# Poly(indenofluorene) (PIF), a Novel Low Band Gap Polyhydrocarbon

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ABSTRACT: This communication describes the synthesis of a novel low band gap hydrocarbon polymer, poly(indenofluorene), PIF, composed of 3,9-di-*tert*-butylindeno[1,2-*b*]fluorene building blocks. The polymer, with high degrees of polymerization (DP > 20), was generated by coupling alkylated 6,6,12,12-tetrachloro-6,12-dihydroindeno[1,2-*b*]fluorene monomers by means of low-valent transition metal [e.g. chromium(0) and nickel(0)] compounds as dehalogenating agents. The cross-conjugated coupling product exhibits a widely red shifted longest wavelength absorption maximum ($\lambda_{max}$ of up to 799 nm). This fact can be interpreted as resulting from the contribution of quinoid states to the electronic ground state. Oligomeric products possessing similar structures were also generated by dehydrohalogenation polymerization, starting from the corresponding 6,12-dihalo-6,12-dihydroindeno[1,2-*b*]fluorenes.

## 1. Introduction

Polymeric chromophores possessing longest wavelength absorption maxima in the near infrared (NIR) region are rare.[1] The most prominent example concerns poly(isothianaphthalene), PITN, which was first synthesized by Wudl et al.[2] PITN and corresponding derivatives show $\lambda_{max}$ values near 1000 nm (band gap energy $E_g$ ca. 1.2 eV). Their $\pi$-topology, namely the tendency to form a benzenoid ring with reference to the annelated 1,2-phenylene subunit, enforces a significant contribution of quinoid states to the electronic ground state and effects the *low* band gap character (Scheme 1).

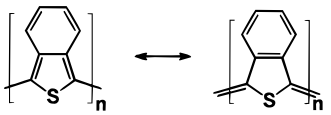
Poly(*p*-phenylenevinylene), PPV, and its substitution products represent one of the most intensively investigated classes of *high* band gap conjugated polymers ($E_g$: 2.2−2.8 eV). A PPV derivative which is diarylated at the vinylene subunit, poly(1,4-phenylene-1,2-diphenylvinylene) (**1**), was first synthesized by Hörhold et al. as a structurally well-defined, yellow, strongly fluorescent, and soluble material, possessing number average molecular weights of up to 20 000.[3]

If two additonal aryl−aryl bonds per repeating unit are introduced into the structural framework of **1** (Scheme 2), a new, until now unknown, polymer, poly(indenofluorene) (PIF) **4**, results, in which planar indeno[1,2-*b*]fluorene sub-units as cyclic building blocks are fitted together at their 6- and 12-positions.

The expected geometry of this novel polymer **4** is a nonplanar one, since there is a strong steric hindrance at the inter-ring linking positions. For related model systems, e.g. 9,9′-bifluorenylidenes, two possible conformations are known: (i) one with a mutual distortion of the fluorenylidene building blocks relative to the olefinic double bonds and (ii) another possessing a geometric distortion within the fluorenylidene subunits under formation of a "butterfly"-like conformation. The literature describes 9,9′-bifluorenylidenes, in which these two alternative variants can be realized with one and the same molecule by way of conformational isomers.[4]

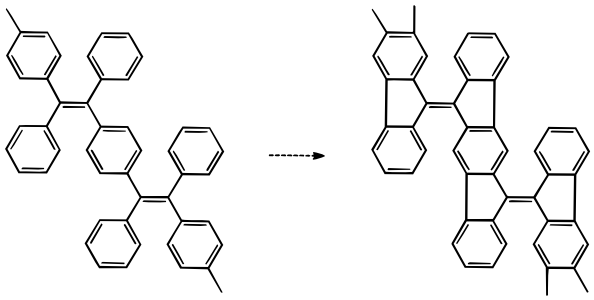
In the case of the polymeric $\pi$-system poly(indeno[1,2-*b*]fluorene) (PIF) **4**, a contribution of quinoid states

**Scheme 1**



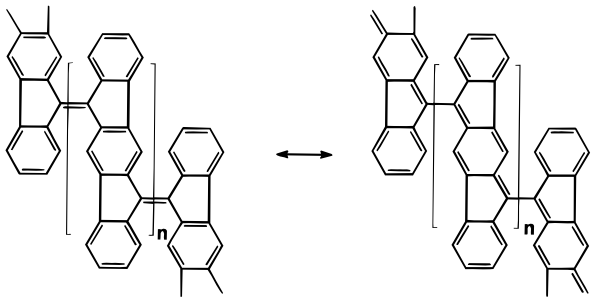

PITN

**Scheme 2**



**1** **4**

**Scheme 3**




to the electronic ground state is possible (Scheme 3). Such a contribution is expected to reduce the band gap energy $E_g$. In additon, the character of the inter-ring bond changes. An increasing single bond character with increasing participation of quinoid states would elongate the distance between the cyclic building blocks as well as favor their mutual distortion.

Within this paper, we will present the synthesis and characterization of poly(indeno[1,2-*b*]fluorene) (PIF) as novel low band gap polyhydrocarbon. To obtain deeper insight into the electronic structure of PIF **4**, we have performed additional calculations of $\pi$-topology and

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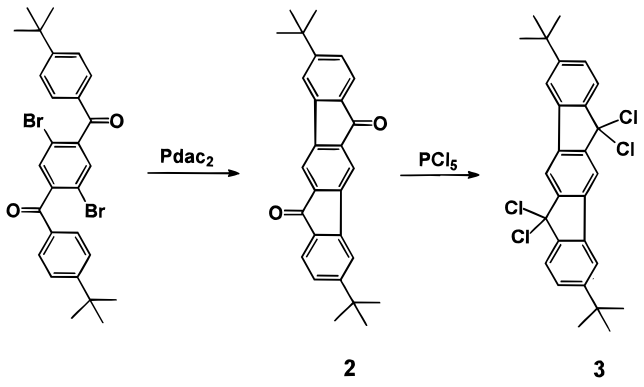
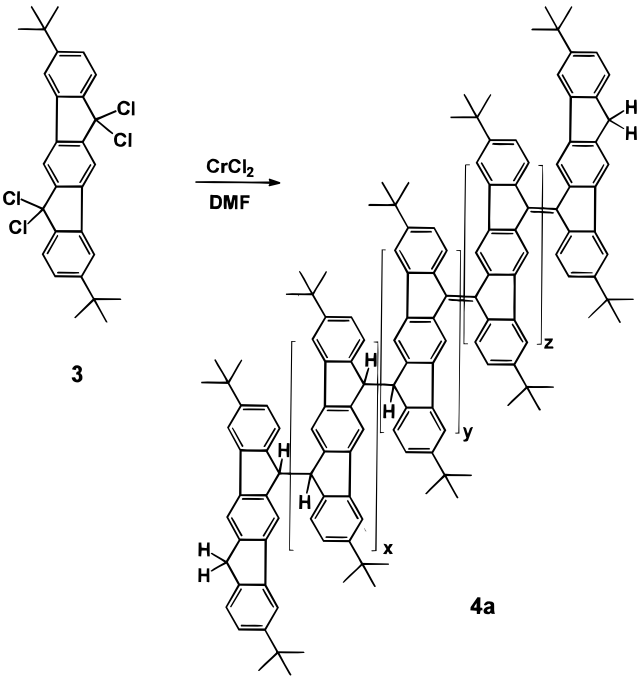
**Scheme 4**




**Scheme 5**

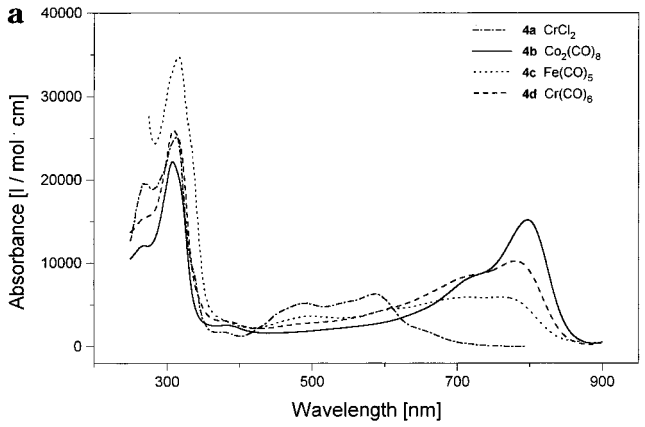



geometry of poly(indeno[1,2-*b*]fluorene) **4**, possessing an infinite chain length.

## 2. Results and Discussion: Synthesis

**2.1. Dehalogenation Polycondensation.** 3,9-Di-*tert*-butyl-6,6,12,12-tetrachloro-6,12-dihydroindeno[1,2-*b*]fluorene (**3**) represents a monomer with the preformed structure of the cyclic buliding blocks of poly(indeno-[1,2-*b*]fluorene) **4**. It can be generated in a two-step synthesis (Scheme 4) starting from 2,5-dibromo-1,4-bis-(4-*tert*-butylbenzoyl)benzene:[5] (i) a twofold intramolecular Pd(0)-catalyzed aryl−aryl coupling (see ref 6) to prepare the diketone **2** in moderate yields (ca. 20−25%), and (ii) the conversion of the diketone **2** into the corresponding "bis-geminal" tetrachloro monomer **3** using phosphorus pentachloride.

3,9-Di-*tert*-butyl-6,6,12,12-tetrachloro-6,12-dihydroindeno[1,2-*b*]fluorene (**3**) was obtained from **2** in high yields (90%) as slightly yellow crystals.[5] Compound **3** is a well suited monomer for a reductive polycondensation to give poly(3,9-di-*tert*-butylindeno[1,2-*b*]fluorene) (**4**). A series of possible dehalogenating coupling methods was listed in the literature.[7,8] Recently, we reported our first experiments by means of chromium(II) salts ($CrCl_2$) (solvent DMF; see ref 5). Hereby, a blue oligomeric reaction product **4a** was obtained (Scheme 5). The



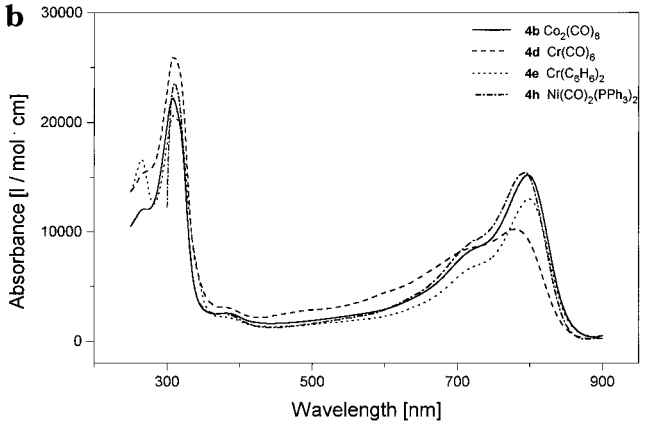




**Figure 1.** (a) UV/vis absorption spectra of the dehalogenation polycondensation products PIF **4a**−**d** (solvent: methylene chloride). (b) UV/vis absorption spectra of the dehalogenation polycondensation products PIF **4b,d,e,h** (solvent: methylene chloride).

oligomers possess a $M_n$ of ca. 2500−4000, corresponding to degrees of polymerization of 6−10 (for $x + y + z$).

The $^1$H-NMR spectra of the completely soluble coupling products exhibit the presence of inter-ring single bonds besides the "regularly" formed olefinic double bonds. The terminal 6- and 12-positions exist as methylene (ar−$CH_2$−ar) groups.

The hydrogen transfer taking place from the solvent (DMF) is somewhat surprising, since other authors did not observe such side reactions during Cr(II)-mediated reductive couplings of noncyclic "bis-geminal" tetrachloro monomers.[8] The hydrogen transfer should be, in our case, strongly related to the steric constraints around the coupling position. The unexpected tendency toward hydrogen transfer determines the length of the chains (via chain termination reactions) as well as the type of inter-ring connection (single or double bond).

The deep color of the oligomeric product **4a** is reflected in its UV/vis spectrum [$\lambda_{max}$: 465 (sh), 489, 560 (sh), 586, 650 (sh) nm]; it represents a superposition of the absorptions of conjugatively linked indenofluorene subunits containing two, three, or more building blocks (see Figure 1a).

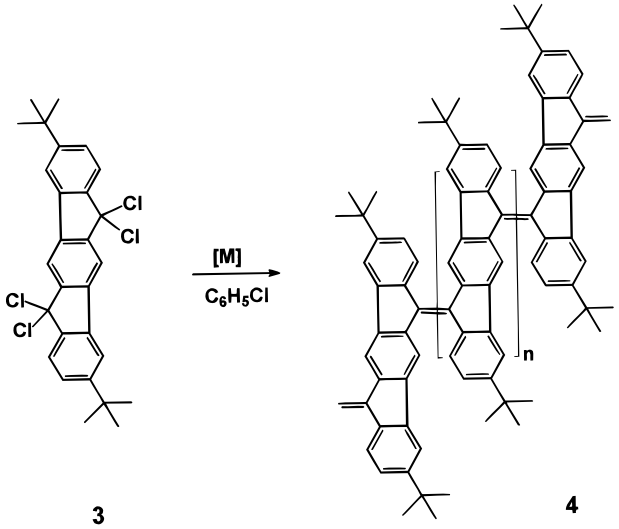
It is understandable that we, however, were not satisfied with our initial results showing low degrees of polymerization and the lack of an extended $\pi$-conjugation.

Therefore, the search for coupling conditions, which effectively suppress the unwanted hydrogen transfer, was an attractive challenge. A very promising alternative is the use of nonpolar, low-valent transition metal

**Table 1. Dehalogenation Polycondensation of the Tetrachloro Monomer 3 to Poly(indenofluorene) PIF 4 with Various Coupling Agents**

| product | coupling agent | yield (%) | $M_n$ (GPC) [$M_n$ (VPO)] | $M_w$ (GPC) [$M_w/M_n$] | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|
| **4b** | $Co_2(CO)_8$ | 93 | 17 000 [8 700] | 40 000 [2.35] | 795 |
| | | 88 | 16 500 [6 400] | 36 000 [2.18] | 790 |
| **4c** | $Fe(CO)_5$ | 97 | 14 500 [6 900] | 32 500 [2.24] | 785 |
| **4d** | $Cr(CO)_6$ | 95 | 12 000 | 28 000 [2.33] | 781 |
| **4e** | $(C_6H_6)_2Cr$ | 90 | 19 500 | 46 000 [2.36] | 799 |
| **4f** | $(C_8H_{12})_2Ni$ | 16 (oligomers) | 3 500 | 15 000 [4.28] | <700 |
| **4g** | $[(C_6H_5)_3P]_3CoCl$ | (no product) | | | |
| **4h** | $[(C_6H_5)_3P]_2Ni(CO)_2$ | 91 | 12 500 | 27 000 [2.16] | 792 |
| **4i** | KO-*t*-$C_4H_9$ | | | | |
| | **5a** as monomer | 75 | 2 400 | 5 300 [2.21] | 762 |
| | **5b** as monomer | 80 | 2 200 | 4 900 [2.23] | 763 |

**Scheme 6**




**3** **4**

complexes as reducing agents (iron, chromium, or cobalt carbonyls; the nickel/bis(cyclooctadiene) or the chromium/bis(benzene) complex; the nickel(0) dicarbonyl/bis(triphenylphosphane) and the cobalt(I)chloride/tris(triphenylphosphane) complex). Using these reagents, the condensation can be performed in nonpolar aromatic solvents like benzene, chlorobenzene, and 1,2-dichlorobenzene, which should be generally inert against H transfer.

Table 1 gives the yields, molecular weights, and longest wavelength absorption maxima of the condensation products **4b**−**4h**.

We obtained the best results with dicobalt octacarbonyl (**4b**), chromium hexacarbonyl (**4d**), the chromium/bis(benzene) (**4e**), and the nickel dicarbonyl/bis(triphenylphosphane) complex (**4h**) as dechlorinating metallorganic reagents (Scheme 6). The condensation is generally accompanied by a color change. The monomer solutions are of pale yellow color, the polymer solutions are deep bluish-black. This color can be overlayed by those of the transition metal species. In the case of transition metal carbonyls as coupling agents, condensation is accompanied by a strong foaming of the mixture. The use of the Ni/COD complex (**4f**) and the cobalt(I) chloride/tris(triphenylphosphane) complex (**4g**) as dehalogenating agents does not lead to polymeric products; only oligomers of short chain length are formed. In the case of $Ni(COD)_2$, the allylic hydrogens of the cyclooctadiene ligand should act as a source for hydrogen transfer, thus limiting the molecular weight of the products.

Simple precipitation into ethanol or methanol, followed by reprecipitation from methylene chloride into acetone gave the desired products **4b**−**e** and **4h** as deep blue powders in high yields (88−97%). Remaining transition metal traces were removed using column chromatography on aluminum oxide. Gel permeation chromatography gives unexpectedly high number average molecular weights $M_n$ of up to 20 000, corresponding to degrees of polymerization up to 55. Direct determinations of absolute values of $M_n$ by means of vapor pressure osmometry (VPO) provide lower values (halved) compared to our GPC measurements (1,2-dichlorobenzene, polystyrene calibration). The doubled molecular weights $M_n$ of the size exclusion chromatographic measurements should be the result of the rigid structure of **4**. Therefore, all GPC data ($M_n$) are to be divided by 2.

The novel, completely soluble polymer PIF **4** forms intensely blue solutions in halogenated hydrocarbons like methylene chloride, chloroform, or tetrachloroethane and in aromatic solvents.

The $^1$H-NMR spectrum of **4b**, **4d**, **4e**, and **4h** provides no evidence for any methylene or methyne groups, resulting from hydrogen transfer under formation of $-CH_2-$ end groups or $>CH-CH<$ inter-ring single bonds. The spectra display four broad signals of aromatic/olefinic hydrogens (**4b**: $\delta$ = 8.88, 8.53, 7.75, 7.34/7.32) and one of the *tert*-butyl groups (18H; $\delta$ = 1.3−1.5). The coupling product **4c** [$Fe(CO)_5$ as dehalogenating agent] displays an additonal signal at $\delta$ = ca. 6.5, which is assigned to the presence of chloro-substituted aromatic rings, formed in a chlorinating side reaction, effected by iron(III)chloride as the byproduct of reductive dehalogenation (see below).

The $^{13}$C-NMR spectrum of poly(3,9-di-*tert*-butylindeno[1,2-*b*]fluorene) (**4b**) consists of one signal block in the aromatic/olefinic region, accompanied by the two signals of the *tert*-butyl side groups [$\delta$ = 35.2 ($-\mathbf{C}(CH_3)_3$), 31.3 ($-C(\mathbf{C}H_3)_3$)]. The aromatic/olefinic region of the spectrum exhibits ten signals of the ten nonequivalent aromatic/olefinic carbon atoms of **4** ($\delta$ = 153.3 [$>\mathbf{C_{ar}}-C(CH_3)_3$], 141.5, 140.4, 139.6, 136.5, 126.9, 124.7, 123.5, 118.8, 117.1). Four signals of weak intensity ($\delta$ = 130.3, 129.1, 127.8, 125.8) are assigned to end groups. There were no signals observed in the region between $\delta$ = 115 and 35, within the detection limit of the method, which could originate from aliphatic carbons. No inter-ring single bonds are, therefore, present in **4b**,**d**,**e**,**h**.

By EPR spectroscopy, no paramagnetic species (iron or cobalt compounds, carbon radicals) are detectable within the detection limit of the method. The elemental analysis of the products **4** are in good agreement with the claimed structure, only small amounts of chlorine are detectable (**4b** 0.37%, **4d**,**e**,**h** 1.2−3.3%), with the exception of **4c** synthesized with iron pentacarbonyl as dechlorinating agent. This polymer contains a surpris-

ingly high amount of chlorine (11.4%), corresponding to more than one chlorine atom per repeating unit. Iron(III) chloride formed during the reductive dehalogenation, should act as a Lewis acid in an electrophilic chlorination of aromatic nuclei. The formation of $>C_{ar}-Cl$ substructures is illustrated by comparing the FTIR spectra of the polymer obtained after coupling with cobalt or chromium carbonyls and the product formed with iron pentacarbonyl. The spectrum of the latter contains two additional intense signals in the region between 650 and 800 $cm^{-1}$ (668, 791 $cm^{-1}$) to be ascribed to the $C_{ar}-Cl$ bond.

The characterization data favor dicobalt octacarbonyl as the most effective dehalogenation agent (high molecular weight; low chlorine content; NMR, no structural defects detactable).

The UV/vis spectra of **4b,d,e,h** (see Figure 1a/b) show the occurrence of the conjugated one-dimensional $\pi$-system, clearly indicated by the sharp absorption edge and the 0−0 transition ($\lambda_{max}$: 781−799 nm) as the most intense absorption band, escorted by one shoulder at ca. 710 nm.

In the cases where high molecular weight, well-defined products are formed (**4b**,**d**,**e**,**h**), the absorption spectra are nearly independent of the coupling agent used within the dehalogenation polycondensations.

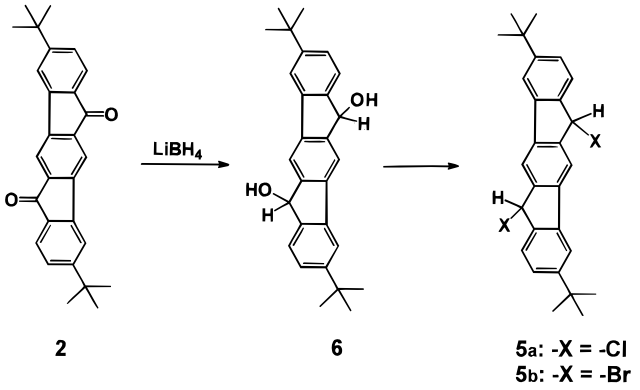
Particularly noteworthy is the position of the longest wavelength absorption band, widely red shifted into the NIR region. Compared to polyacetylene[9] and polydiacetylenes,[10] as other typical hydrocarbon polymers with low band gap energies, the $\lambda_{max}$ of PIF **4** is red shifted by more than 100 nm. Conjugated, but insoluble, polyhydrocarbons possessing a ribbon structure, as described by Schlüter and co-workers, exhibit $\lambda_{max}$ values betweeen 500 and 600 nm.[11] Only the hitherto unknown polyarylene poly(*peri*-naphthalene) is predicted to show a comparably low HOMO/LUMO energy difference (band gap energy) as extrapolated by Koch and Müllen in model studies (pentarylene: $\lambda_{max}$ 745 nm).[12] To our knowledge, **4** is the polyhydrocarbon possessing the lowest band gap energy known and characterized as a structurally defined neutral macromolecule.

Poly(3,9-di-*tert*-butylindeno[1,2-*b*]fluorene) (**4**) is characterized by an unexpectedly high chemical stability, especially when considering other conjugated polyhydrocarbons with comparably low band gap energies (polyacetylenes, polydiacetylenes). PIF is stable against atmospheric influences like air, moisture, and daylight. The UV/vis spectra remain nearly unchanged over time periods of several months.

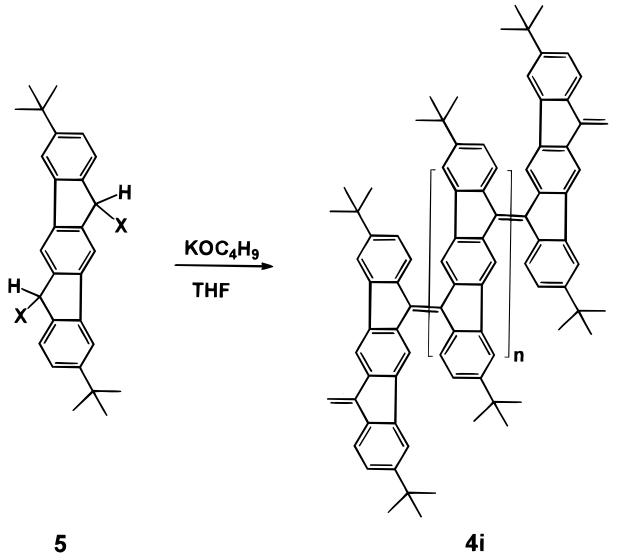
**2.2. Dehydrohalogenation Polymerization.** Parallel to our dehalogenation polycondensations in the synthesis of polymer **4**, we have performed additional experiments to generate **4** via a dehydrohalogenation polymerization, following a procedure described for several PPV derivatives (base-induced dehydrohalogenation using KO-*t*-$C_4H_9$ in THF).[13]

We have, therefore, synthesized the corresponding dichloro and dibromo monomers **5a** and **5b** in a two-step synthesis starting from the diketone **2** (Scheme 7). The polymerization of **5** (with KO-*t*-$C_4H_9$ in THF) gives, in spite of the strong steric hindrance at the coupling positions, the desired product **4i** (Scheme 8; see Table 1). **4i** possesses a similar structure (NMR, UV/vis absorption) when compared with the corresponding dehalogenation condensation products **4b,d,e,h**. However, the molecular weights are low ($M_n$ < 3000) when

**Scheme 7**




**Scheme 8**




compared to those of the dehalogenation polymers **4b,d,e,h.** The $^1$H-NMR spectrum of **4i** displays the four broad aromatic/olefinic signals of PIF ($\delta$ = 8.76, 8.41/8.31, 7.64/7.55, 7.29) which were also observed for the dehalogenation products **4b,d,e,h**. In addition, the spectra exhibit low-intensity signals at $\delta$ = 8.76, 8.55, 8.19, 7.99, 7.74, 7.42, and 6.88/6.71 that should be assigned to end groups (oligomeric nature of the products) and defects. These findings are reflected in the UV/vis spectra of **4i**, which display a slightly hypsochromically shifted longest wavelength absorption maximum ($\Delta\lambda_{max}$: ca. 40 nm) centered at ca. 750 nm (see Figure 2). This hypsochromic shift is accompanied by a broadening of the absorption edge, thus indicating that the convergence limit of the optical properties is not yet reached in the oligomeric dehydrohalogenation products **4i**.

## 3. Band Gap and Geometry Calculations

For our calculations, polymer **4** was regarded as an infinite 1D system for which the Born−Karman conditions are fulfilled. In order to estimate the bond length alternation (Peierls distortion)[14] of the polymer, a generalized Su−Schrieffer−Heeger (SSH) model was used.[15] This approach (the SSH−PPP model) incorporates a linear electron−lattice coupling, a harmonic bond-strain potential,[16] and a $\pi-\pi$ electron-electron interaction, corresponding to the the Pariser−Parr−Pople (PPP) approximation.[17]

The calculations were carried out with the following parametrization:[15] $\beta$ = −2.4 eV (resonance integral); *a*

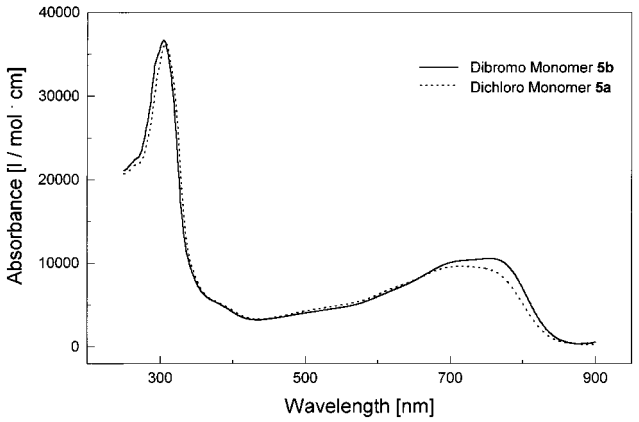



**Figure 2.** UV/vis absorption spectra of the dehydrohalogenation polymerization products PIF **4i** (solvent: methylene chloride).

**Chart 1**

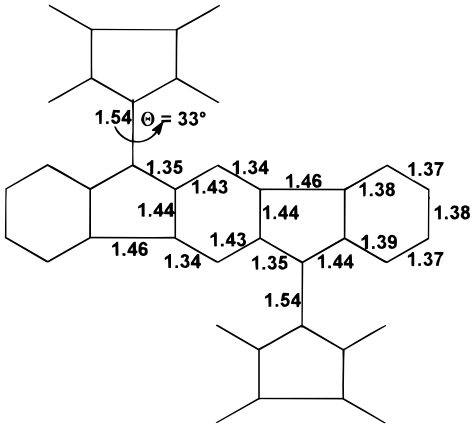
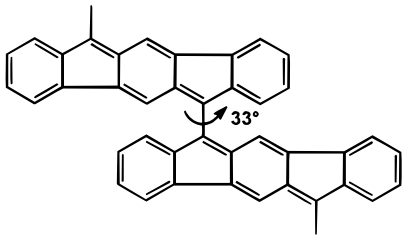



**Chart 2**




= 3.21 eV/A (electron−lattice coupling constant); $K$ = 24.6 eV/A$^2$ (spring constant).

The two-electron Coulomb integrals were calculated by means of the Mataga−Nishimoto approximations.[18] The dihedral angle $\theta$ (see Chart 1) was estimated by means of a quantum-chemical AM1 method based on a cluster containing three indenofluorene building blocks[19] (SPARTAN Program System[20]).

The calculated equilibrium geometry (Chart 1; bond lengths in Å) corresponds to a valence formula given in Chart 2.

As shown in ref 21, the energy gap ($E_g$) of a $\pi$-conjugated system possessing a singlet ground state is given by the expression

$$E_g^{\,2} = (D_{top} + D_{geom} + D_{1,corr})^2 + D_{2,corr}^{\,2} \qquad (1)$$

($D_{top} + D_{geom}$ is the energy gap calculated in a one-electron approximation).

The topological ($D_{top}$) and geometrical ($D_{geom}$) contributions to the energy gap have been calculated using a Hückel−Hubbard version of the Bloch method[22] (see also ref 23). For the calculation of the geometrical factor ($D_{geom}$) the Mulliken formula[24] was used with the following dependence of the resonance integrals on the bond length R:

$$\beta(R) = \beta(R_0)\, S(R)/S(R_0) \cos \Theta$$

($R_0 = 1.40$ Å; $S$ are the overlap integrals calculated with $Z_C = 3.25$).

The correlation corrections $D_{1,corr}$ and $D_{2,corr}$ have been calculated using standard values of the resonance integral and the one-center Coulomb integral.[23]

Table 2 gives the calculated components for the $E_g$ of polymer **4**. The minor difference between the calculated and measured $E_g$'s ($E_{g,calc} - E_{g,exp}$: ca. 0.2 eV) should be the result of the finite chain length of the real polymeric systems (influence of end groups). This point, as well as the introduction of the solubilizing *tert*-butyl groups, was neglected in our calculations (based on infinite 1D systems for which the Born−Karman conditions are fulfilled).

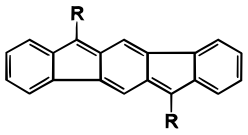
**Table 2. Energy Gap Components (in eV) for the Energy Gap $E_g$ of 4, Calculated by Means of Eq 1**

| $D_{top} + D_{geom}$ | $D_{1,corr}$ | $D_{2,corr}$ | $E_{g,calc}$[a] |
|---|---|---|---|
| 0.62 | 0.43 | 1.36 | 1.72 |

[a] $E_g$,exp: 1.55 eV ($\lambda_{max}$: 799 nm, PIF **4e**).

As a result of our calculations and the experimental optical energy gap observed for PIF **4** we conclude that quinoid states dominate the electronic ground state of poly(indenofluorene) **4**, and, therefore, act as the key chromophore.

9,12-Diphenylindeno[1,2-*b*]fluorene (**7**) (R = $-C_6H_5$) as a model compound for the "quinoid subunit" present




**R: -$C_6H_5$ , -H**

**7**

in **4** exhibits a $\lambda_{max}$ of 543 nm (2.28 eV[25]), theoretical calculations (geometry-AM1 method[19]) provide a HOMO/LUMO energy difference of 2.34 eV ($\lambda_{max}$: 530 nm ($f$ = 1.148) for a related model compound, indeno[1,2-*b*]-fluorene **7** (R = −H).

## 4. Conclusions

We have presented the synthesis and characterization of a novel, structurally defined low band gap polyhydrocarbon, poly(3,9-di-*tert*-butylindeno[1,2-*b*]fluorene) (PIF) **4**, with an energy gap $E_g$ of ca. 1.55 eV ($\lambda_{max}$ up to 799 nm).

Now, further experiments are planned to study the photoluminescence of PIF as well as the nonlinear optical characteristics. Conjugated $\pi$-systems possessing widely red shifted absorption maxima, combined with a sharp band edge (no absorptions in the region between 1.0 and 1.8 $\mu$m), are particularly attractive subjects to study third-order NLO effects and for potential applications in optoelectronics. Initial measurements gave a $\chi^{(3)}$ value of $2 \times 10^{-11}$ esu for **4a** (oligomers with interrupted conjugation) and $7 \times 10^{-10}$ esu for the conjugated PIF **4d** (degenerate four wave mixing, DFWM).

## 5. Experimental Part

**Reagents.** The solvents used were commercial p.a. quality. The monomer 3,9-di-*tert*-butyl-6,6,12,12-tetrachloro-6,12-di-

hydroindeno[1,2-*b*]fluorene (**3**) was synthesized according to ref 5. The transition metal agents were used without further purification.

**A typical dehalogenation polycondensation to poly-(3,9-di-*tert*-butylindeno[1,2-*b*]fluorene)s was conducted in the following manner (4b−h).** 3,9-Di-*tert*-butyl-6,6,12,-12-tetrachloro-6,12-dihydroindeno[1,2-*b*]fluorene (**3**) [560 mg (1.13 mmol)] was suspended in 30 mL of chlorobenzene. The resulting suspension was stirred under an argon atmosphere at 90 °C. After it reached this temperature, the coupling agent was added in one portion. The following amounts were used: dicobalt octacarbonyl ($Co_2(CO)_8$) (1.03 g, 3.0 mmol), iron pentacarbonyl ($Fe(CO)_5$) (1.17 g, 6.0 mmol), chromium hexacarbonyl ($Cr(CO)_6$) (1.32 g, 6.0 mmol), bis(benzene)chromium-(0) ($(C_6H_6)_2Cr$) (1.25 g, 6.0 mmol), bis(1,5-cyclooctadiene)nickel-(0) ($(C_8H_{12})_2Ni$) (1.65 g, 6.0 mmol), tris(triphenylphosphane) cobalt(I) chloride ($[(C_6H_5)_3P]_3CoCl$) (5.28 g, 6.0 mmol), and bis-(triphenylphosphane)nickel(0) dicarbonyl ($[(C_6H_5)_3P]_2Ni(CO)_2$) (3.83 g, 6.0 mmol).

With metal carbonyls as dechlorinating agents the mixture strongly foams after 2−4 min, indicating the onset of the reaction. After 20 min, the mixture was poured into 300 mL of methanol, and the precipitate formed was collected by filtration and washed carefully with methanol, water, 2 N hydrochloric acid, and methanol, until the filtrate was colorless. Remaining metal traces were removed using column filtration on thermally activated, neutral aluminum oxide (eluent: methylene chloride).

Yields of polymers **4** (after drying *in vacuo*): **4b**, 376 mg (93%); **4c**, 390 mg (97%); **4d**, 382 mg (95%); **4e**, 362 mg (90%); **4f**, 64 mg (16%); **4h**, 366 mg (91%). Anal. Calc for **4b**, $(C_{28}H_{26})_n$ (362.51)$_n$: C, 92.77; H, 7.23. Found: C, 90.75; H, 6.97; Cl, 0.37.

**4b**: $M_n$: 17 000, $M_w$: 40 000, $M_w/M_n$ 2.35 (GPC, PS calibration); $M_n$ 8700 (vapor pressure osmometry; solvent, toluene; 50 °C); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ = 8.88, 8.53, 7.75, 7.34/7.32, (8H), 1.3−1.5 [−C(C**H**$_3$)$_3$; 18H]; $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ = 153.3 [**C**$_{ar}$−C(CH$_3$)$_3$], 141.5, 140.4, 139.6, 136.5, 126.9, 124.7, 123.5, 118.8, 117.1, 35.1 [**C**(CH$_3$)$_3$], 31.3 [−C(**C**H$_3$)$_3$] (low-intensity signals: (end groups) 130.3, 129.1, 127.8, 125.8).

**4c**: $M_n$ 14 500, $M_w$ 32 500, $M_w/M_n$ 2.27 (GPC, PS calibration); $M_n$ 6900 (vapor pressure osmometry; solvent, toluene, 50 °C); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ = 8.82, 8.43, 7.68, 7.33, 6.64 (8H), 1.3−1.4 [−C(C**H**$_3$)$_3$; 18H]; $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ = 153.2 [**C**$_{ar}$−C(CH$_3$)$_3$], 147.6 (**C**$_{ar}$−Cl), 142.8, 140.4, 139.8, 136.5, 126.3, 124.0, 118.2, 116.0, 35.1[-**C**(CH$_3$)$_3$], 31.2 [−C(**C**H$_3$)$_3$].

**4d**: $M_n$ 12 000, $M_w$ 28 000, $M_w/M_n$ 2.33 (GPC, PS calibration); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ = 8.80, 8.47, 7.67, 7.30 (8H), 1.2−1.5 [−C(C**H**$_3$)$_3$; 18H].

**4e**: $M_n$ 19 500, $M_w$ 46 000; $M_w/M_n$ 2.36 (GPC, PS calibration); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ = 8.87, 8.51, 7.72, 7.37/7.32 (8H), 1.3−1.5 [−C(C**H**$_3$)$_3$; 18H].

**4h**: $M_n$ 12 000, $M_w$ 27 000, $M_w/M_n$ 2.25 (GPC, PS calibration); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ = 8.82, 8.43, 7.65, 7.38, 6.6 (s) (8H), 1.3−1.6 [−C(C**H**$_3$)$_3$; 18H].

**3,9-Di-*tert*-butyl-6,12-dihydroxy-6,12-dihydroindeno-[1,2-*b*]fluorene (6).** To a stirred suspension of 3,9-di-*tert*-butylindeno[1,2-*b*]fluorene-6,12-dione **(2)** (1.00 g, 2.53 mmol) in 40 mL of dry THF was added a 2 M $LiBH_4$ solution in THF (4 mL, 8 mmol) as a single portion.

The reaction mixture was refluxed under argon for 2 h. After cooling to room temperature, the suspension was hydrolyzed with 100 mL of an 1 M aqueous $Na_2SO_3$ solution. The precipitate formed was washed with ethanol. Recrystallization from toluene gave 0.99 g (98%) of the dialcohol **6** as yellow crystals.

$^1$H-NMR (500 MHz, 100 °C; $C_2D_2Cl_4$): $\delta$ = 7.89 (s, 2H), 7.71 (s, 2H), 7.53 (d, 2H), 7.35 (d, 2H), 5.58 (s, 2H, −O**H**), 2.33 (s, 2H), 1.40 (s, 18H). $^{13}$C-NMR (125 MHz, 100 °C, $C_2D_2Cl_4$): $\delta$ = 152.9, 147.7, 143.2, 140.4, 139.9, 129.0, 128.2, 124.6, 116.8, 74.8, 34.9, 31.5. MS (70 eV), *m*/*z*: 398 [M$^+$]. Anal. Calc for $C_{28}H_{30}O_2$ (398.3): C, 84.38; H, 7.59. Found: C, 84.37; H, 7.69.

**3,9-Di-*tert*-butyl-6,12-dichloro-6,12-dihydroindeno[1,2-*b*]fluorene (5a).** 3,9-Di-*tert*-butyl-6,12-dihydroxy-6,12-dihydroindeno[1,2-*b*]fluorene (**6**) (0.44 g, 1.10 mmol) was refluxed with $SOCl_2$ (0.59 g, 5.00 mmol)/20 mL of dry benzene/0.5 mL of dry DMF for 24 h. Then the solvent was evaporated *in vacuo*, and the resulting residue was recyrstallized from toluene to give 0.35 g of 3,9-di-*tert*-butyl-6,12-dichloro-6,12-dihydroindeno[1,2-*b*]fluorene (**5a**) (72%) as yellow crystals.

$^1$H-NMR (500 MHz, 100 °C, $C_2D_2Cl_4$): $\delta$ = 7.92 (s, 2H), 7.73 (s, 2H), 7.55 (d, 2H), 7.39 (d, 2H), 5.92 (s, 2H), 1.41 (s, 18H). $^{13}$C-NMR (125 MHz, 100 °C, $C_2D_2Cl_4$): $\delta$ = 154.8, 147.4, 142.5, 141.9, 140.9, 127.4, 126.1, 119.3, 118.1, 58.2, 36.4, 32.3. MS (70 eV), *m*/*z*: 434 [M$^+$]. Anal. Calc for $C_{28}H_{28}Cl_2$ (434.2): C, 77.23; H, 6.48; C, 16.28. Found: C, 77.02; H, 6.39; Cl, 16.05.

**3,9-Di-*tert*-butyl-6,12-dibromo-6,12-dihydroindeno[1,2-*b*]fluorene (5b).** 3,9-Di-*tert*-butyl-6,12-dihydroxy-6,12-dihydroindeno[1,2-*b*]fluorene **(6)** (1.01 g, 2.15 mmol) was suspended in 20 mL of dry $CHCl_3$. Then bromotrimethylsilane (2.30 g, 15 mmol) was added as a single portion. The reaction mixture was stirred under argon at 50 °C for 48 h. The solvent was removed *in vacuo*, and the resulting residue was recrystallized from toluene to give 1.14 g of 3,9-di-*tert*-butyl-6,12-dibromo-6,12-dihydroindeno[1,2-*b*]fluorene **(5b)** (87%) as yellow crystals.

$^1$H-NMR (500 MHz, 100 °C, $C_2D_2Cl_4$): $\delta$ = 7.91 (s, 2H), 7.72 (s, 2H), 7.55 (d, 2H), 7.38 (d, 2H), 6.03 (s, 2H), 1.40 (s, 18H). $^{13}$C-NMR (125 MHz; 100 °C; $C_2D_2Cl_4$): $\delta$ = 153.5, 146.5, 141.8, 140.6, 139.5, 127.5, 126.7, 118.2, 117.3, 46.3, 33.2, 31.7. MS (70 eV), *m*/*z*: 524 [M$^+$]. Anal. Calc for $C_{28}H_{28}Br_2$ (523.9) C, 64.14; H, 5.38; Br, 30.48. Found: C, 64.66; H, 5.28; Br, 29.96.

**A typical dehydrohalogenation polymerization to poly(3,9-di-*tert*-butylindeno[1,2-*b*]fluorene)s was conducted in the following manner (4i).** To a stirred suspension of 3,9-di-*tert*-butyl-6,12-dibromo-6,12-dihydroindeno[1,2-*b*]fluorene **(5b)** (400 mg, 0.76 mmol) in 15 mL of dry THF was added dropwise a solution of 1.0 g (8.18 mmol) of KO-*t*-$C_4H_9$ in 20 mL of dry THF over a time period of 20 min at 0 °C under argon. The color of the reaction mixture changed to deep blue. The mixture was stirred at room temperature for 24 h. Then two-thirds of the solvent was removed *in vacuo*, and the resulting mixture was poured into 200 mL of methanol. The resulting precipitate was filtered off and carefully washed with water. The product was redissolved in a minimum of $CHCl_3$ and then reprecipitated into methanol. The resulting polymer was dried *in vacuo* to yield 216 mg of **4i** (80%) as a deep blue powder.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.76, 8.41/8.31, 7.64/7.55, 7.29, 1.1−1.4 [−C(C**H**$_3$)$_3$; 18H]; low-intensity signals at 8.76, 8.55, 8.19, 7.99, 7.74, 7.42, 6.88/6.71.

**Measurements.** $^1$H- and $^{13}$C-NMR data were obtained on a Bruker AMX 500 and a VARIAN Gemini 200 spectrometer. The UV/vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer (solutions in methylene chloride). Gel-permeation chromatographic (GPC) analysis utilized PL-gel columns (three columns, 10 $\mu$m gel, pore widths 500, $10^4$, and $10^5$ Å) connected with UV/vis detection. All GPC analyses were performed on solutions of the polymers in 1,2-dichlorobenzene at 70 °C (concentration of the polymer 2 g/L). The calibration was based on polystyrene standards with narrow molecular weight distribution. VPO was carried out on a solution of **4** in toluene at 50 °C.

The mass spectra were recorded on a Finnigan TRIO 2000 (EI) and a ZAB2-SE-FPD (FD) mass spectrometer.

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## References and Notes

(1) Müllen, K.; Scherf, U. *Makromol. Chem., Macromol. Symp.* **1993**, *69*, 23.

(2) Wudl, F.; Heeger, A. J.; Kobayashi, M. *J. Org. Chem.* **1984**, *49*, 3382.
(3) Hörhold, H.-H.; Helbig, M.; Raabe, D.; Opfermann, J.; Scherf, U.; Stockmann, R.; Weiss, D. *Z. Chem.* **1987**, *27*, 126.
(4) (a) Kortüm, G. *Ber. Bunsen-Ges. Phys. Chem.* **1974**, *78*, 391. (b) Beck, A.; Gompper, R.; Polborn, K.; Wagner, H.-U. *Angew. Chem.* **1993**, *105*, 1424.
(5) Scherf, U. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 575.
(6) Ames, D. E.; Opalko, A. *Tetrahedron* **1984**, *40*, 1919.
(7) (a) Bistmann, H.-J.; Klein, O. Alkene, Cycloalkene und Arylalkene. In *Houben-Weyl: Methoden der Organischen Chemie*; Müller, E., Ed.; Thieme: Stuttgart, 1972; Vol. 5/1b, p 424. (b) Hajos, A. Reduktion mit Metallhydriden und komplexen Hydriden. In *Houben-Weyl*: *Methoden der Organischen Chemie*, 2nd ed.; Kropf, H., Ed.; Thieme: Stuttgart and New York, 1981; Vol. 4/1d, p 286.
(8) (a) Hörhold, H.-H.; Gottschald, J.; Opfermann, J. *J. Prakt. Chem.* **1977**, *319*, 611. (b) Hörhold, H.-H.; Raabe, D. *Acta Polym.* **1979**, *30*, 86.
(9) Feldblum, A.; Kaufman, J. H.; Etemad, S.; Heeger, A. J.; MacDiarmid, A. G. *Phys. Rev. B* **1982**, *26*, 815.
(10) Wegner, G. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 495.
(11) (a) Schlüter, A.-D.; Löffler, M.; Enkelmann, V. *Nature* **1994**, *368*, 83. (b) Löffler, M.; Schlüter, A.-D.; Gessner, K.; Saenger, W.; Toussaint, J.-M.; Bredas, J.-L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2209. (c) Schlicke, B.; Schirmer, H.; Schlüter, A.-D. *Adv. Mater.* **1995**, *7*, 544.
(12) Koch, K.-H.; Müllen, K. *Chem. Ber.* **1991**, *124*, 2091.
(13) (a) Gilch, H. G.; Wheelwright, W. I. *J. Polym. Sci., Part A1* **1966**, *4*, 1337. (b) Hörhold, H.-H.; Opfermann, J. *Makromol. Chem.* **1970**, *131*, 105.
(14) Peierls, E. *Quantum Theory of Solids*; Oxford University Press: London, 1955.
(15) Karabunarliev, S.; Baumgarten, M.; Müllen, K.; Tyutyulkov, N. *Chem. Phys.* **1994**, *179*, 421.
(16) Su, W.-P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, *42*, 1698; *Phys. Rev. B* **1980**, *22*, 2099.
(17) (a) Pariser, R.; Parr, R. H. *J. Chem. Phys.* **1953**, *21*, 466, 767. (b) Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.
(18) Mataga, N.; Nishimoto, K. *Z. Phys. Chem.* **1957**, *13*, 140.
(19) Stewart, J. J. P. MOPAC 6.00, QCPE, No. 455.
(20) SPARTAN Program System, Version 3.0, Wavefunction Inc., Irvine, CA.
(21) Tyutyulkov, N.; Dietz, F. *Chem. Phys.* **1993**, *171*, 293.
(22) Polansky, O. E.; Tyutyulkov, N. *MATCH* (*Commun. Math. Chem.*) **1977**, *3*, 149.
(23) Tyutyulkov, N.; Dietz, F.; Klein, J.; Schmalz, T. *Int. J. Quantum Chem.* **1994**, *51*, 173.
(24) Mulliken, R. S. *J. Chem. Phys.* **1949**, *46*, 497, 675.
(25) Scherf, U. *Synth. Met.* **1993**, *55*−*57*, 767.

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