Thermocleavable Low Band Gap Polymers and Solar Cells Therefrom with Remarkable Stability toward Oxygen

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ABSTRACT: Thermocleavable esters of low band gap monomers and polymers based on diphenyldithienylthienopyrazine were prepared by incorporating carboxylic acid functionalities into the system. A series of different ester groups were prepared and the temperature of elimination of the ester group was studied. The lowest temperatures of elimination obtained were in the range 220−240 °C for tertiary esters giving the free acid. The highest temperatures of elimination were found for primary esters that also lead to decomposition of the molecule. Only the tertiary esters offer a good degree of control over the chemistry in the thermocleaved product. The photovoltaic performance of the polymers prepared was tested under simulated sunlight (1000 W m^{-2}, AM1.5G, 72 °C) and the best power conversion efficiency that could be reached for devices with an active area of 3 cm^2 was up to 0.4% in an ITO/PEDOT/polymer−PCBM/aluminum device geometry. The best performing polymer material was subjected to lifetime studies in four different atmospheres (dry nitrogen, dry oxygen, humid nitrogen and the ambient atmosphere). The best stability was observed in nitrogen while the devices showed nearly the same degree of stability in dry oxygen. In both the ambient atmosphere and the humid nitrogen atmospheres the devices degraded quickly. Finally the stability was compared with two other polymer systems that are known to give stable devices, poly(3-hexylthiophene) (P3HT) and native polythiophene (PT) obtained from the thermocleavable poly(3-(2-methylhexyloxycarbonyl)dithiophene) (P3MHOCT). The performance of the materials reported here was inferior to the performance of P3HT and PT in terms of power conversion efficiency (PCE). The photovoltaic parameters as studied under continuous illumination were however much more stable than those of the reference compounds.

Introduction

The processing requirements of functional materials and polymers are key to the successful application in active devices such as polymer solar cells.[1] In addition to processing there is, in the context of polymer solar cells, increasing focus on preparation of efficient materials with low optical band gaps[1b] and materials that give stable devices. Polymer solar cell devices most often rely on a thin multilayer structure with exact requirements of the nanomorphology of the individual layers. One of the advantages of the technology is that the individual layers can be prepared by solution processing thus gaining considerably in the potential speed, simplicity and lowered cost. However, the formation of multilayer structures based on organic materials such as polymers require that the deposition of subsequent layers does not affect the previously deposited layers. In practical terms this poses a major challenge and has only been solved with some success by following one of three possible strategies or a combination thereof.

(1) Orthogonal solvents for different layers.

(2) Cross-linking after film formation.

(3) Removal of solubilizing groups by thermocleavage.

The use of orthogonal solvents is the simplest and most facile approach. While it is not generic, in the sense that one may encounter combinations of materials for which no orthogonal solvents can be devised, it is commonly employed either intentionally or because there are no other alternatives with the materials at hand. A good example is the use of a PEDOT:PSS layer spincoated from polar solvents such as water followed by another layer spincoated from an organic solvent such as dichlorobenzene.[2] Cross-linking has been employed only rarely as the possibility for cross-linkage has to be engineered into the material. One of the best known examples involved the use of solubilizing sidechains containing an oxetane group that can be cross-linked by a ring opening polymerization.[3] The last approach involving solubilizing groups that can be removed after the film is prepared is the most appealing from the solar cell point of view since all the advantages of solution processing are available up until the film has been produced. After the film has been prepared the side chains take up a considerable part of the volume of the film and are passive in terms of carrier transport and light absorption. There are obvious challenges in controlling the purity, structure and morphology of the film material after the removal of the solubilizing groups but it is reasonable to assume that these can be overcome. The most

Table 1. List of TGA Data for 6a−m, 8b−d, 8i−l

compound	ester elimination (°C)	weight loss (%) calculated	found
6a	410[a]	23.7	36
6b	333	26.7	25
6c	325	31.8	34
6d	332	26.7	25
6e	360[a]	21.1	22
6f[b]		22.4	
6g	326[a]	20.1	17
6h	300[a]	22.9	15
6i	266	27.8	18
6j	225	26.7	26
6k	197	20.1	18
6l	246	19.7	10
6m[b]		22.4	
8b	329	24.0	25
8c	325	28.9	28
8d	325	24.0	24
8i	254	25.6	15
8j	225	24.0	21
8k	206	18.0	8
8l	*c*	17.6	6

[a] Molecule decomposes at first inflection. [b] Insufficient TGA data. [c] Broad derivative peak with no maximum (see Supporting Information).

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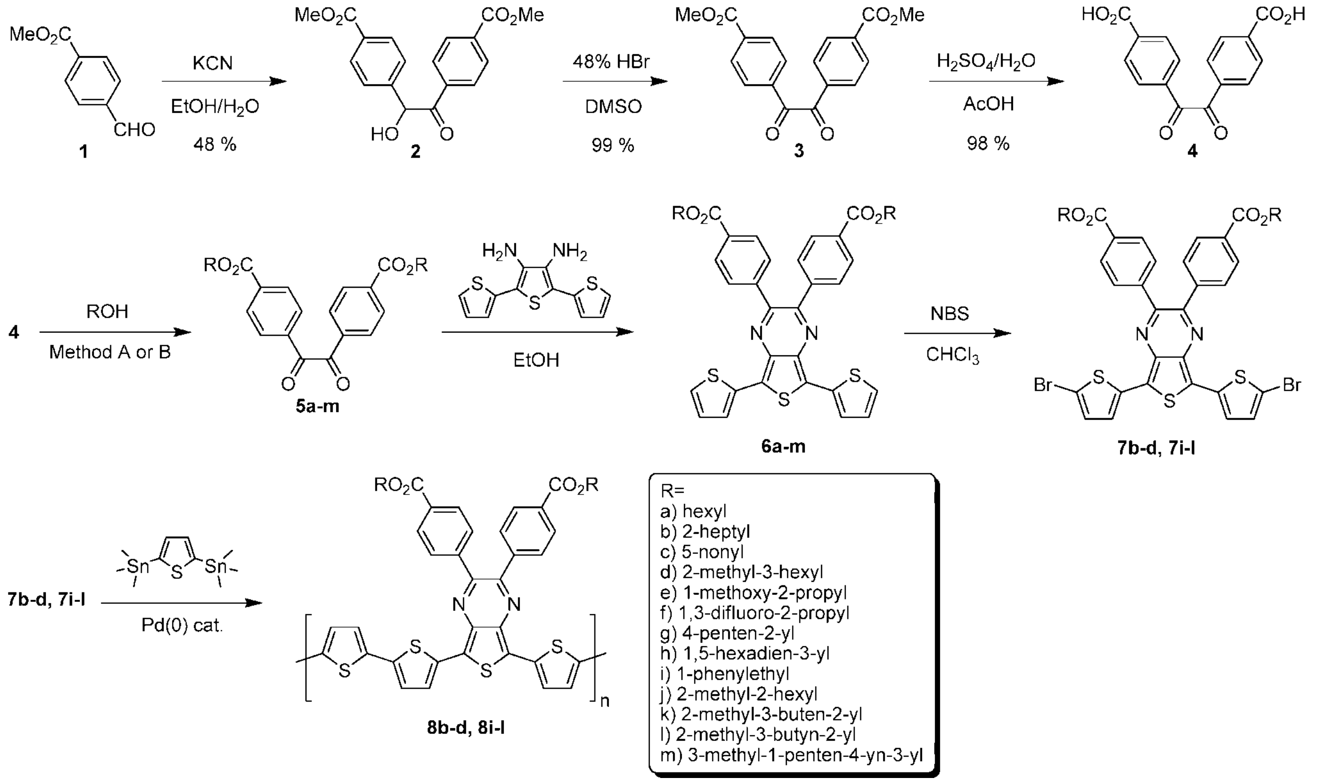
Table 2. Photovoltaic Parameters of the Materials Reported with and without Thermocleavage[a]

polymer	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)	cleaving temp (°C)[b]	solubility in DCB
8b	1.52	0.14	0.25	0.05	25	easy to dissolve
	0.41	0.16	0.26	0.017	310	
8c	2.1	0.4	0.29	0.25	25	hard to dissolve
	0.36	0.14	0.27	0.013	310	
8d	2.55	0.41	0.29	0.3	25	easy to dissolve
	0.24	0.08	0.26	0.005	310	
8j	2.4	0.46	0.36	0.4	25	easy to dissolve
	1.94	0.4	0.33	0.25	230	

[a] The devices had a glass/ITO/PEDOT:PSS/polymer:PCBM/Al geometry and the performance was recorded immediately after preparation in the ambient atmosphere (1000 W m^{-2}, AM1.5G, 72 ± °C, humidity 30 ± 5% rh). [b] The duration of cleaving at 230 °C was 1 min and at 310 °C was 10 min.

Scheme 1. Synthesis of the Dithienylthienopyrazines 6a−m and the Polymers 8b−d, 8i−l with Thermocleavable Benzoate Esters Substituted on the Pyrazine Ring[a]



[a] Method A: 1,1′-carbonyldiimidazole, pyridine. Method B: DMAP, Sc(OTf)$_3$, *N,N*′-diisopropylcarbodiimide.

recent developments are the thermocleavable ester groups[4] and the dithiocarbamate precursor route.[5] The thermocleavable ester groups have been explored in the context of polymer solar cells giving stable operation,[6] stable nanostructures[7] and multilayer tandem cells.[8] The use of thermocleavable materials offer several advantages. Most importantly the side chains that constitute a significant proportion of the final film are alleviated and ideally the final film comprises only the active component. Furthermore, in the case of carboxylic esters attached to thiophenes the processing offer removal of the esters at lower temperatures and the acid groups at higher temperatures allowing for multistep processing.[4b] One aim is to achieve as low a temperature of elimination of the ester group as possible and the purpose of this work was to establish this in the context of choice of ester alcohol, mode of preparation of the ester using the monomers for model studies, extending this to the polymers, evaluate these materials in solar cells and finally to establish their stability performance when subjected to different conditions comprising both inert, ambient and model atmospheres presenting either water or oxygen on their own.

Experimental Section

4,4′-Bis(methyloxycarbonyl)benzoin (2). Methyl 4-formylbenzoate (**1**) (50 g, 305 mmol, 1 equiv) was stirred in 99% ethanol (150 mL) and water (50 mL). Potassium cyanide (6 g, 92.1 mmol, 0.3 equiv) was added, and the reaction mixture was stirred at room temperature for 15 min. The product was filtered, washed with water (3 × 200 mL) and dried at 70 °C in vacuum. Yield: 48 g (48%), light yellow solid. M_p = 140−141 °C. ^{1}H NMR (DMSO): δ = 8.09 (d, 2H, J = 8.6 Hz), 8.00 (d, 2H, J = 8.6 Hz), 7.90 (d, 2H, J = 8.3 Hz), 7.55 (d, 2H, J = 8.3 Hz), 6.46 (s, 1H), 6.15 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (DMSO): δ = 199.0, 166.4, 165.9, 145.0, 138.8, 133.7, 129.7, 129.7, 129.6, 129.5, 127.9, 76.2, 52.9, 52.5.

4,4′-Bis(methyloxycarbonyl)benzil (3). To a stirred solution of **2** (74 g, 225 mmol) in DMSO (510 mL) was added slowly 105 mL 48% aqueous hydrobromic acid. The solution was heated to 55 °C for 24 h after which 500 mL water was added and the product was filtered, washed with water (3 × 200 mL) and dried at 70 °C in vacuum. Yield: 72.5 g (99%), yellow solid. M_p = 197−198 °C. ^{1}H NMR (CDCl$_3$): δ = 8.19 (d, 4H, J = 7.5 Hz), 8.06 (d, 4H, J = 7.5 Hz), 3.97 (s, 6H). ^{13}C NMR (CDCl$_3$): δ = 192.9, 165.8, 135.7, 135.5, 130.1, 129.9, 52.7.

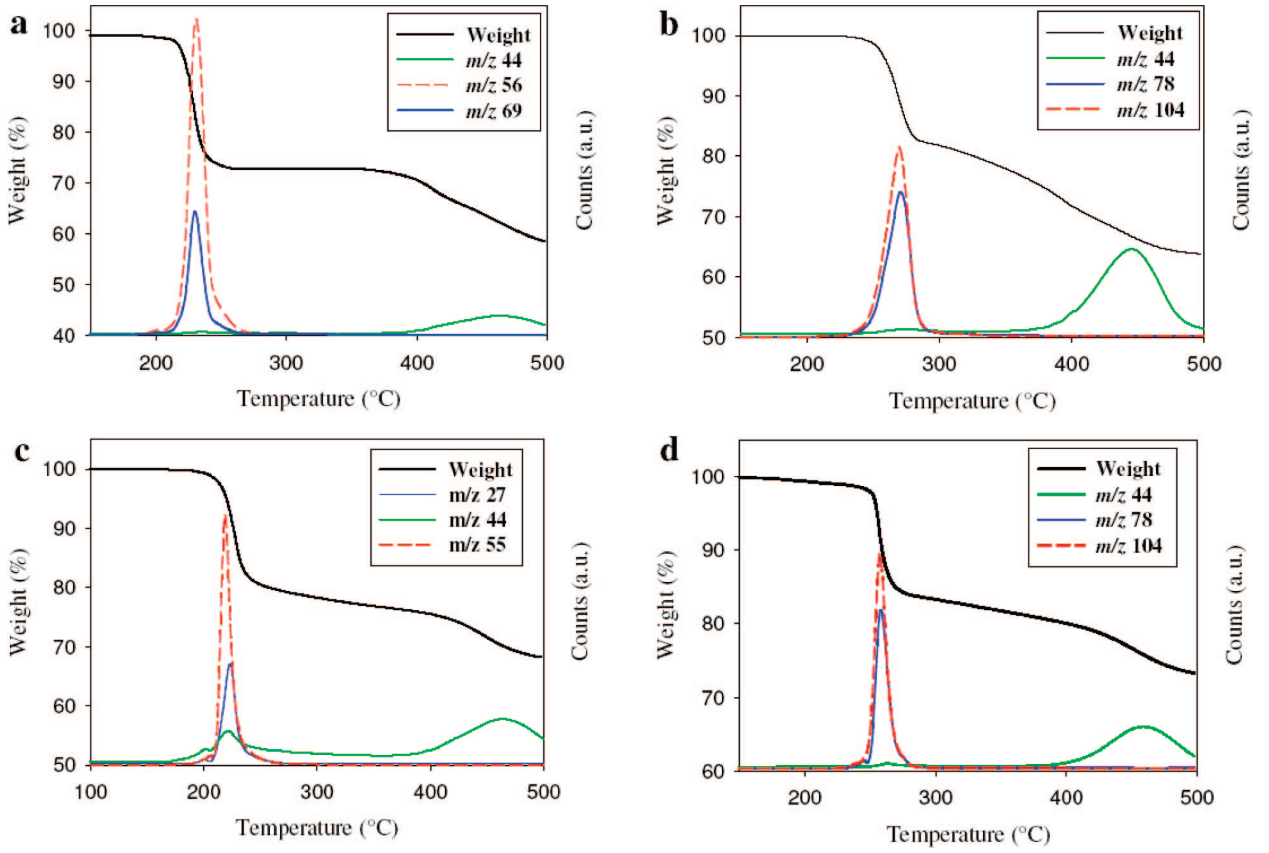


Figure 1. (a) TGA−MS of **6j**, (b) TGA−MS of **6i**, (c) TGA−MS of **8j**, and (d) TGA−MS of **8i**. The first inflection accounts for the ester elimination and the second weight loss around 400−500 °C is decomposition. The red and blue curves correspond to loss of alkenes and the green curves corresponds to loss of carbon dioxide.

4,4′-Bis(hydroxycarbonyl)benzil (4). **3** (5 g, 15.3 mmol) was mixed in acetic acid (350 mL) and a 4:1 H_2SO_4/H_2O solution (175 mL). The reaction mixture was heated to reflux and stirred for 10 h after which 250 mL water was added and the mixture was cooled on ice. After cooling the product was filtered, washed with water (3 × 20 mL) and dried at 70 °C in vacuum. Yield: 4.5 g (98%), pale yellow solid. M_p > 300 °C. ^{1}H NMR (DMSO): $\delta = 13.54$ (s, 2H), 8.15 (d, 4H, $J = 7.0$ Hz), 8.08 (d, 4H, $J = 7.0$ Hz). ^{13}C NMR (DMSO): $\delta = 193.8$, 166.8, 136.9, 135.5, 130.5, 130.5.

General Procedure for the Preparation of Primary and Secondary Diesters (Method A). *4,4′-Bis(hexyloxycarbonyl)benzil (**5a**).* **4** (500 mg, 1.68 mmol, 1 equiv) and 1,1′-carbonyldiimidazole (557 mg, 3.44 mmol, 2.05 equiv) were mixed in dry pyridine (5 mL) and stirred at 50 °C under argon for 1 h. 1-Hexanol (439 μL, 3.52 mmol, 2.1 equiv) was added and the reaction mixture was heated to reflux for 10 h. After TLC showed reaction completion the pyridine was evaporated in vacuum. The residue was added saturated $NaHCO_3$ (30 mL) and extracted with ether (3 × 30 mL). The combined organic phase was dried ($MgSO_4$), filtered and concentrated in vacuum. Dry column chromatography (silica gel 15−40 μm, eluted with EtOAc/Heptane, gradient 1−5% EtOAc) afforded **5a**. Yield: 625 mg (80%), yellow solid. $M_p = 140-141$ °C. ^{1}H NMR ($CDCl_3$): $\delta = 8.18$ (d, 4H, $J = 8.5$ Hz), 8.05 (d, 4H, $J = 8.5$ Hz), 4.36 (t, 4H, $J = 6.7$ Hz), 1.83−1.74 (m, 4H), 1.49−1.39 (m, 4H), 1.39−1.29 (m, 8H), 0.95−0.86 (m, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 192.9$, 165.4, 135.9, 135.7, 130.1, 129.8, 65.9, 31.4, 28.6, 25.6, 22.5, 13.9. HRMS-FAB: *m*/*z* calcd for $C_{28}H_{35}O_6$ [M + H]$^+$, 467.2434; found, 467.2430.

General Procedure for the Preparation of Tertiary Diesters (Method B). *4,4′-Bis(2-methylhexan-2-yloxycarbonyl)benzil (**5j**).* A suspension of **4** (300 mg, 1.01 mmol, 1 equiv), DMAP (258 mg, 2.11 mmol, 2.1 equiv), scandium triflate (49.5 mg, 0,101 mmol, 0.1 equiv) and 2-methyl-2-hexanol (302 μL, 2.11 mmol, 2.1 equiv) in dry methylene chloride (5 mL) was stirred at room temperature under argon for 30 min. *N*,*N*′-Diisopropylcarbodiimide (331 μL, 2.11 mmol, 2.1 equiv) was added and the reaction mixture was heated to reflux and stirred for 24 h. The reaction mixture was concentrated on celite in vacuum. Dry column chromatography (silica gel 15−40 μm, eluted with EtOAc/Heptane, gradient 1−5% EtOAc) afforded **5j**. Yield: 388 mg (78%), yellow oil. ^{1}H NMR ($CDCl_3$): $\delta = 8.08$ (d, 4H, $J = 8.5$ Hz), 7.99 (d, 4H, $J = 8.5$ Hz), 1.92−1.80 (m, 4H), 1.55 (s, 12H), 1.42−1.25 (m, 8H), 0.94−0.82 (m, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 193.1$, 164.2, 137.5, 135.5, 129.9, 129.6, 84.4, 40.6, 26.1, 26.0, 22.9, 13.9. HRMS-FAB: *m*/*z* calcd for $C_{30}H_{39}O_6$ [M + H]$^+$, 495.2747; found, 495.2735.

General Procedure for the Condensation. *Bis(2-methylhexan-2-yl) 4,4′-(5,7-Di(thiophen-2-yl)thieno-[3,4-b]pyrazine-2,3-diyl)dibenzoate (**6j**).* **5j** (567 mg, 1.15 mmol, 1 equiv), [2,2′;5′,2″]terthiophene-3′,4′-diamine hydrochloride (397 mg, 1.26 mmol, 1.1 equiv) and triethylamine (3.44 mmol, 0.480 mL, 3 equiv) was mixed in 99% ethanol (20 mL). The reaction mixture was heated to reflux and stirred for 15 h. After the reaction was complete the mixture was cooled on ice followed by filtration of the product. The product was washed with 99% ethanol (3 × 5 mL) and dried at 50 °C in vacuum.Yield: 730 mg (86%), dark purple solid. $M_p = 197-198$ °C. ^{1}H NMR ($CDCl_3$): $\delta = 7.97$ (d, 4H, $J = 8.3$ Hz), 7.67−7.60 (m, 6H), 7.40 (dd, 2H, $J = 5.1$, 1.0 Hz), 7.11 (dd, 2H, $J = 5.1$, 3.7 Hz), 1.96−1.86 (m, 4H), 1.60 (s, 12H), 1.44−1.34 (m, 8H), 0.94 (t, 6H, $J = 6.9$, 6.9 Hz). ^{13}C NMR ($CDCl_3$): $\delta = 165.0$, 151.3, 142.6, 137.3, 134.5, 132.4, 129.8, 129.3, 127.3, 126.9, 125.6, 124.9, 83.7, 40.8, 26.2, 26.1, 23.0, 14.0. HRMS-FAB: *m*/*z* calcd for $C_{42}H_{44}N_2O_4S_3$ [M + H]$^+$, 736.2463; found, 736.2466.

General Procedure for the NBS Bromination. *Bis(2-methylhexan-2-yl) 4,4′-(5,7-Bis(5-bromothiophen-2-yl)thieno[3,4-b]pyrazine-2,3-diyl)dibenzoate (**7j**).* **6j** (1 g, 1.36 mmol, 1 equiv) was dissolved in dry chloroform (70 mL). Then NBS (483 mg, 2.71 mmol, 2 equiv) was added slowly and the reaction mixture was stirred at room temperature in the dark for 20 min. After completed reaction

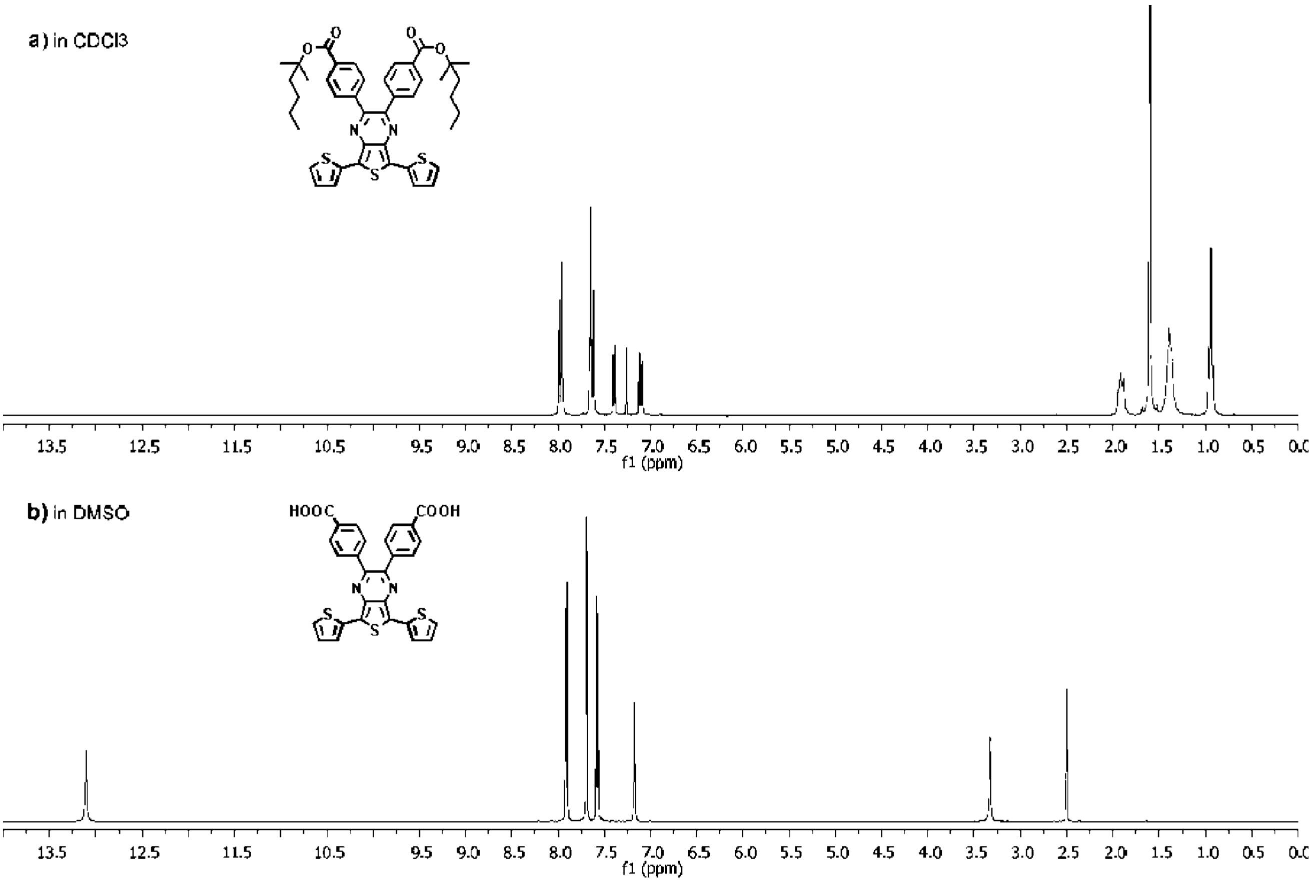


Figure 2. ^{1}H NMR spectra of **6j** (a) from before and after (b) heating to 233 °C for 30 min under argon.

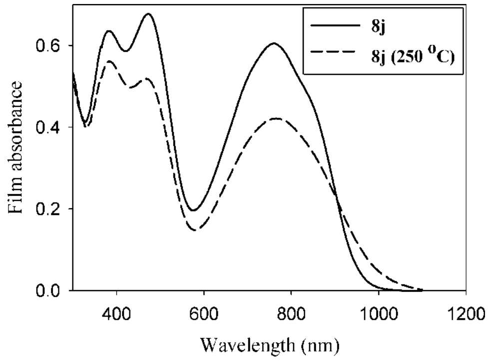


Figure 3. UV−vis for a spincoated film of **8j** on a glass substrate as measured in a transmission geometry. The spectrum for the thermocleaved film is also shown (heated to 250 °C for 1 min).

the mixture was washed with water (3 × 50 mL), dried ($MgSO_4$), filtered and concentrated in vacuum affording **7j**. Yield: 1.13 g (93%), dark purple solid. M_p = 185−186 °C.

^{1}H NMR ($CDCl_3$): δ = 7.98 (d, J = 8.4 Hz, 4H), 7.58 (d, J = 8.4 Hz, 4H), 7.22 (d, J = 4.0 Hz, 2H), 7.01 (d, J = 4.0 Hz, 2H), 1.97−1.87 (m, 4H), 1.61 (s, 12H), 1.46−1.33 (m, 8H), 0.94 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 165.1, 152.0, 142.1, 137.3, 135.6, 132.7, 129.9, 129.8, 129.3, 124.8, 124.3, 115.1, 83.8, 40.8, 26.2, 26.1, 23.0, 14.0.

General Procedure for the Stille Coupling Polymerization. *Poly{bis(2-methylhexan-2-yl) 4,4′-(5-(2,2′-bithiophen-5-yl)-7-(thiophen-2-yl)thieno[3,4-b]pyrazine-2,3-diyl)dibenzoate} (8j).* **7j** (200 mg, 0.22 mmol, 1 equiv), 2,5-bis(trimethylstannyl)thiophene (92 mg, 0.22 mmol, 1 equiv), Pd_2dba_3 (20 mg, 0.022 mmol, 0.1 equiv) and tri(o-tolyl)phosphine (54 mg, 0.18 mmol, 0.8 equiv) was dissolved in dry toluene (50 mL). The reaction mixture was heated to reflux for 24 h under argon. Then the mixture was poured into 150 mL methanol and the polymer was allowed to precipitate. Finally the polymer **8j** was filtered and purified by Soxhlet extraction with MeOH,hexane and $CHCl_3$. Yield: 169 mg (92%), dark green solid. ^{1}H NMR (CD_2Cl_2): δ = 8.18−6.37 (m, 14H), 2.30−0.45 (m, 30H). SEC ($CHCl_3$): M_w = 39429, M_n = 20410, M_p = 17839, and PD = 1.932.

Thermal Analysis. The sample holders were carefully weighed and the samples introduced followed by drying for 24 h at 50 °C in vacuum. The thermogravimetric analysis was then carried out using heating rate of 10 °C min^{-1}. The carrier gas used was argon and the exhaust gases were passed through a mass spectrometer allowing for the simultaneous acquisition of mass data. A series of masses relevant to the degradation process were specifically followed such as CO_2, alkyl chain fragments and fluorine when relevant (see Supporting Information for each material).

Solar Cell Preparation. Glass substrates with pre-etched 100 nm thick layer of ITO and a sheet resistivity of 8−12 Ω square^{-1} purchased from LumTec were cleaned by consecutive ultrasonication in isopropanol and distilled water for 10 min each followed by drying immediately prior to use. A layer of PEDOT:PSS purchased from Aldrich as a 1.3 wt % aqueous solution was spin coated on top of ITO at a rotational speed of 2800 rpm and the slides were annealed at 160 °C for 5 min. Subsequently, the samples were transported into a glovebox and the active layer was applied as a blend of the polymer and [60]PCBM in a 1:1 ratio (20 mg mL^{-1} in dichlorobenzene) by spin coating onto the glass/ITO/PEDOT:PSS substrates. The samples were then dried at room temperature (25 °C) or heated to the desired cleaving temperature (see Tables 1 and 2). An aluminum metal electrode was evaporated on top after the thermal annealing to complete the devices. The devices had an active area of 3 cm^2 and were tested for photovoltaic performance and stability.

Device Characterization. The photovoltaic performance was tested under a solar simulator (KHS575) where the irradiance and emission spectrum were observed using an optical spectrum

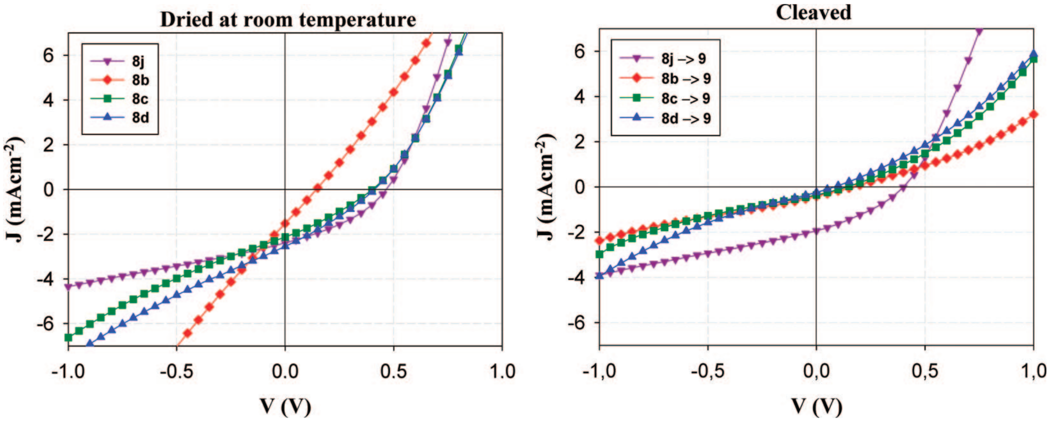
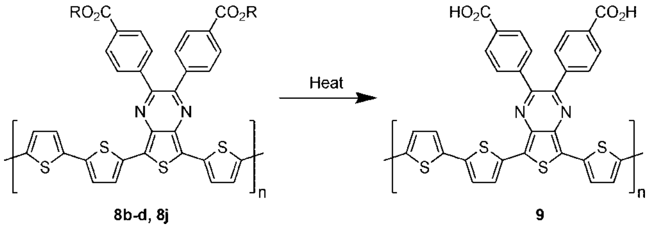


Figure 4. IV-curves for the different polymers uncleaved (left) and cleaved (right). The polymers **8b**, **8c**, and **8d** were cleaved at 310 °C for 10 min and the polymer **8j** was cleaved at 230 °C for 1 min.

Table 3. Summary of the Ranges of Performance Obtained for All Polymers (8b, 8c, 8d and 8j) in Pristine and Thermocleaved Form (1000 W m^{-2}, AM1.5G, 72 ± °C, Humidity 30 ± 5% rh)

J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	cleaving temp (°C)
1.52−2.55	0.14−0.46	0.25−0.36	0.05−0.4	25
0.24−1.94	0.08−0.4	0.26−0.33	0.005−0.25	230−310

Scheme 2. Thermocleavage of the the Polymer Materials 8b, 8c, 8d, or 8j All Lead to the Same Polymer Material 9



analyzer in conjunction with a precision radiometer from Eppley Laboratories. The spectrum during characterization of the solar cell efficiency was AM1.5G with an incident light power of 1000 W m^{-2}. The solar simulator is Class AAA from 400−800 nm, over the area of the cell and for the duration of the experiment. No corrections for mismatch were performed.

Stability Measurements. The stability measurements were performed in a stainless steel chamber[6f] with quartz windows and controlled atmosphere. Four different atmospheric conditions were applied to the chambers by continuously introducing the following gas mixtures: (1) nitrogen atmosphere 99.999% (oxygen <2 ppm, humidity <2 ppm); (2) dry oxygen atmosphere 99.5% (humidity <2 ppm); (3) ambient atmosphere (20 ± 5% relative humidity); (4) humid nitrogen 99.999% (oxygen <2 ppm, 95 ± 5% relative humidity). The main impurity in the 99.5% pure oxygen is nitrogen. The temperature during all experiments was 30 ± 2 °C and the incident light intensity was 330 W m^{-2}. The setup is automated and employ IV-measurements at intervals of 10 min using a Keithley 2400 through a switch matrix based on a Keithley 7705 contained in a Keithley 2700.[6f]

Results and Discussion

Synthesis. The synthetic steps involved in the preparation of the dithienylthienopyrazines with thermocleavable esters are outlined in Scheme 1. The benzils **5a−m** were made by a four step synthetic sequence employing a standard benzoin condensation of methyl 4-formylbenzoate (**1**) and potassium cyanide. The reaction was very fast and no heating was required. The insoluble benzoin **2** was oxidized using 48% aqueous hydrobromic acid in dimethyl sulfoxide[9] affording the benzil **3** that was then hydrolyzed in an aqueous acid to give the diacid **4**. The esterifications of the primary and secondary esters **5a−i** employed 1,1′-carbonyldiimidazole as the acylating agent (method A). Tertiary esters are notoriously difficult to synthesize and a series of techniques were attempted. Transformation of **4** into the diacid chloride followed by direct reaction with the tertiary alcohols (2-methyl-2-hexanol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyn-2-ol, 3-methyl-1-penten-4-yn-3-ol) or by adding freshly precipitated AgCN[10] was ineffective. Other acylating agents such as 2,2′-dipyridyl disulfide/PPh$_3$,[11] 2-chloro-1-methylpyridinium iodide[12] and 2-chloro-3,5-dinitropyridine[4a] all failed. The latter method has proven useful for monoesterification albeit in low yield that makes its use impractical for diesterification. A procedure reported by Zhao et al.[13] turned out to work efficiently. The method employs a catalytic amount of scandium triflate in combination with *N*,*N*′-diisopropylcarbodiimide and DMAP (method B). Very good yields of the tertiary diesters **5j−m** (78−81%) were obtained. Finally, the diphenyldithienyl thienopyrazines **6a−m** were prepared by a known procedure[14] where the benzils **5a−m** were condensed with [2,2′;5′,2″]terthiophene-3′,4′-diamine.[15] The polymers of **6b−d** and **6i−l** were also made. Activation of the monomers was done by a NBS bromination and was followed by a Stille coupling polymerization with 2,5-bis(trimethylstannyl)thiophene giving **8b−d** and **8i−l**.

Thermal Behavior. The relative stability of the dithienylthienopyrazines with thermocleavable benzoate esters substituted on the pyrazine ring, **6a−m**, was investigated by thermogravimetric analysis (TGA) and thermogravimetric analysis in conjunction with mass spectrometry of the carrier gas (TGA−MS) in the temperature range 50−500 °C (Table 1). The thermogravimetric data in table 1 are consistent with earlier pyrolysis studies of esters.[16] As expected elimination of an alkene from the tertiary diesters **6j−l** take place at lower temperatures than the secondary diesters **6b−i**. The primary diester **6a** eliminated with decomposition at a significantly higher temperature. The presence of an inductively (σ bond) electron withdrawing β substituent on the alcohol is known to slow down the rate of ester pyrolysis.[17] **6e** eliminate at 360 °C which is 35 °C higher than the elimination temperature of **6c** that bears a β alkyl substituent.

A double bond substituent at the β carbon can reduce the elimination temperature moderately as observed by comparing **6g** with **6b** and **6d**. **6h** eliminates hexatriene at around 300 °C which is approximately 25 °C lower compared to **6c**. We ascribe this to an activation of the adjacent C_{β}−H bond that assist the elimination. The double bond substituents apparently contribute to other reactions (weight losses) at the higher temperatures as **6g** and **6h** decompose at the elimination temperatures. Furthermore, we observed that **6e**, **6h**, and **6m** showed a slight weight

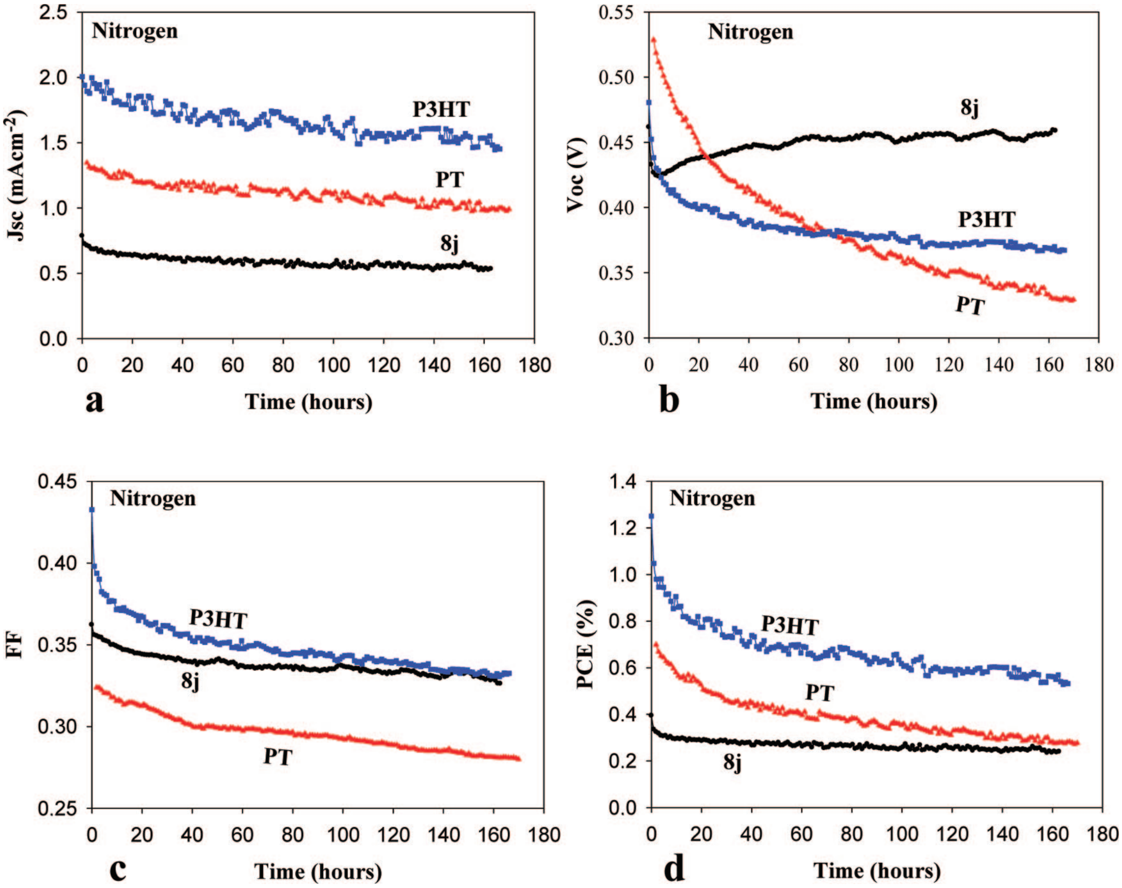


Figure 5. Comparison of the decay of the photovoltaic parameters for P3HT, PT, and **8j** polymers with a Glass/ITO/PEDOT:PSS/polymer:PCBM/Al device geometry in a nitrogen atmosphere (330 W m^{-2}, 30 °C, oxygen <2 ppm, water <2 ppm).

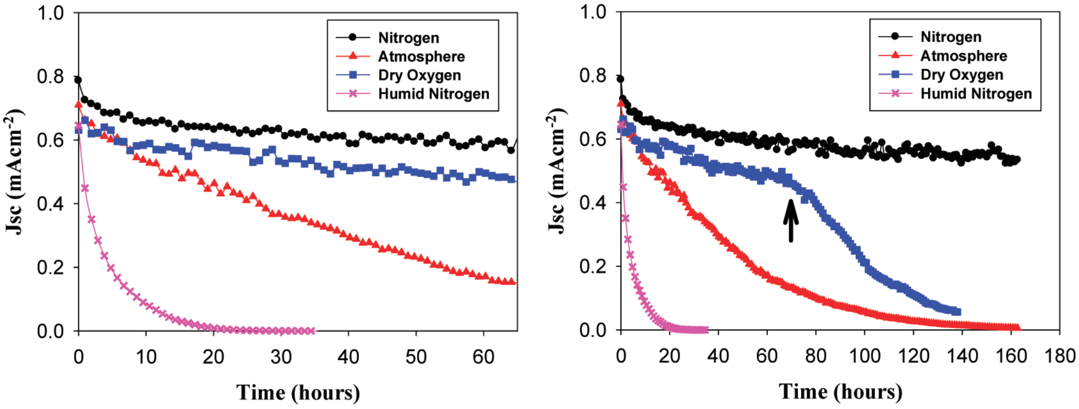


Figure 6. Decay of devices with configuration Glass/ITO/PEDOT:PSS/**8j**:PCBM/Al under conditions of: pure nitrogen atmosphere 99.999% (oxygen <2 ppm, humidity <2 ppm), dry oxygen atmosphere 99.5% (humidity <2 ppm), ambient atmosphere (20 ± 5% relative humidity), humid nitrogen 99.999% (oxygen <2 ppm, 95 ± 5% relative humidity). The temperature was 30 ± 2 °C and the incident light intensity was 330 W m^{-2} (left). The same experiment was repeated for a longer period of time while introducing ambient atmosphere after 70 h (see arrow) thus reducing the oxygen level by a factor of 5 and increasing the humidity by a factor of 10^5 whereupon rapid degradation sets in thereafter (right).

loss at low temperatures. We found no identifiable mass peaks corresponding to the solvent and also rule out the possibility for solvent loss as the samples were dried prior to analysis in a vacuum oven at 50 °C for 24 h. It is possible that these materials are subject to chemical reactions in the solid state (ie. a Cope reaction for **6h** and **6m** or elimination of methanol for **6e**). We currently have no explanation for these observations other then it being an elimination reaction or an electrocyclic reaction followed by an elimination reaction giving fragments that we did not observe in our mass spectra. **6i** has a 1-phenylethyl ester where the π bonded substituent contributes to the activation of the adjacent C$_\beta$−H. It has a simple TGA curve where the first inflection is responsible for the elimination of styrene (Figure 1). The phenyl substituent decrease the temperature for the first weight loss even further compared to **6g** and **6h.**

The tertiary diesters **6j**−**l** eliminate in the temperature range 197−246 °C. **6k** eliminates at a lower temperature compared to **6j** which may arise from the double bond activation as described above. **6l** eliminate 14 °C higher compared to **6j** and we conclude that a triple bond is not as activating as the double bond in this position (α carbon). The observed weight loss for the compounds **6g**, **6h**, **6i**, **6k**, and **6l** all show weight loss at the first inflection which is significantly lower than the calculated value. Since all these fragments have multiple unsaturations after the elimination we ascribe this to polymerization reactions of these materials in the matrix of the material or to cross-linking. Analysis of the materials after the first weight loss by NMR was used to establish whether the ester could be used efficiently as a solubilizing group that can be removed quantitatively by a simple thermal treatment (Figure 2). NMR analysis after heating compound **6a−m** at the temperature of the first weight loss for 15 min. under argon showed that compounds **6a**, **6e−h**, **6m** could not be used for the preparation of the diacid. While the esters may eliminate liberating an alkene the materials also decompose at the given temperature. The ^{1}H NMR spectra of **6j** from before and after the pyrolysis clearly shows that the diester has been transformed into the diacid (Figure 2). Spectrum b in Figure 3 shows no aliphatic protons and the protons from the carboxylic acid appear at 13.08 ppm. From the TGA−MS data it was possible to track evolution of various small molecules and fragments as a function of the temperature. As expected the signals for the observed fragments peak in the same temperature range as the weight losses. The mass signals that we focused on were carbon dioxide and fragments for even and uneven alkenes. As shown earlier[4b] for tertiary esters of polythiophene several weight loss mechanisms may be observed and the advantage of studying the monomer was that the effects of the polymer matrix on the weight loss mechanisms were possibly eliminated.

The primary ester showed loss of both alkene and carbon dioxide starting at around 300 °C peaking at around 400 °C. For the secondary alkyl esters two loss mechanisms could be distinguished as elimination of the ester at the lower temperature (around 300 °C) and loss of carbon dioxide at a higher temperature (425 °C). The weight loss of the secondary alkyl esters corresponded well with the calculated loss while some decarboxylation was evident from a small mass peak of carbon dioxide during the first loss peak. The secondary esters with unsaturations, branching, fluorine and methoxy substituents showed more complex weight loss curves. It would seem that the only useful materials in this series are the simple secondary and tertiary esters. In terms of achieving a lower temperature for the thermocleavage this limits the choice to simple tertiary esters. The only secondary ester that works well is the ester with a phenyl group α to the alcohol and no other unsaturations. As discussed above the simplest secondary alcohol with an α-phenyl group gives styrene upon elimination and this gave an incomplete weight loss. While successfully achieving a lower temperature of elimination this alone does not grant usefulness. The elimination reaction also has to complete the weight loss and the polymer material that is the end product should be insoluble.

Polymers. The polymerization of the monomer materials was achieved through selective bromination of **6b−d** and **6i−l** using NBS to give **7b−d** and **7i−l**. These monomers were then polymerized by Stille cross coupling using bis(2,5-trimethylstannyl)thiophene. This gave the polymers **8b−d** and **8i−l** in good yield. The polymer materials had a low band gap as expected. A major requirement for processing into thin films is that the polymer materials are soluble in organic solvents. While the thermal behavior could be studied for all the polymers, not all of them had a good solubility. The molecular weights for the materials were in the 40000−70000 g mol^{-1} range and the polydispersity was around 2 as expected (see Supporting Information). The only polymers that were readily soluble, could be analyzed, processed into thin films and showed a useful thermal behavior were thus **8b**, **8c**, **8d**, and **8j**.

Only **8j** could be cleaved at an acceptably low temperature. The UV−vis spectrum of a film of **8j** spincoated from chlorobenzene is shown in figure 3. A film absorbance of 1 was easily reached with a very good film quality. The color of the film is olive green and the band gap of **8j** in the film was estimated from the crossing point of the tangent on the absorption edges[18] and was 950 nm or 1.3 eV. The observed band gap is as expected from earlier studies on the same polymer backbone[14] and similar polymers.[19] Upon thermocleavage of the film by heating it at 250 °C for 1 min a color change is observed whereby the film changes to a more brown color. The associated changes in the absorption spectrum are a less intense absorption and a smaller band gap with a band gap of 1010 nm or 1.2 eV. There may be several explanations for the lower absorption intensity.

First, the associated change in film thickness and dielectric constant may lead to changes in the reflection phenomena that also contribute to the intensities in the observed absorption spectrum for a solid film in a transmission geometry. Second, the intensity of absorption quite often decreases as the band gap is lowered. After the short thermal treatment the film maintained the optical quality and was completely insoluble in organic solvents.

Photovoltaic Performance. All of the polymer materials presented in Scheme 1 were intended for use in solar cell devices. Some of the polymer materials however were not very soluble and did not process well into films and the photovoltaic performance obtained for these were either not possible to establish or very poor. Consequently only **8b**, **8c**, **8d**, and **8j** were studied in solar cells. The devices were prepared in duplicate and were after spincoating of the active layer either processed directly into a solar cell by evaporation of the aluminum electrode or subjected to a thermal treatment at the temperature of thermocleavage immediately before evaporation of the aluminum electrode. The results obtained are shown in table 2.

A general observation was that the devices performed significantly worse after thermocleavage as indicated by a decrease in voltage and current. Some examples of IV-curves for uncleaved and cleaved devices are shown in figure 4 (see also Supporting Information). The best performing material was **8j**, which show a decreased performance upon thermocleavage, but maintained a significant performance. We chose to repeat the preparation of devices based on all polymers and obtained results in the ranges outlined in table 3.

It should be noted that polymer solar cells based on thermocleavable materials present additional complexity in terms of processing as compared to materials such as P3HT. In the case of P3HT heating of the device film leads to crystallization and changes in the morphology of the device film that significantly influences the device performance. In the case of thermocleavable materials these effects also take place, but in addition, the chemistry of the device film change and as the chemistry changes so do the processes relating to crystallization and changes in morphology. This has been observed in the case of P3MHOCT where the chemistry of the device film can be processed into three distinct forms starting from the same device film.[4b,20] This allowed for the preparation of devices with a PCE of up to 1.5%.[20]

This implies that not only the temperature of thermal annealing and the duration but also the speed of heating becomes influential. In the case of the polymers presented here the polymer esters (**8b**, **8c**, **8d**, or **8j**) are all chemically different materials. Heating them to the temperature of thermocleavage gives, in principle, the same product as polymer **9** (Scheme 2). The difference in device performance is thus not related to the molecule but rather how the final device film was obtained. Thus the same material can present different levels of performance depending on how it was processed. The chemistry of the sidechains may influence the morphology before thermocleavage, and if the process of thermocleavage is faster than the changes in morphology upon heating, this may also allow for the preparation of different final film morphologies. It has been shown that the morphology is stable in the final thermocleaved form when using a temperature of thermocleavage[7] below T_g and the kinetics of the film formation in such a case is important. A final issue is the completion of the thermocleavage in the final film. It is likely that thermocleavage under a given set of conditions lead only to a partially cleaved film that then present chemistry corresponding to both the uncleaved and cleaved material to varying degrees.[20] In the experiments performed here the films were completely cleaved and a detailed study of varying the degree of thermocleavage warrants further study.

In Figure 4, the performance of some of the devices are shown as IV-curves in the cleaved and uncleaved state. The drastic decrease of the performance for polymers **8b**, **8c** and **8d** is probably due to high cleaving temperature (310 °C) and long cleaving time (10 min), while thermocleavage of **8j** resulted in very little decrease of performance. In the case of earlier reported cleaving of P3MHOCT the performance dropped around 10-fold when cleaved to P3CT and then improved 15-fold when cleaved further to PT.[20]

Stability Studies. We chose to subject the best performing material **8j** to detailed stability studies. Polymer solar cells are inherently unstable under intense illumination and will degrade through a large number of coexisting paths. Some of the paths involve reactants such as water and oxygen from the atmosphere that will dominate the course of degradation if allowed to access the active layer during operation. Their efficient removal efficiently eliminates the associated degradation processes, and other slower processes become readily observable (ie. morphological changes, interlayer diffusion, reactions at interfaces, photochemistry). To get an overview of the stability of the **8j** in relation to other known polymers and as a function of atmospheric reactants we performed two studies. One comparative study in an inert atmosphere and a study where devices were subjected to different atmospheres during continuous (uninterrupted) illumination.

Figure 5 shows the degradation of devices prepared in the same manner employing respectively P3HT, PT, and **8j**. The performance of **8j** is inferior to both P3HT and PT while the photovoltaic parameters are much more stable in time. The P3HT device was annealed at 150 °C for 5 min after evaporation of the aluminum electrode. PT devices were prepared by heating P3MHOCT−PCBM films to 310 °C before evaporation of the aluminum electrode. The decay in the photovoltaic parameters were not affected significantly by the thermocleavage at 230 °C and the stability of **8j** is thus concluded to be very good without cleavage while there are processing advantages of thermocleaved **8j**. Cleaving **8j** at a higher temperature (310 °C) reduced the photovoltaic performance drastically and the decay of V_{oc} and FF was much faster.

When subjecting **8j** devices to four different atmospheres to establish the inherent stability in nitrogen and the effect of water and oxygen taken separately and finally in combination in the real atmosphere it was found that oxygen had little effect on the stability as shown in Figure 6. The interesting finding was that the presence of pure oxygen at high concentration (i.e., five times more than in the ambient atmosphere) does not seem to speed up degradation significantly and we would rate **8j** as stable toward oxygen under illumination. Humidity however was found to profoundly influence the stability leading to rapid degradation that is complete within less than 20 h whereas the absence of water leads to moderately stable operation.

Conclusion

In conclusion, the application of esters as solubilizing groups that allow for removal by a simple thermal treatment is limited to simple secondary and tertiary esters where the alcohol is saturated in order to ensure that the alkene that is eliminated is removed efficiently without undesired side reactions. The lowest temperatures of elimination were found to be achieved when employing tertiary esters as expected. In contrast to the systems where the ester reside on a thiophene ring we found that no decarboxylation takes place prior to decomposition, and it is thus not possible to access the native system without the carboxylic acid groups by a thermal treatment. We showed that a monomer relevant to low band gap polymer systems could be prepared with solubilizing groups that allow for removal by a thermal treatment of around 200−225 °C. We further prepared the polymer materials from the monomers and found that only the polymers with secondary and tertiary esters are useful and the solubility requirements make the choice of side chain functionality limited. The band gaps of the materials were in the 1.2−1.3 eV range and the operational stability was found to be very good compared to model materials such as P3HT and PT. In addition polymer solar cells in a glass/ITO/PEDOT:PSS/polymer:PCBM/Al were found to be very stable toward oxygen during operation. In pure oxygen the device decay was similar to inert conditions. This is in stark contrast to conjugated materials containing vinylene bonds that are very sensitive toward oxygen. The devices decayed rapidly in the presence of water (with and without oxygen present) and removal of water from this type of device gives devices with stability that exceeds hundreds of hours.

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Supporting Information Available: Text giving general procedures and characterization data (including structural diagrams) and figures showing TGA and TGA−MS data, NMR spectra, IPCE curves for **8j**, and plots of the photovoltaic response as a function of incident light intensity. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338. (b) Bundgaard, E.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 954–985. (c) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 58–77.

(2) Hadipour, A.; de Boer, B.; Wildeman, J.; Kooistra, F. B.; Hummelen, J. C.; Turbiez, M. G. R.; Wienk, M. M.; Janssen, R. A. J.; Blom, P. W. M. *Adv. Funct. Mater.* **2006**, *16*, 1897–1903.

(3) (a) Barche, J.; Janietz, S.; Ahles, M.; Schmechel, R.; von Seggern, H. *Chem. Mater.* **2004**, *16*, 4286–4291. (b) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature* **2003**, *421*, 829–833.

(4) (a) Liu, J. S.; Kadnikova, E. N.; Liu, Y. X.; McGehee, M. D.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 9486–9487. (b) Bjerring, M.; Nielsen, J. S.; Nielsen, N. C.; Krebs, F. C. *Macromolecules* **2007**, *40*, 6012–6013.

(5) (a) Nguyen, L. H.; Günes, S.; Neugebauer, H.; Sariciftci, N. S.; Banishoeib, F.; Henckens, A.; Cleij, T.; Lutsen, L.; Vanderzande, D. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2815–2828. (b) Banishoeib, F.; Adriaensens, P.; Berson, S.; Guillerez, S.; Douheret, O.; Manca, J.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1026–1034. (c) Banishoeib, F.; Henckens, A.; Fourier, S.; Vanhooyland, G.; Breselge, M.; Manca, J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D.; Nguyen, L. H.; Neugebauer, H.; Sariciftci, N. S. *Thin Solid Films* **2008**, *516*, 3978–3988.

(6) (a) Krebs, F. C.; Spanggaard, H. *Chem. Mater.* **2005**, *17*, 5235–5237. (b) Krebs, F. C.; Norrman, K. *Prog. Photovolt. Res. Appl.* **2007**, *15*, 697–712. (c) Bjerring, M.; Nielsen, J. S.; Siu, A.; Nielsen, N. C.; Krebs, F. C. *Sol. Energ. Mater. Sol. Cells* **2008**, *92*, 772–784. (d) Krebs, F. C. *Sol. Energ. Mater. Sol. Cells* **2008**, *92*, 715–726. (e) Jørgensen,

M.; Norrman, K.; Krebs, F. C. *Sol. Energ. Mater. Sol. Cells* **2008**, *92*, 686–714. (f) Gevorgyan, S. A.; Jørgensen, M.; Krebs, F. C. *Sol. Energ. Mater. Sol. Cells* **2008**, *92*, 736–745.
(7) Andreasen, J. W.; Jørgensen, M.; Krebs, F. C. *Macromolecules* **2007**, *40*, 7758–7762.
(8) Hagemann, O.; Bjerring, M.; Nielsen, N. C.; Krebs, F. C. *Sol. Energ. Mater. Sol. Cells* **2008**, *92*, 1327–1335.
(9) Floyd, M. B.; Du, M. T.; Fabio, P. F.; Jacob, L. A.; Johnson, B. D. *J. Org. Chem.* **1985**, *50*, 5022–5027.
(10) Takimoto, S.; Inanaga, J.; Katsuki, T.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2335.
(11) Mukaiyama, T.; Matsueda, R.; Suzuki, M. *Tetrahedron Lett.* **1970**, 1901–1904.
(12) Mukaiyama, T.; Usui, M.; Shimada, E.; Saigo, K. *Chem. Lett.* **1975**, 1045–1048.
(13) Zhao, H.; Pendri, A.; Greenwald, R. B. *J. Org. Chem.* **1998**, *63*, 7559–7562.
(14) Petersen, M. H.; Hagemann, O.; Nielsen, K. T.; Jørgensen, M.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 996–1009.
(15) Mangeney, C.; Lacroix, J.-C.; Chane-Ching, K. I.; Jouini, M.; Villain, F.; Ammar, S.; Jouini, N.; Lacaze, P.-C. *Chem. Eur. J.* **2001**, *7*, 5029–5040.
(16) Houtman, J. P. W.; van Steenis, J.; Heartjes, P. M. *Recl. Trav. Chim.* **1946**, *65*, 781.
(17) Chuchani, G.; Martín, I.; Hernández, J. A.; Rotinov, A.; Fraile, G. *J. Phys. Chem.* **1980**, *84*, 944–948.
(18) Bundgaard, E.; Krebs, F. C. *Macromolecules* **2006**, *39*, 2823–2831.
(19) (a) Campos, L. M.; Toncheva, A.; Günes, S.; Sonmez, G.; Neugebauer, H.; Sariciftci, N. S.; Wudl, F. *Chem. Mater.* **2005**, *17*, 4031–4033. (b) Wienk, M. M.; Turbiez, M. G. R.; Struijk, M. P.; Fonrodona, M.; Janssen, R.A. J. *Appl. Phys. Lett.* **2006**, *88*, 153511.
(20) Gevorgyan, S. A.; Krebs, F. C. *Chem. Mater.* **2008**, *20*, 4386–4390.

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