G. *J. Chem. Phys.* **2000**, *113*, 10002–10012. (b) Jespersen, K. G.; Beenken, W. J. D.; Zaushitsyn, Y.; Yartsev, A.; Andersson, M.; Pullerits, T.; Sundstrom, V. *J. Chem. Phys.* **2004**, *121*, 12613–12617.

(25) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589–599.

(26) Cornil, J.; Beljonne, D.; Bredas, J. *J. Chem. Phys.* **1995**, *103*, 842–849.

(27) dos Santos, D.; Beljonne, D.; Cornil, J.; Bredas, J. *Chem. Phys.* **1998**, *227*, 1–10.