ChemPubSoc Europe

DOI: 10.1002/chem.201403623

CHEMISTRY
A European Journal
Full Paper

Functional Molecules

Solubility and Crystallizability: Facile Access to Functionalized π-Conjugated Compounds with Chlorendylimide Protecting Groups

Jan Gebers,[a] Damien Rolland,[a] Roman Marty,[a] Stéphane Suàrez,[a] Luca Cervini,[a] Rosario Scopelliti,[b] Jan Cornelius Brauer,[a] and Holger Frauenrath*[a]

Abstract: Functional π-conjugated molecules are relevant for the preparation of new organic electronic materials with improved performance. However, their synthesis is often rendered difficult by their inherently low solubility, and the permanent attachment of solubilizing groups may change the properties of the material. Here, we introduced the chlorendylimidyl moiety as a new temporary protecting group for the straightforward large-scale synthesis of protected quarter-, sexi-, octathiophene, and perylene bisimide diamine and dicarboxylic acid derivatives. The obtained chlorendylimides and chlorendylimidyl active esters were highly soluble in organic solvents, and optical spectroscopy confirmed the low tendency of the compounds to aggregate in solution. At the same time, they could be conveniently purified by recrystallization or precipitation. Single-crystal X-ray structures obtained for most compounds showed supramolecular motifs highlighting the role of the rigid, polychlorinated chlorendyl moieties in their crystallization. The obtained protected diamine and dicarboxylic acid derivatives were easily deprotected and converted into various amide-substituted oligothiophenes and perylene bisimides that are of interest as new functional materials for organic electronic thin film or nanowire devices.

Introduction

Organic electronic materials from π-conjugated molecules or polymers have become highly relevant for applications in organic field-effect transistors,[1–2] photovoltaics,[3] light-emitting diodes,[4] as well as chemical sensors[5] and other building blocks of nanoelectronic devices.[6] Materials from oligothiophene and perylene bisimide derivatives are among the best-studied p-type and n-type organic semiconductors, respectively.[7–8] Whereas the performance of these materials relies on efficient π–π stacking of the molecules in the solid state, these interactions at the same time hamper the synthesis due to the low solubility of products and intermediates. Therefore, the introduction of flexible substituents at the π-conjugated core, such as (branched) alkyl chains, dendrons, and polymers, is often used to induce entropy-driven solubility.[9–12] Whereas this facilitates the synthesis and characterization of precursors and products as well as their processing from solution, the presence of bulky or branched substituents may have undesirable effects on the supramolecular arrangement and thus on the desired electric properties of the final materials.[10,13] Therefore, the preparation of solely end-functionalized oligothiophenes or perylene bisimides would be desirable, but remains a synthetic challenge. To this end, intriguing synthetic pathways have been developed in recent years, including functionalized molecular precursors of organic electronic materials.[9,13–24] However, most of the employed syntheses are convergent and hence tedious, and they are often limited in versatility and reaction scale when the preparation of a larger number of similar derivatives is desired.

Here, we report a versatile synthetic approach to the divergent synthesis of end-functionalized oligothiophenes and perylene derivatives on large scale. Our synthesis relies on the use of chlorendylimides as new (temporary) protecting groups for either amines or carboxylic acids. Chlorendic acid derivatives are inexpensive and readily available since they have been widely used as insecticides and fire-retardant additives for polymers.[25–26] To the best of our knowledge, however, their application in protecting-group chemistry has never been investigated. All chlorendylimide-protected intermediates and products exhibited a significantly enhanced solubility in organic solvents, as compared with the parent compounds or even some of their alkyl-substituted derivatives. At the same time, the chlorendylimide moiety rendered most compounds excellently crystallizable, which allowed us to perform all synthetic steps on the multi-gram scale and purify the products by recrystallization or precipitation, avoiding column chromatography. Single-crystal X-ray structures of various molecules revealed common packing features that might be attributed to

[a] Dr. J. Gebers, D. Rolland, Dr. R. Marty, Dr. S. Suàrez, L. Cervini, Dr. J. C. Brauer, Prof. Dr. H. Frauenrath
Institute of Materials, École Polytechnique Fédérale de Lausanne (EPFL), EPFL–STI–IMX–LMOM
MXG 037, Station 12, 1015 Lausanne (Switzerland)
Fax: (+41) 21-69-35270
E-mail: holger.frauenrath@epfl.ch

[b] Dr. R. Scopelliti
Institute of Chemical Science and Engineering
École Polytechnique Fédérale de Lausanne (EPFL)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403623.

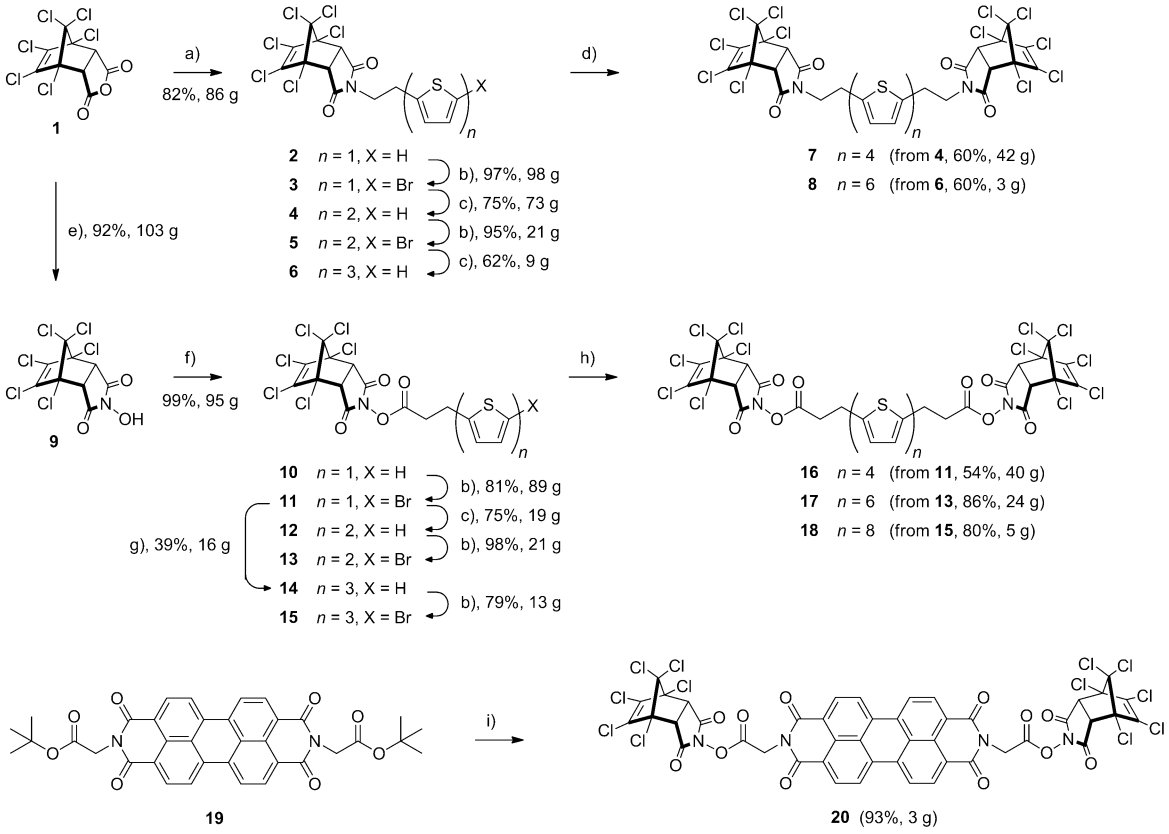
the dominant role of the chlorendylimide residue for their crystallization.

We were thus able to prepare chlorendylimide-substituted oligothiophenes up to the octamers and perylene bisimides through a straightforward solution-phase synthesis on large reaction scales with isolated yields of up to 40 g. The protected oligothiophene or perylene bisimide diamines and dicarboxylic acids represent versatile building blocks that can be reacted with a variety of electrophiles or nucleophiles, respectively. As first examples, we readily employed them in the synthesis of amide-substituted quaterthiophenes, sexithiophenes, octathiophenes, and perylene bisimides, which are of interest as materials for organic electronic thin film devices or organic nanowires.[27–31]

Results and Discussion

The synthesis of the desired amino- and carboxylic acid-functional quaterthiophenes, sexithiophenes, octathiophenes, and perylene bisimides started from the inexpensive chlorendic acid anhydride **1** (Scheme 1). Thus, condensation of chlorendic anhydride **1** with 2-(2-aminoethyl)thiophene led to the thiophene chlorendylimide **2** on the 86 g scale (82% yield) after recrystallization. Subsequent bromination of **2** with *N*-bromosuccinylimide (NBS) in *N*,*N*-dimethylformamide (DMF) afforded 98 g (97%) of the bromothiophene **3**. Moreover, the reaction sequence from **1** to **3** could also be performed using crude **2** without further purification in the second step, allowing us to perform the reaction on an increased scale (155 g) with improved overall yield of the isolated product (91% over two steps). Bithiophene chlorendylimide **4** was then conveniently prepared by Stille coupling to 2-(tributylstannyl)thiophene on a scale of 73 g (75%). By repetition of this bromination/Stille coupling sequence, the corresponding bromobithiophene **5** and the terthiophene **6** were accessible on the 21 g (95%) and 9 g scale (62%), respectively. Finally, the quaterthiophene and sexithiophene chlorendylimides **7** and **8** were synthesized by a Pd^{II}-catalyzed oxidative homocoupling using AgF or $AgNO_3$/KF as oxidants.[32–33] Purification of the final compounds proved to be straightforward due to their high solubility and crystallizability. Thus, simple filtration of the reaction mixture over silica gel to remove Ag particles furnished pure **7** on the 42 g scale (60%) that was recrystallized from toluene or dimethylsulfoxide (DMSO). The pure sexithiophene **8** was obtained in a yield of 3 g (60%) by extraction of the crude product with hot DMSO from which the product immediately crystallized upon cooling of the solvent.

In a similar way, we synthesized quaterthiophene, sexithiophene, and octathiophene derivatives with chlorendylimidyl active esters as temporary protecting groups (Scheme 1). Thus,



Scheme 1. Synthesis of the chlorendylimides and chlorendylimidyl active esters. Reaction conditions: a) Thiophene-2-ethylamine, Et_3N, toluene, reflux; b) NBS, DMF, RT; c) 2-tributyltin-thiophene, $[Pd(PPh_3)_2Cl_2]$ or $[Pd(PPh_3)_4]$, DMF or MeCN, 80 °C; d) $AgNO_3$, KF, $[Pd(PhCN)_2Cl_2]$, DMSO, 80 °C; e) $H_2NOH{\cdot}HCl$, K_2CO_3, water, reflux; f) thiophene-2-propionic acid, EDCI, DPTS, CH_2Cl_2; g) 5-tributyltin-2,2′-bithiophene, $[Pd(PPh_3)_2Cl_2]$, DMF 100 °C; h) 5,5′-bis(tributylstannyl)-2,2′-bithiophene, $[Pd(PPh_3)_4]$, DMF, 80 °C; i) TFA, $CHCl_3$, reflux, then **9**, DIC, DMF, 40 °C.

reaction of chlorendic anhydride **1** with hydroxylamine hydrochloride under basic conditions afforded 103 g (92%) of chlorendyl hydroxylimide **9**. Subsequent esterification of 3-(2-thienyl)propionic acid with **9** promoted by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) and 4-(dimethylamino)-pyridinium *p*-toluenesulfonate (DPTS)[34] resulted in ester **10** in quantitative yield. The same bromination/Stille coupling sequence as above then led to the bromothiophene active ester **11** (89 g, 81%) that was converted to the bithiophene active ester **12** (19 g, 75%) after gel filtration to remove the symmetric diester side product (8%). Compound **12** was then brominated to furnish the corresponding bromobithiophene active ester **13** (21 g, 98%). Likewise, Stille coupling of **11** with 5-tri-*n*-butylstannyl-2,2′-bithiophene yielded the terthiophene active ester **14** (16 g, 39%) after gel filtration to remove the quaterthiophene and diester side products. The terthiophene **14** was then brominated to obtain the bromoterthiophene active ester **15** (13 g, 79%). Whereas the sensitivity of the active ester functions towards bases precluded using the oxidative homocoupling protocol applied to the chlorendylimides above, the final quarterthiophene, sexithiophene, and octathiophene active esters **16**, **17**, and **18** could be prepared by Stille coupling of 5,5′-bis(tri-*n*-butylstannyl)-2,2′-bithiophene to **11**, **13**, or **15**, respectively. Thus, the quaterthiophene active ester **16** was obtained from bromothiophene **11** as a microcrystalline yellow powder in 54% yield on a 40 g scale after precipitation of the crude product from a slurry in diisopropylether/THF/toluene (3:1:1) and washing with diisopropylether and then pentane. Similarly, Stille coupling to the bromobithiophene **13** furnished the sexithiophene active ester **17** as a microcrystalline orange powder in 86% yield on a 24 g scale after resuspension in the same solvent mixture and filtration. Finally, Stille coupling to bromoterthiophene **15** resulted in the octathiophene active ester **18** as a red powder in 80% yield on a 5 g scale after resuspension in toluene and filtration.

To further test the versatility of the chosen approach, we also investigated the use of chlorendylimidyl active esters in the synthesis of functional perylene bisimide derivatives (Scheme 1). Different from our previously described in situ coupling approach,[28] perylene bisanhydride was reacted with glycine *tert*-butyl ester hydrochloride to afford the diglycyl-substituted perylene bisimide **19** (6 g, 73%), which was subsequently converted to the perylene bisimide diester **20** by trifluoroacetic acid (TFA)-promoted deprotection followed by formation of the active ester using diisopropylcarbodiimide (DIC) as a coupling reagent. The isolated product was obtained as a microcrystalline red powder on a 3 g scale in 93% yield after precipitation of the crude product from THF into diisopropylether.

The use of the chlorendylimide moiety has therefore enabled us to obtain a variety of protected, amine- or acid-functionalized π-conjugated molecules and building blocks. Notably, all intermediates and products displayed good to excellent solubility in various organic solvents (Table 1), which is in contrast to other oligothiophene and perylene bisimide derivatives that typically have solubilities of less than 3–4 g L^{-1} (for α-quaterthiophene in $CHCl_3$).[35–36] The quaterthiophene bisimide **7**, for instance, was soluble in THF or DMSO up to concentrations of about 100 g L^{-1}, whereas up to 3 g L^{-1} of the sexithiophene bisimide **8** could be dissolved in hot DMSO. Likewise, the active esters **16**, **17**, and **20** proved to be well soluble in polar organic solvents such as THF, DMSO, or DMF. Even the octathiophene active ester **18** remained (poorly) soluble in several solvents, allowing for successful follow-up reactions (see below). Moreover, almost no chromatographic purification steps had to be performed since all compounds could be readily precipitated or recrystallized. In this way, we obtained X-ray-quality single crystals of all intermediates and final products **2**–**13**, whereas **14**–**20** were furnished as microcrystalline powders.

Table 1. Solubilities of the chlorendylimides and chlorendylimidyl active esters in different organic solvents [g L^{-1}].

Solvent	7	8	16	17	18	20
heptane	0	0	0	0	0	0
toluene	3	0.2	34	0.3	<0.1	0.9
Et_2O	0	0	1.3	<0.1	<0.1	0.2
CH_2Cl_2	8	0.1	186	0.4	<0.1	1.3
THF	98	0.8	230	1	<0.1	303
DMSO	87	3	350	0.9	<0.1	394
MeOH	0	0	n.a.	n.a.	n.a.	n.a.
H_2O	0	0	n.a.	n.a.	n.a.	n.a.

The molecular packing in the crystal structures of intermediates **2**–**13** shared several common features (Figures 1 and 2 and the Supporting Information, Figure S1–S14). Notably, their *N*-chlorendylimide and oligothiophene fragments were always separated into different layers. All bi- and terthiophenes assumed a herringbone packing within their layer, with both edge-to-face and parallel-displaced arrangements resulting in several C···C short contacts of 3.4–3.6 Å. More prominently, a face-to-face stacking of one of the electron-rich thiophene rings with the electron-poor succinyl imide fragment of the *N*-chlorendylimide moiety was encountered in several examples, with a typical C···S short contact between the thiophene sulfur atom and one of the carbonyl carbons of the imide of 3.3–3.4 Å. The close packing of the unsymmetrically substituted oligothiophenes in the herringbone pattern was achieved by interdigitation, thus accommodating the steric demand of the attached *N*-chlorendylimides with their van der Waals radius of roughly 8 Å. As a result, each oligothiophene layer was flanked by two *N*-chlorendylimide layers, and multiple Cl···Cl short contacts of 3.3–3.5 Å, Cl···O short contacts of 2.8–3.1 Å with the imide carbonyl oxygens, as well as O···C short contacts of the latter with the carbonyl carbons of a neighboring chlorendylimide were observed. In the case of all bromothiophene derivatives (**3**, **5**, **11**, and **13**), the interdigitation of the oligothiophenes was organized such that the bromine atoms appeared to "participate" in the halogen-rich *N*-chlorendylimide layers, with several Br···Cl short contacts of 3.4–3.6 Å, respectively. Moreover, Br···O short contacts of 2.9–3.3 Å were observed with the imide carbonyl oxygen atoms.

The two different crystal structures of the quaterthiophene bisimide **7**·toluene and **7**·DMSO obtained by recrystallization from toluene or DMSO, respectively, as well as the structure of

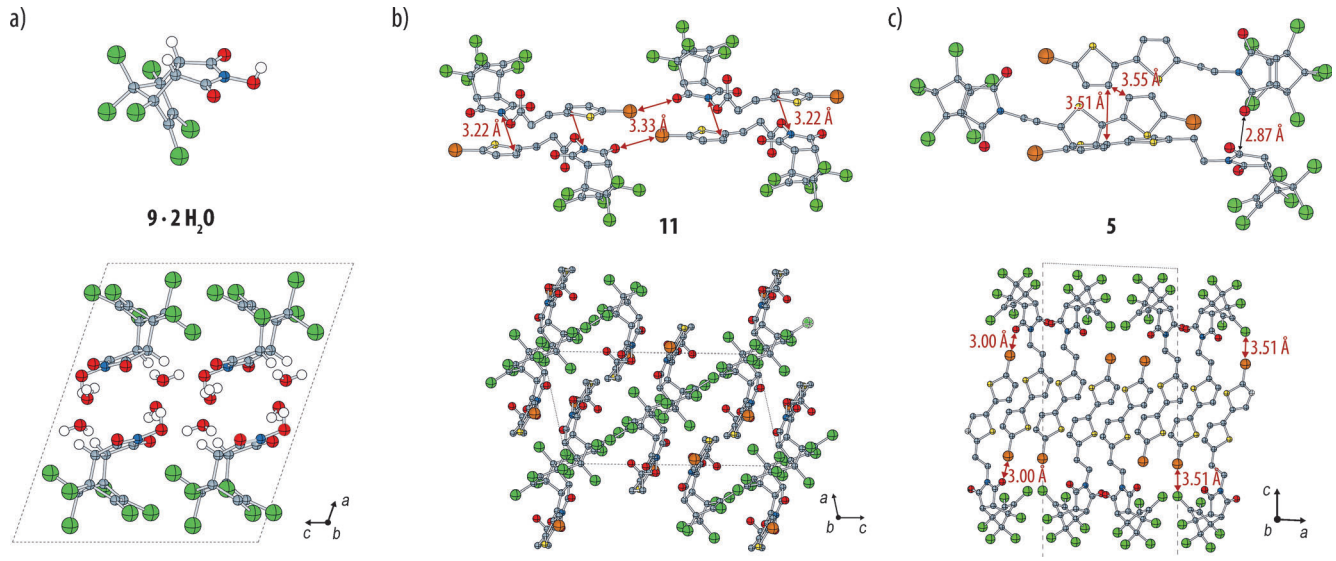


Figure 1. Single-crystal X-ray structures of a) the chorendylhydroxylimide **9** in a cocrystal with water; b) the bromothiophene chlorendylimide active ester **11**, and c) the bromobithiophene chlorendylimide **5**, chosen as representative examples of the packing patterns observed for **2–13**. All crystal structures showed a packing of the π-conjugated segments and the chlorendylimide residues into separate layers, with multiple Cl···Cl short contacts between the chlorendylimide moieties (see **11** and **5**). All unsymmetric bi- and terthiophenes (such as **5**) featured an interdigitated herringbone packing of the π-conjugated segments. Additional supramolecular interactions observed in the structures **2–13** include π–π stacking between the thiophene rings and succinimide moieties, imide–imide interactions, as well as Br···Cl or Br···O short contacts for brominated derivatives such as **11** and **5**. See also the Supporting Information, Figures S1–S14 for the single-crystal X-ray structures of the other intermediates.

the sexithiophene bisimide **8** were dominated by the same placement of the *N*-chlorendylimides oligothiophenes into separate layers, with similar Cl···Cl, Cl···O, and O···C short contacts. However, they were still distinctly different from the crystal structures of the intermediates described above because the symmetric attachment of the two terminal *N*-chlorendylimides did not allow for an interdigitated packing of the oligthiophenes.

The quaterthiophene cores in **7**·DMSO were organized into layers with a herringbone arrangement (Figure 2). However, the tilt angle of the quaterthiophene long axis with respect to the layer normal of 56° was much larger than typically observed tilt angles in oligothiophenes, such as 24° in the parent quaterthiophene (α4T).[37] Moreover, the oligothiophene layer was "interrupted" by channels containing DMSO solvate molecules along the [1 0 0] axis. In the case of **7**·toluene (Figure 2; the Supporting Information, Figure S7), the *N*-chlorendylimides and quaterthiophenes were packed into separate layers. Notably, the molecules did not assume a herringbone packing. Instead, parallel-displaced π–π interactions was observed, with carbon–sulfur short contacts of 3.73 Å and a large tilt angle of 70° of the quaterthiophene long axis relative to the layer normal. Moreover, a parallel-displaced π–π interaction with a C···S short contact of less than 3.6 Å was observed between one of the thiophenes and the succinylimide fragment of a neighboring molecule. The oligothiophene layer was again interrupted by channels of toluene solvate molecules along the [0 1 0] direction. Finally, the sexithiophene bisimide **8** featured a herringbone packing with a remarkably large tilt angle of 68° of the oligothiophene long axes with respect to the layer normal (Figure 2 and the Supporting Information, Figure S8).

The normalized UV/Vis spectra (Figure 3) of the oligothiophene chlorendylimides **4**, **6**, **7**, and **8** in CH_2Cl_2, as well as the oligothiophene active esters **12**, **14**, **16**, and **17** in THF solutions at concentrations of up to $c = 0.5\ mmol\,L^{-1}$ showed absorption maxima at 311, 360, 400, 440, and 309, 360, 401, 440 nm respectively, in excellent agreement with the absorption spectra expected for molecularly disperse bi-, ter-, quarter-, and sexithiophenes.[24,38] Likewise, the UV/Vis spectra of the perylene bisimide active ester **20** in THF up to a concentration of $c = 0.1\ mmol\,L^{-1}$ showed maxima at 523, 487, and 457 nm, that is, the typical features of non-aggregated perylene bisimides.[39] Plots of the UV/Vis absorption spectra for a broad range of concentrations did not show any appearance of new bands or a shift of the absorption bands when following Lambert–Beer's law up to concentrations of at least $6\ mmol\,L^{-1}$ (**7**), $30\ \mu mol\,L^{-1}$ (**8**), $7\ mmol\,L^{-1}$ (**16**), $0.7\ mmol\,L^{-1}$ (**17**), and $1\ mmol\,L^{-1}$ (**20**), indicating that the molecules did not aggregate in the investigated concentration range (the Supporting Information, Figures S15–S17). The corresponding fluorescence emission spectra in solution exhibited well-defined bands with Stokes shifts on the order of 60–70 nm and maxima at 372, 436, 460, and 513 nm for the chorendylimides, 370, 435, 460, and 511 nm for the active esters, as well as 532 nm for the perylene derivative, all similar to those previously reported for molecularly disperse solutions of such compounds.[38–39] The emission spectra did not change in shape for different excitation wavelengths, proving that the absorption peaks originated from a single type of species in each case. Only the octathiophene active ester **18** showed a broadened UV/Vis absorption band with features reminiscent of a vibronic fine structure, and the emission spectra were dependent on the excitation wavelength even in dilute solution ($c =$

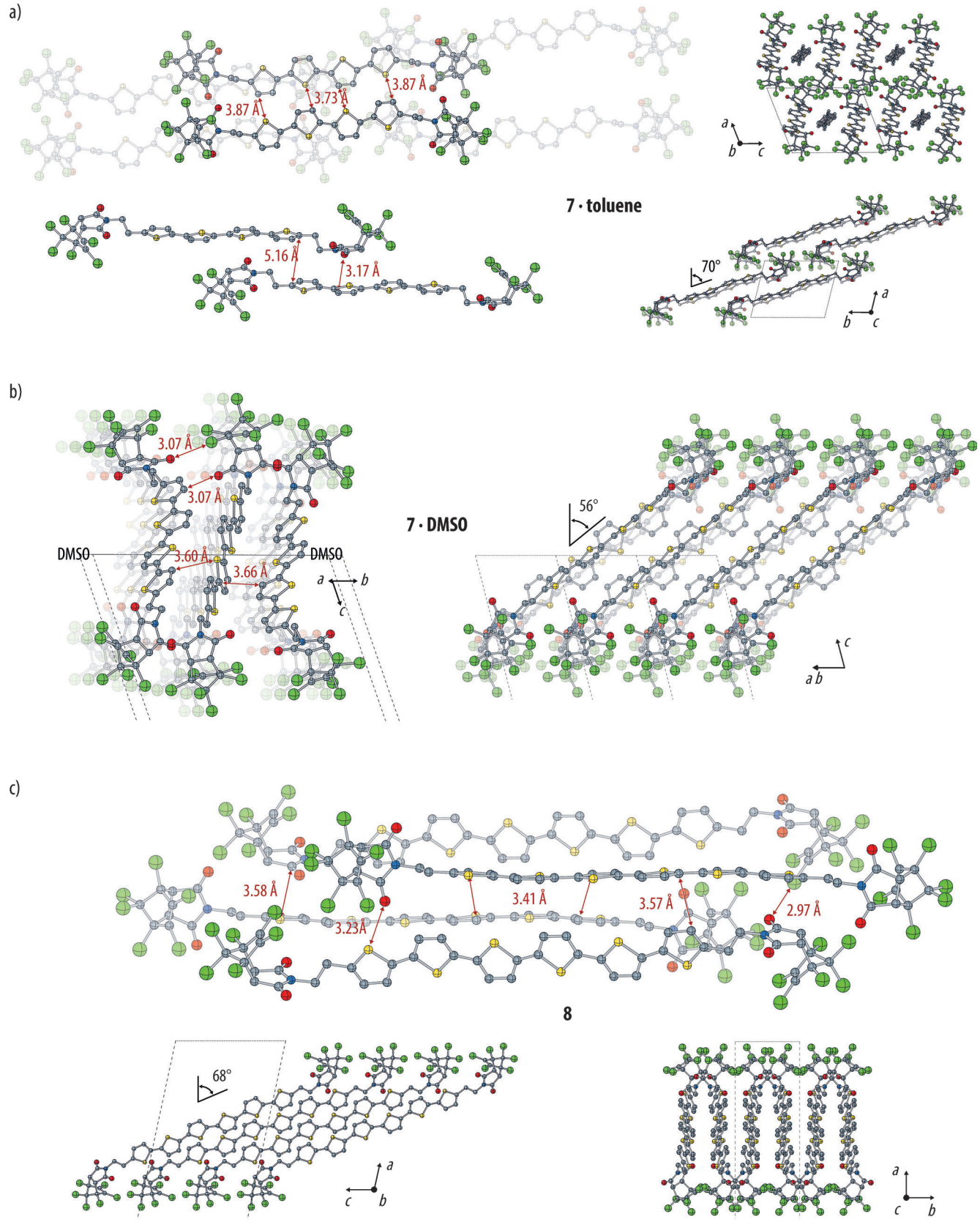


Figure 2. Representations of the single-crystal X-ray structures along different crystallographic directions of the quaterthiophene bischlorendylimide **7** in crystal structures comprising a) toluene and b) DMSO solvate molecules, as well as c) the sexithiophene bischlorendylimide **8**. In all three structures, compounds **7** and **8** formed layered structures with the two terminal chlorendylimides placed on the layer surfaces. Inside the layers, the mismatch in spatial demand between the chlorendylimide residues and the π-conjugated segments resulted in large tilt angles between the long axis and the layer normal of the π-conjugated segments. The oligothiophenes assumed a herringbone packing with both edge-to-face and face-to-face pairs of molecules (as shown for **7**·DMSO and **8**), with the notable exception of **7**·toluene, which only showed a strongly displaced π–π stacking with carbon–sulfur short contacts of 3.73 Å.

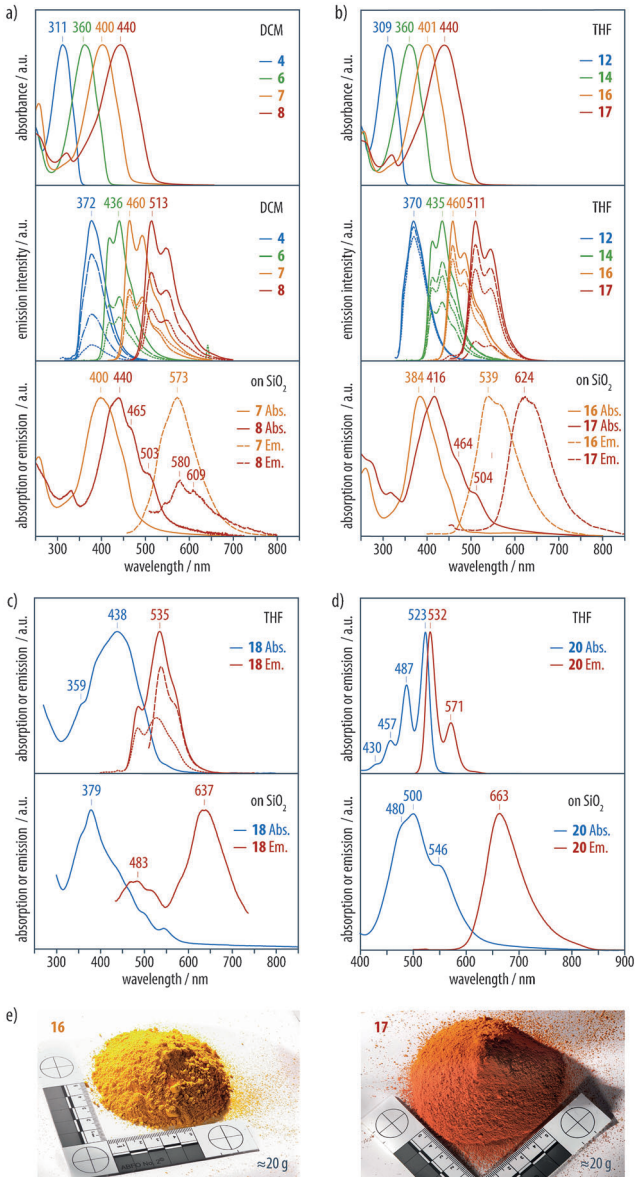


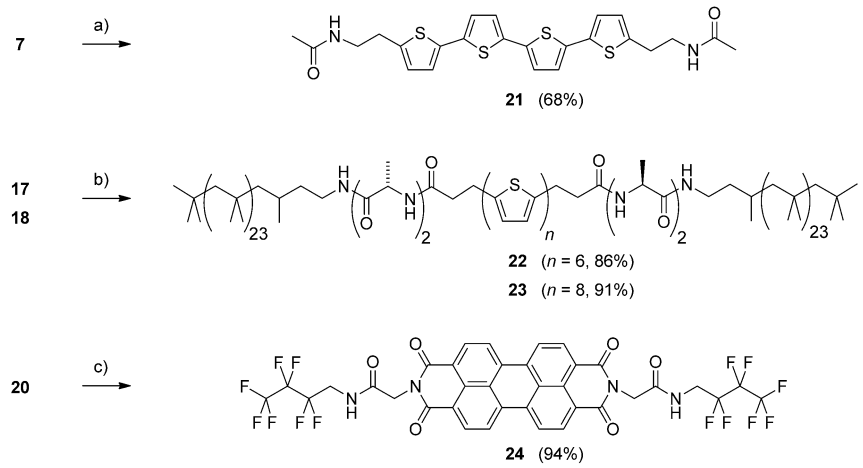
Figure 3. a–d) Normalized UV/Vis absorption spectra and the corresponding normalized fluorescence emission spectra in solution, as well as the solid-state absorption and emission spectra of thin films cast from DMSO (**7**, **8**) or THF (**16, 17, 18, 20**) onto fused silica substrates; the different fluorescence emission spectra were measured at the following excitation wavelengths (in the order of decreasing emission intensity): Compound **4** (310, 300, 340, 280 nm), **6** (360, 400, 320 nm), **7** (400, 360, 440 nm; solid state 400 nm), **8** (440, 400, 480 nm; solid state 440 nm), **12** (313, 300, 325 nm), **14** (360, 390, 330, 320 nm), **16** (400, 425, 375 nm; solid state 384 nm), **17** (439, 465, 410, 320 nm; solid state 413 nm), **18** (445, 500, 390 nm; solid state 380 nm), **20** (457 nm; solid state 480 nm); e) Photographs of the microcrystalline powders **16** and **17** (samples of 20 g each).

2 μmol L), indicating the presence of spectroscopic aggregates in THF solution.

UV/Vis and fluorescence spectroscopy on thin films cast from organic solvents onto fused silica substrates proved that the chlorendylimides **7** and **8**, the active esters **16**–**18**, and the perylene derivative **20** gave rise to spectroscopic aggregates in the solid state. For instance, the absorption maxima of the active esters **16**–**18** and the perylene **20** were significantly blueshifted in the solid state, the sexithiophenes **8** and **17** as well as the octathiophene **18** exhibited a vibronic fine structure, and all fluorescence emission spectra experienced a drastic redshift of up to 130 nm, as compared with the solution-phase spectra. Nevertheless, all compounds retained some fluorescence in the solid state (the Supporting Information, Figure S18).

Our findings therefore suggest that, although the chlorendylimidyl-protected oligothiophene and perylene derivatives did exhibit some electronic interactions between the chromophores in the solid state, they only displayed a low tendency for aggregation in organic solution (with the exception of octathiophene **18**). This finding is supposedly the reason for the fact that they can be handled straightforwardly in solution up to relatively high concentrations. At the same time, the protected amine and carboxylic acid groups are representative examples of functionalities that can be used in reactions with electrophiles or nucleophiles, respectively, to obtain a variety of functionalized π-conjugated compounds. In our hands, they proved to be versatile synthetic precursors for the preparation of various amide-functionalized π-conjugated molecules by simple transformations (Scheme 2). The thus-obtained products are valuable compounds for the investigation of the hydrogen-bonding-directed crystallization or solution-phase self-assembly towards organic electronic materials and devices. For instance, the quaterthiophene chlorendylimide **7** was straightforwardly converted into the quaterthiophene bis(acetamide) **21** by deprotection through hydrazinolysis followed by acetylation with acetic anhydride in typical yields of 60–70% over two steps on reaction scales of up to 1 g. The resulting quaterthiophene bis(acetamide) **21** could be further purified by sublimation and was used to prepare crystalline thin films by physical vapor deposition to fabricate organic field-effect transistors.[40]

The oligothiophene or perylene bisimide active esters **16**–**18** and **20** were even more convenient precursors because the chlorendylimidyl esters served as temporary protecting groups that were sufficiently stable during their synthesis but could be directly converted into the corresponding amide-functional derivatives in a single step by simple addition of the desired amine without the addition of a base or coupling reagent. This was even true for the octathiophene active ester **18** that was treated straightforwardly with amines, despite its somewhat lower solubility. Thus, the sexi- and octathiophene chlorendylimidyl active esters **17** and **18** were coupled to the free amine terminus of L-alanyl-L-alanyl-poly(isobutylene) in THF. The corresponding polymer-oligopeptide-substituted sexi- and octathiophenes **22** and **23** were isolated in yields of 1.2 g (86%) and 751 mg (91%), respectively, after purification by repeated precipitation from THF into MeOH in both cases (Scheme 2). Such derivatives serve to prepare well-defined organic nanowires by solution-phase self-assembly.[28–30] Similarly, treating the chlorendylimidyl active ester of the diglycyl-substituted perylene bisimide **20** with 2,2,3,3,4,4,4-heptafluorobutyl amine in DMSO at room temperature furnished the corresponding bis(heptafluorobutylamide) **24** isolated as a crystalline dark-red powder in a yield of 94% on a 2 g scale (Scheme 2). In this



Scheme 2. Synthesis of various amide-functionalized π-conjugated molecules from different chlorendylimidyl precursors (for hydrogen-bonding-directed crystallization or solution-phase self-assembly). Reaction conditions: a) $H_2N{-}NH_2{\cdot}H_2O$, THF, reflux, then Ac_2O, DMSO, 100 °C; b) PIB_{19}-Ala_2-H, THF, RT; c) 2,2,3,3,4,4,4-heptafluorobutyl amine, DMSO, RT.

case, the product precipitates directly from the reaction mixture, and purification only involved filtration and washing. This polyfluorinated, and hydrogen-bonded product may give rise to air-stable n-type semiconducting crystalline thin films[41] with improved crystalline order.

Conclusion

The use of chlorendyl imides as (temporary) protecting groups for either amines or carboxylic acids, represents a versatile tool for the synthesis of end-functionalized π-conjugated molecules on large reaction scales. In this context, the chlorendylimide moieties fulfill the double task of enhancing the solubility of all intermediates and products while, at the same time, improving their crystallizability. This unusual property profile is supposedly due to the chlorendylimides' unique combination of steric demand, rigidity, and polarity, which may also prove to be useful for the solution of other synthetic challenges in organic chemistry. As a result, the synthesis and purification at all stages was facilitated because almost no column chromatography was required, and all compounds could be conveniently prepared on reaction scales of up to several tens of grams, including the notoriously difficult-to-handle end-substituted octathiophene and perylene bisimide derivatives. Moreover, the chlorendylimidyl-protected amines and acids are useful precursors in subsequent reactions with electrophiles or nucleophiles, respectively, which allowed us to synthesize a variety of end-functionalized π-conjugated compounds in a divergent synthetic approach. This is particularly true for the chlorendylimidyl active esters that serve as temporary protecting groups and can be directly reacted with free amines without the use of any additional reactants. We used them, for example, to prepare various amide-functional oligothiophenes or perylene bisimides straightforwardly. The thus obtained products do not comprise sterically demanding substituents anymore and are therefore highly suited for use in organic electronics. In particular, the hydrogen-bonded π-conjugated molecules described here are important precursors for the fabrication of organic electronic materials and devices and have already shown promising properties in organic field-effect transistors or in organic nanowire devices.[28–30,40,42]

Experimental Section

Syntheses

2-Chlorendylimidylethylthiophene (2): 2-(Thien-2-yl)ethylamine (38.6 g, 303 mmol) was dissolved in toluene (300 mL) and chlorendic anhydride **1** (114 g, 306 mmol) was added. The reaction mixture was heated at reflux using a Dean–Stark trap for 4 h. It was then cooled to room temperature, and the solvent was removed in vacuo to yield the crude product (149 g) as a colorless solid, which was typically used without further purification for the next reaction. The pure thiophene **2** can be obtained by concentrating the reaction mixture to half of its volume; the product starts to crystallize upon cooling. Typical yields are around 80% of pure product in the form of colorless crystals. Crystals of **2** suitable for single-crystal X-ray analysis were obtained by slow evaporation or cooling of a solution in toluene over a few hours. R_f (CH_2Cl_2): 0.70; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.99$ (m, 2H, CH_2), 3.72 (m, 2H, CH_2), 3.84 (s, 2H, 2 C*H*), 6.87 (dd, $J = 3.4$, 1.0 Hz, 1H, Ar-*H*), 6.93 (dd, $J = 3.5$, 5.1 Hz, 1H, Ar-*H*), 7.16 ppm (dd, $J = 1.1$, 5.1 Hz, 1H, Ar-*H*). ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 27.8$, 40.6, 52.0, 79.4, 104.2, 124.5, 126.0, 127.3, 131.0, 138.9, 169.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 234 nm (9800 L mol^{-1} cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{15}H_9Cl_6NO_2SNa$: 501.8348 $[(M+2)+Na]^+$; found: 501.8349; elemental analysis calcd (%) for $C_{15}H_9Cl_6NO_2S$: C 37.53, H 1.89, N 2.92; found: C 37.76, H 1.80, N 2.78.

2-Bromo-5-chlorendylimidylethylthiophene (3): The crude product **2** (149 g) was dissolved in DMF (500 mL), and NBS (56.7 g, 319 mmol) was added. The flask was shielded from light with aluminum foil, and the solution was stirred overnight. The reaction mixture was then poured into 1 M HCl (3.5 L), and the precipitate was filtered off, taken up in acetone (750 mL), and precipitated once more into 1 M HCl (3.5 L). After filtration, the precipitate was dried at 80 °C in vacuo to yield the pure bromothiophene **3** (155 g, 278 mmol, 91% over 2 steps) as a colorless powder. Crystals of **3** suitable for single-crystal X-ray analysis were obtained by slow evaporation or cooling of a solution in toluene over a few hours. R_f (CH_2Cl_2): 0.70; M.p. (DSC in N_2): 154–156 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.89$ (m, 2H, CH_2), 3.66 (m, 2H, CH_2), 3.85 (s, 2H, 2 C*H*), 6.63 (d, $J = 3.7$ Hz, 1H, Ar-*H*), 6.87 ppm (d, $J = 3.7$ Hz, 1H, Ar-*H*); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 28.1$, 40.1, 52.0, 79.3, 104.2, 110.5, 126.5, 130.0, 130.9, 140.6, 169.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 nm (10300 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd for $C_{15}H_8BrCl_6NO_2S$ 554.7585 $[M]^+$; found: 554.7586; elemental analysis calcd (%) for $C_{15}H_8BrCl_6NO_2S$: C 32.23, H 1.44, N 2.51; found: C 32.29, H 1.27, N 2.37.

5-Chlorendylimidylethyl-2,2′-bithiophene (4): Bromothiophene **3** (96.6 g, 173 mmol) was dissolved in DMF (250 mL), and 2-(*n*-tributylstannyl)-thiophene (67.7 g, 181 mmol) was added. Argon was

bubbled through the solution for 30 min. Then, the reaction mixture was heated to 100 °C. Bis(triphenylphosphine)palladium(II) chloride (1.21 g, 1.73 mmol) was added, and the solution was stirred for 3 h. The reaction mixture was then cooled to room temperature and extracted four times with *n*-heptane (250 mL). The DMF phase was then poured into water (1.5 L). The precipitate was filtered off and dried at 90 °C in vacuo. The solid residue was then dissolved in CH_2Cl_2 and filtered over silica gel. After removal of the solvent, the residue was purified by fractionating crystallization from CH_2Cl_2/MeOH (2:1). The pure bithiophene **4** (73.2 g, 130 mmol, 75%) was obtained as a colorless crystalline solid. Crystals of **4** suitable for single-crystal X-ray analysis were obtained by slow evaporation of a solution in toluene over a few days. R_f (CH_2Cl_2): 0.70; M.p. (DSC in N_2): 159–161 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.95$ (m, 2H, C*H*$_2$), 3.73 (m, 2H, C*H*$_2$), 3.85 (s, 2H, 2 C*H*), 6.77 (dt, $J = 0.8$, 3.6 Hz, 1H, Ar-*H*), 6.99 (m, 2H, Ar-*H*), 7.11 (dd, $J = 1.1$, 3.6 Hz, 1H, Ar-*H*), 7.19 ppm (dd, $J = 1.2$, 5.1 Hz, 1H, Ar-*H*); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 28.0$, 40.3, 52.0, 79.3, 104.2, 123.6, 123.7, 124.4, 126.7, 127.9, 130.9, 136.5, 137.3, 138.0, 169.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 309 nm (13 800 L mol^{-1} cm^{-1}); HRMS (MALDI): *m/z* calcd (%) for $C_{19}H_{11}Cl_6NO_2S_2^+$: 560.8333 $[M+2]^+$; found: 560.8360; elemental analysis calcd (%) for $C_{19}H_{11}Cl_6NO_2S_2$: C 40.60; H 1.97; N 2.49; found: C 40.09; H 1.84; N 2.30.

5-Bromo-5′-chlorendylimidylethyl-2,2′-bithiophene (5): NBS (6.46 g, 36.3 mmol) was added to a solution of bithiophene **4** (20.0 g, 35.6 mmol) in DMF (150 mL). The flask was shielded from light with aluminum foil, and the solution was stirred overnight. The reaction mixture was then poured into 1 M HCl (800 mL). The precipitate was filtered off, taken up in acetone (400 mL), and precipitated once more into 1 M HCl (1.30 L). After filtration, the precipitate was dried at 70 °C in vacuo to yield bromobithiophene **5** (21.9 g, 34.2 mmol, 96%) as a colorless powder. Crystals of **5** suitable for single-crystal X-ray analysis were obtained by slow evaporation of a solution in toluene over about 1 week. R_f (CH_2Cl_2): 0.70; M.p. (DSC in N_2): 145–147 °C. ^{1}H NMR (400.13 MHz, [D$_6$]DMSO): $\delta =$ 2.86 (m, 2H, C*H*$_2$), 3.61 (m, 2H, C*H*$_2$), 4.14 (s, 2H, 2 C*H*), 6.94 (d, $J =$ 3.6 Hz, 1H, Ar-*H*), 7.09 (d, $J = 3.9$ Hz, 1H, Ar-*H*), 7.14 (d, $J = 3.6$ Hz, 1H, Ar-*H*), 7.20 ppm (d, $J = 3.9$ Hz, 1H, Ar-*H*); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 28.0$, 40.3, 52.0, 79.4, 104.2, 111.0, 123.7, 124.0, 126.8, 130.7, 130.9, 135.5, 138.6, 138.8, 169.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) 318 nm (15 800 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd for $C_{19}H_{10}BrCl_6NO_2S_2^+$: 636.7462 $[M]^+$; found: 636.7461; elemental analysis calcd (%) for $C_{19}H_{10}BrCl_6NO_2S_2$: C 35.60; H 1.57; N 2.18; found: C 35.13; H 1.46; N 2.04.

5-Chlorendylimidylethyl-2,2′:5′,2′-terthiophene (6): The bromobithiophene **5** (15.0 g, 23.4 mmol) was dissolved in DMF (50 mL), and 2-(*n*-tributylstannyl)-thiophene (9.00 g, 24.1 mmol) was added. Argon was bubbled through the solution for 30 min. Then, the reaction mixture was heated to 100 °C. Bis(triphenylphosphine)palladium(II) chloride (164 mg, 0.24 mmol) was added, and the solution was stirred overnight. The reaction mixture was cooled to room temperature and extracted three times with *n*-heptane (50 mL). The DMF phase was then concentrated to dryness, and the residue was dissolved in CH_2Cl_2 and filtered over silica gel. After removal of the solvent, the residue was purified by fractionating crystallization from acetone. The pure terthiophene **6** (9.28 g, 14.4 mmol, 62%) was obtained as pale-yellow crystalline solid. Crystals of **6** suitable for single-crystal X-ray analysis were obtained by slow evaporation of a solution in toluene over about 2 weeks. R_f (CH_2Cl_2): 0.70; M.p. (DSC in N_2): 217–219 °C; ^{1}H NMR (400.13 MHz, [D$_6$]DMSO): $\delta = 2.87$ (m, 2H, C*H*$_2$), 3.62 (m, 2H, C*H*$_2$), 4.14 (s, 2H, 2 C*H*), 6.95 (d, $J =$ 3.6 Hz, 1H, Ar-*H*), 7.10 (dd, $J = 3.6$, 5.1 Hz, 2H, Ar-*H*), 7.17 (d, $J =$ 3.6 Hz, 1H, Ar-*H*), 7.21 (d, $J = 3.8$ Hz, 1H, Ar-*H*), 7.25 (d, $J = 3.8$ Hz, 1H, Ar-*H*), 7.33 (dd, $J = 1.1$, 3.6 Hz, 1H, Ar-*H*), 7.21 ppm (dd, $J = 1.1$, 5.1 Hz, 1H, Ar-*H*); ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 27.5$, 39.3 (under DMSO signal), 51.74, 78.8, 103.9, 124.1, 124.2, 124.6, 124.8, 125.6, 127.2, 128.4, 130.3, 134.7, 135.2, 135.2, 136.0, 138.7, 170.22 ppm; UV/Vis (DCM): λ_{max} (ε) = 360 nm (22 100 L mol^{-1} cm^{-1}); HRMS (QTOF): *m/z* calcd for $C_{23}H_{13}Cl_6NO_2S_3^+$: 642.8205 $[M+2]^+$; found: 642.8241; elemental analysis calcd (%) for $C_{19}H_{10}Cl_6NO_2S_3$: C 42.88; H 2.03; N 2.17; found: C 42.81; H 1.85; N 1.48.

5,5‴-Bis(chlorendylimidylethyl)-2,2′:5′,2″:5″,2‴-quaterthiophene (7): The bithiophene **4** (70.0 g, 125 mmol), $AgNO_3$ (43.0 g, 253 mmol), and KF (14.5 g, 250 mmol) were dissolved in DMSO (400 mL) under argon atmosphere. Bis(benzonitrile)palladium(II) chloride (2.40 g, 6.26 mmol) was added, and the flask was shielded from light with aluminum foil. The mixture was heated to 85 °C and stirred overnight. Then, the same amounts of $AgNO_3$, KF, and bis(benzonitrile)palladium(II) chloride were added once again, and the reaction mixture was stirred at 85 °C for another 5 h before the solvent was removed in vacuo. The resulting residue was loaded onto silica gel (500 mL) from a THF solution (2 L) and purified by filtration over silica gel (THF). The filtrate was concentrated in vacuo and the residue was suspended in CH_2Cl_2 (500 mL). The suspended solid was then collected by filtration and dried in air to give the pure quaterthiophene **7** (42.3 g, 60%) as a yellow powder. Crystals of **7** suitable for single-crystal X-ray analysis were either obtained by slow evaporation of a solution in toluene over a few days, or by slow cooling of hot saturated solutions in DMSO. R_f (CH_2Cl_2): 0.57; M.p. (DSC in N_2): 248–250 °C; ^{1}H NMR (400.13 MHz, [D$_6$]DMSO): $\delta = 2.87$ (m, 2H, C*H*$_2$), 3.63 (m, 2H, C*H*$_2$), 4.14 (s, 2H, 2 C*H*), 6.96 (d, $J = 3.6$ Hz, 1H, Ar-*H*), 7.19 (d, $J = 3.6$ Hz, 1H, Ar-*H*), 7.23 (d, $J = 3.8$ Hz, 1H, Ar-*H*), 7.29 ppm (d, $J = 3.8$ Hz, 1H, Ar-*H*); ^{13}C NMR (100.62 MHz, [D$_6$]DMSO): $\delta = 15.2$, 27.5, 51.8, 78.8, 103.9, 124,3, 124.8, 125.1, 127.3, 130.4, 134.6, 134.6, 135.5, 138.9, 170.3 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 399 nm (40 200 L mol^{-1} cm^{-1}); HRMS (ESI): *m/z* calcd (%) for $C_{38}H_{20}Cl_{12}N_2O_4S_4^+$: 1115.6563 $[M]^+$; found: 1115.6537.

5,5‴′-Bis(chlorendylimidylethyl)-2,2′:5′,2″:5″,2‴:5‴,2‴′:5‴′,2‴″-sexithiophene (8): The terthiophene **6** (5.0 g, 7.76 mmol) and AgF (1.97 g, 15.5 mmol) were dissolved in dry DMSO (50 mL) under an argon atmosphere. Bis(benzonitrile)palladium(II) chloride (298 mg, 0.78 mmol) was added, and the flask was shielded from light with aluminum foil. The mixture was heated to 85 °C for 2 d. Then, the same amounts of AgF and bis(benzonitrile)palladium(II) chloride were added once again, and the reaction mixture was stirred at 85 °C for another 2 d. The reaction mixture was cooled to room temperature and diluted with THF (100 mL). The resulting precipitate was collected by filtration. After careful washing with CH_2Cl_2 and drying, a continuous extraction of the precipitate with hot DMSO (≈200 °C) from the same filter yielded pure sexithiophene **8** (3.02 g, 60%) in the form of orange-red crystals. Crystals of **8** suitable for single-crystal X-ray analysis were obtained by cooling of hot saturated solutions in DMSO over about 10 min. R_f (CH_2Cl_2): 0.57; ^{1}H NMR (400.13 MHz, [D$_6$]DMSO, 120 °C): $\delta = 2.95$ (m, 4H, C*H*$_2$), 3.66 (m, 4H, C*H*$_2$), 4.14 (s, 4H, 2 C*H*), 6.93 (m, 2H, Ar-*H*), 7.16 (m, 2H, Ar-*H*), 7.21 (m, 2H, Ar-*H*), 7.28 ppm (m, 6H, Ar-*H*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 440 nm (61 100 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd for $C_{46}H_{24}Cl_{12}N_2O_4S_6^+$: 1279.6317 $[M]^+$; found: 1279.6318.

Chlorendic hydroxylimide (9): Hydroxylamine hydrochloride (18.7 g, 269 mmol) was added to a solution of potassium carbonate (18.6 g, 134 mmol) in water (800 mL). After stirring for 5 min, chlorendic anhydride **1** (100 g, 269 mmol) was added. The resulting mixture was heated to reflux (130 °C) for 24 h and then cooled to 0 °C. The obtained precipitate was filtered off, washed with water, dried under air flow and then in vacuo to afford **9** as a grey

powder (96.0 g, 92%) that can directly be used for subsequent reactions, or further be purified by fractionated recrystallization from MeOH to obtain a white solid (73 g, 70%). Crystals of **9** suitable for single-crystal X-ray analysis were obtained by slow recrystallization from THF solutions after the addition of MeOH (THF/MeOH 1:10) over a few hours. R_f (CH_2Cl_2/MeOH 10:1): 0.32; M.p.: 252–254 °C; ^{1}H NMR (400.13 MHz, [D$_6$]DMSO): δ = 4.07 (s, 2H, 2 *CH*), 11.50 ppm (s, 1H, *OH*); ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 49.1, 78.7, 103.7, 130.5, 166.2 ppm; HRMS (ESI): *m/z* calcd for $C_9H_2Cl_6NO_3^-$: 383.8141 $[M-H]^-$; found: 383.8143; elemental analysis calcd (%) for $C_9H_3Cl_6NO_3$: C 28.09; H 0.78; N 3.63; found: C 27.86; H 0.96; N 3.43.

Chlorendylimidyl-3-(thien-2-yl)propanoate (10): 3-(Thien-2-yl)propionic acid (28.5 g, 182 mmol), **9** (70.6 g, 182 mmol), and DPTS (53.8 g, 182 mmol) were dissolved in CH_2Cl_2 (1 L) and EDCI (45.6 g, 237 mmol) was added. The reaction mixture was stirred for 4 h, washed with water (4 times), and finally with brine. The organic phase was dried over $MgSO_4$ and solvent was removed to yield the product (95.3 g, 99%) as a brownish solid. Crystals suitable for single-crystal X-ray analysis of thiophene active ester **10** were obtained by slow recrystallization from CH_2Cl_2 solutions after the addition of MeOH (CH_2Cl_2/MeOH 1:5) over a few hours. R_f (CH_2Cl_2): 0.60; M.p.: 146–148 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.95 (t, *J* = 7.6 Hz, 2H, C*H*$_2$C(O)), 3.26 (t, *J* = 7.6 Hz, 2H, C*H*$_2$-Ar), 3.96 (s, 2H, 2C*H*), 6.86 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 6.90–6.95 (m, 1H, Ar-*H*), 7.16 ppm (dd, *J* = 1.2, 5.2 Hz, 1H, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$, 50 °C): δ = 24.9, 33.0, 50.0, 79.3, 104.1, 124.2, 125.4, 127.2, 131.6, 141.3, 162.9, 166.6 ppm. UV/vis (THF): λ_{max} (ε) = 233 nm (10500 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd for $C_{16}H_9Cl_6NO_4S$ 520.8378 $[M]^+$; found: 520.8381; elemental analysis calcd (%) for $C_{16}H_9Cl_6NO_4S$: C 36.67; H 1.73; N 2.67; found: C 36.61; H 1.58; N 2.54.

Chlorendylimidyl-3-(2-bromothien-5-yl)-propanoate (11): The thiophene active ester **10** (95.1 g, 181 mmol) was dissolved in DMF (500 mL) and cooled to 0 °C before adding NBS (32.9 g, 185 mmol). The reaction flask was shielded from light with aluminum foil, and the reaction mixture was stirred overnight. Diisopropyl ether (500 mL) was added, and the mixture was cooled to 0 °C. Then, water was added, and the aqueous phase was extracted twice with diisopropyl ether (200 mL). The combined organic phases were washed three times with water. Brown crystals of **11** (76.5 g, 70%) formed from the organic phase overnight. By repeating the previous purification/crystallization procedure with the supernatant, a second fraction of **11** (12.7 g) was collected. Thus, a total of 89.1 g (81%) of pure **11** was obtained. Crystals of **11** suitable for single-crystal X-ray analysis were obtained by slow recrystallization from CH_2Cl_2 solutions after the addition of MeOH (CH_2Cl_2/MeOH 1:5) over a few hours. R_f (CH_2Cl_2): 0.65; M.p.: 115–117 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.91 (t, *J* = 7.6 Hz, 2H, C*H*$_2$C(O)), 3.17 (t, *J* = 7.6 Hz, 2H, C*H*$_2$-Ar), 3.96 (s, 2H, 2 *CH*) 6.62 (d, *J* = 3.6 Hz, 1H, Ar-*H*), 6.87 ppm (d, *J* = 3.6 Hz, 1H, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$, 50 °C): δ = 25.2, 32.7, 50.0, 79.3, 104.1, 110.5, 126.0, 130.1, 131.6, 142.9, 162.8, 166.4 ppm; UV/Vis (THF): λ_{max} (ε) = 237 nm (10200 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd for $C_{16}H_9BrCl_6NO_4S$: 598.7483 $[M]^+$; found: 598.7496; elemental analysis calcd (%) for $C_{16}H_8BrCl_6NO_4S$: C 31.87; H 1.34; N 2.32; found: C 31.91; H 1.26; N 2.25.

Chlorendylimidyl-3-(2,2′-bithien-5-yl)propanoate (12): A 500 mL Schlenk flask was charged with 2-(tributylstannyl)thiophene (14.6 mL, 45.8 mmol), compound **11** (25.1 g, 41.6 mmol), and acetonitrile (100 mL). Bis(triphenylphosphine)palladium(II) chloride (584 mg, 2 mol%, 0.92 mmol) was then added. The reaction mixture was stirred overnight at 80 °C and then extracted five times with heptane. A careful filtration over silica gel (CH_2Cl_2) afforded the product as a light-yellow solid (19.0 g, 75%). Crystals of **12** suitable for single-crystal X-ray analysis were obtained by slow recrystallization from CH_2Cl_2 solutions after the addition of MeOH (CH_2Cl_2/MeOH 1:5) over a few hours. R_f (CH_2Cl_2): 0.65; M.p.: 162–164 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.96 (t, *J* = 7.6 Hz, 2H, C*H*$_2$C(O)), 3.23 (t, *J* = 7.6 Hz, 2H, C*H*$_2$-Ar), 3.96 (s, 2H, 2 C*H*), 6.73–6.80 (m, 1H, Ar-*H*), 6.95–7.04 (m, 2H, 2 Ar-*H*), 7.11 (dd, *J* = 1.2 Hz, 3.6 Hz, 1H, Ar-*H*), 7.18 ppm (dd, *J* = 3.6, 5.2 Hz, 1H, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$, 50 °C): δ = 25.1, 32.9, 50.0, 79.3, 104.1, 123.8, 123.9, 124.4, 126.2, 127.9, 131.6, 136.4, 137.6, 140.5, 162.8, 166.5 ppm; UV/Vis (THF): λ_{max} (ε) = 309 nm (13900 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd $C_{20}H_{11}Cl_6NO_4S_2$: 602.8255 $[M]^+$; found: 602.8262; elemental analysis calcd (%) for $C_{20}H_{11}Cl_6NO_4S_2$: C 39.63; H 1.83; N 2.31; found: C 39.75; H 1.79; N 2.24.

Chlorendylimidyl-3-(5-bromo-2,2′-bithien-5′-yl)-propanoate (13): A solution of **12** (18.9 g, 31.2 mmol) in DMF (200 mL) was cooled to 0 °C before adding NBS (5.68 g, 31.89 mmol). The flask was shielded from light with aluminum foil, and the reaction mixture was stirred overnight at room temperature. Then, it was poured into water and the resulting slurry was stirred overnight. The precipitate was filtered off, washed with deionized water, taken up in THF, and reprecipitated into water. After stirring overnight, the precipitate was filtered off, washed with water, redissolved in CH_2Cl_2 and dried over Mg_2SO_4. Solvent removal afforded the product as a light-yellow solid (21.0 g, 98%). Crystals of **13** suitable for single-crystal X-ray analysis were obtained by slow recrystallization from CH_2Cl_2 solutions after the addition of MeOH (CH_2Cl_2/MeOH, 1:5) over a few hours. R_f (CH_2Cl_2): 0.65; M.p.: 116–118 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.95 (t, *J* = 7.6 Hz, 2H, C*H*$_2$C(O)), 3.21 (t, *J* = 7.6 Hz, 2H, C*H*$_2$-Ar), 3.96 (s, 2H, 2 *CH*), 6.75 (d, *J* = 3.6 Hz, 1H, Ar-*H*), 6.84 (d, *J* = 3.6 Hz, 1H, Ar-*H*), 6.92 (d, *J* = 3.6 Hz, 1H, Ar-*H*), 6.94 ppm (d, *J* = 3.6 Hz, 1H, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$, 50 °C): δ = 25.1, 32.8, 50.0, 79.3, 104.1, 111.1, 123.9, 124.2, 126.3, 130.8, 131.6, 135.4, 139.1, 141.0, 162.8, 166.5 ppm; UV/vis (THF): λ_{max} (ε) = 319 nm (17900 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd for $C_{20}H_{10}BrCl_6NO_4S_2$: 680.7360 $[M]^+$; found: 680.7373; elemental analysis calcd (%) for $C_{20}H_{10}BrCl_6NO_4S_2$: C 35.07; H 1.47; N 2.04; found: C 35.14; H 1.41; N 1.95.

Chlorendylimidyl-3-(2,2′:5′,2″-terthiophen-5″-yl)propanoate (14): A dried 500 mL Schlenk flask was charged with 5-(tributylstannyl)2,2′-bithiophene **25** (28.1 g, 61.7 mmol; see below), dry and degassed DMF (150 mL), and **11** (35.4 g, 58.7 mmol). Bis(triphenylphosphine)palladium(II) chloride (824 mg, 2 mol%, 1.2 mmol) was added. The reaction mixture was stirred overnight at 80 °C and then extracted five times with heptane (500 mL). It was subsequently poured in water and stirred overnight at room temperature. The precipitate was filtered off, washed with deionized water, taken up in THF, and reprecipitated into water. After stirring overnight, the precipitate was filtered off, washed with water, redissolved in chloroform and dried over Mg_2SO_4. Purification by a short column chromatography (2 L SiO_2, CH_2Cl_2) afforded terthiophene **14** as a light-yellow solid (15.8 g, 39%). R_f (CH_2Cl_2): 0.60; M.p.: 170–172 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.96 (t, *J* = 7.6 Hz, 2H, C*H*$_2$C(O)), 3.23 (t, *J* = 7.6 Hz, 2H, C*H*$_2$-Ar), 3.96 (s, 2H, 2 C*H*), 6.77 (d, *J* = 3.6 Hz, 1H, Ar-*H*), 6.96–7.09 (m, 4H, Ar-*H*), 7.16 (dd, *J* = 1.2, 4.0 Hz, 1H, Ar-*H*), 7.22 ppm (dd, *J* = 1.2, 5.2 Hz, 1H, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$, 50 °C): δ = 25.1, 32.8, 50.0, 79.2, 104.1, 123.8, 123.9, 124.3, 124.5, 124.6, 126.3, 128.0, 131.6, 136.1, 136.4, 136.4, 137.3, 140.6, 162.8, 166.4 ppm; UV/Vis (THF): λ_{max} (ε) = 360 nm (24500 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd for $C_{24}H_{13}Cl_6NO_4S_3$: 685.8211 $[M+H]^+$; found: 685.8236; elemental analysis calcd (%) for $C_{24}H_{12}Cl_6NO_4S_3$ C 41.88, H 1.90, N 2.04; found: C 41.96, H 1.92, N 2.15.

Chlorendylimidyl-3-(5-bromo-2,2′:5′,2″-terthiophen-5″-yl)propanoate (15): A solution of **14** (15.0 g, 21.7 mmol) in DMF (150 mL) was cooled to 0 °C before adding NBS (3.95 g, 22.2 mmol). The reaction flask was shielded from light with aluminum foil, and the reaction mixture was stirred overnight at room temperature. Next, it was poured into water and the resulting suspension was stirred overnight. The precipitate was filtered off, washed with deionized water, taken up in THF, and reprecipitated into water. After stirring overnight, the precipitate was filtered off, washed with water, dissolved in CH_2Cl_2, and dried over $MgSO_4$. Filtration over silica gel (CH_2Cl_2) afforded bromoterthiophene **15** as a light-yellow solid (13.1 g, 79%). R_f (CH_2Cl_2): 0.60; M.p.: 176–178 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.96$ (t, $J = 7.6$ Hz, 2H, CH_2C(O)), 3.23 (t, $J = 7.6$ Hz, 2H, CH_2-Ar), 3.97 (s, 2H, 2 C*H*), 6.77 (d, $J = 3.6$ Hz, 1H, Ar-*H*), 6.90 (d, $J = 4.0$ Hz, 1H, Ar-*H*), 6.94–7.02 ppm (m, 4H, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$, 50 °C): $\delta = 25.1$, 32.8, 49.9, 79.2, 104.1, 111.2, 123.9, 124.0, 124.3, 124.8, 126.4, 130.9, 131.6, 135.2, 135.8, 136.9, 138.8, 140.9, 162.8, 166.5 ppm; UV/Vis (THF): λ_{max} (ε) = 366 nm (24.5); HRMS (APPI): *m/z* calcd for $C_{24}H_{13}BrCl_6NO_4S_3$: 763.7316 $[M+H]^+$; found: 763.7351; elemental analysis calcd (%) for $C_{24}H_{12}BrCl_6NO_4S_3$: C 37.58; H 1.58; N 1.83; found: C 37.78; H 1.52; N 1.87.

2,2′:5′,2″:5″,2‴-quaterthiophene-5,5‴-di(propan-3-oic acid) di(chlorendylimidyl ester) (16): Degassed dry DMF (500 mL), degassed 5,5′-bis(tibutylstannyl)-2,2′-bithiophene **26** (45.5 g, 61.1 mmol; see below), and **11** (75.6 g, 125 mmol) were placed in a dried 1 L Schlenk flask. Tetrakis(triphenylphosphine)palladium (353 mg, 0.5 mol%, 0.3 mmol) was added, and the reaction mixture was stirred overnight at 80 °C. DMF was evaporated in vacuo, paying careful attention to keeping the mixture in an inert atmosphere. The residue was subsequently suspended at 60 °C in a mixture of diisopropyl ether (300 mL), toluene (100 mL) and THF (100 mL), and the resulting slurry was stirred overnight. The yellow precipitate was filtered off and washed with diisopropyl ether (100 mL) and pentane (100 mL). The filtrate was concentrated and diluted with dry diisopropyl ether (100 mL) and dry toluene (25 mL) at 60 °C. The yellow precipitate that slowly formed upon stirring was filtered off and washed with diisopropyl ether and pentane. Both fractions were combined to afford quaterthiophene **16** as a yellow microcrystalline solid (40.2 g, 54%). R_f (CH_2Cl_2): 0.38; M.p.: 134–136 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.97$ (t, $J = 7.6$ Hz, 2H, CH_2C(O)), 3.23 (t, $J = 7.6$ Hz, 2H, CH_2-Ar), 3.97 (s, 2H, 2 C*H*), 6.77 (d, $J = 3.6$ Hz, 1H, Ar-*H*), 6.98 (d, $J = 3.6$ Hz, 1H, Ar-*H*), 7.01 (d, $J = 3.6$ Hz, 1H, Ar-*H*), 7.04 ppm (d, $J = 3.6$ Hz, 1H, Ar-*H*); ^{13}C NMR (151 MHz, $CDCl_3$, 50 °C): $\delta = 25.2$, 32.8, 50.0, 79.3, 104.1, 123.9, 124.4, 124.5, 126.4, 131.6, 136.1, 136.1, 136.5, 140.7, 162.8, 166.5 ppm; UV/Vis (THF): λ_{max} (ε) = 401 nm (38 500 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd for $C_{40}H_{20}Cl_{12}N_2O_8S_4$: 1203.6359 $[M]^+$; found: 1203.6361; elemental analysis calcd (%) for $C_{40}H_{20}Cl_{12}N2O_8S_4$: C 39.70; H 1.67; N 2.31; found C 39.59; H 1.69; N 2.11.

2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene-5,5⁗′-di(propan-3-oic acid) di(chlorendylimidyl ester) (17): 5,5′-Bis(tibutylstannyl)-2,2′-bithiophene **26** (15.3 g, 20.6 mmol; see below) and **13** (28.8 g, 42.1 mmol) were dissolved in dry and degassed DMF (200 mL) in a dried 500 mL Schlenk flask. Tetrakis(triphenylphosphine)palladium (477 mg, 2 mol%, 0.41 mmol) was added, and the mixture was stirred overnight at 80 °C. DMF was subsequently removed in vacuo, and the orange residue was dispersed in a mixture of diisopropyl ether (100 mL), toluene (30 mL) and dry THF (30 mL). The mixture was gently heated at reflux (85 °C) for about 15 min. The precipitate was filtered off and washed with three times with diisopropyl ether to afford pure sexithiophene **17** as an orange microcrystalline powder (24.4 g, 86%). R_f (CH_2Cl_2): 0.36; M.p.: 260 °C. ^{1}H NMR (400.13 MHz, [D$_2$]TCE, 80 °C): $\delta = 3.01$ (t, $J = 7.6$ Hz, 4H, CH_2C(O)), 3.29 (t, $J = 7.6$ Hz, 4H, CH_2-Ar), 4.00 (s, 4H, 2 C*H*), 6.84 (d, $J = 3.6$ Hz, 2H, Ar-*H*), 7.02–7.17 ppm (m, 10H, Ar-*H*); ^{13}C NMR (151 MHz, [D$_2$]TCE, 60 °C): $\delta = 24.6$, 32.2, 49.3, 78.6, 123.5, 123.9, 124.1, 124.2, 125.9, 131.0, 135.2, 135.2, 135.5, 135.7, 136.1, 140.3, 162.3 ppm; UV/Vis (THF): λ_{max} (ε) = 440 nm (51 800 L mol^{-1} cm^{-1}); HRMS (APPI): *m/z* calcd for $C_{48}H_{24}Cl_{12}N_2O_8S_6$ 1367.6114 $[M]^+$; found: 1367.6103; elemental analysis calcd (%) for $C_{48}H_{24}Cl_{12}N_2O_8S_6$: C 41.94; H 1.76; N 2.04; found: C 40.73; H 1.71; N 1.79.

2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗′′:5⁗′′-octathiophene-5,5⁗′′-di(propan-3-oic acid) di(chlorendylimidyl ester) (18): A dried 250 mL Schlenk flask was charged with 5,5′-bis(tributylstannyl)2,2′-bithiophene **26** (3.15 g, 4.23 mmol), **15** (6.48 g, 8.45 mmol), and dry and degassed DMF (110 mL). Tetrakis(triphenyl-phosphine)-palladium(0) (244 mg, 0.21 mmol, 5 mol%) was added and the reaction mixture was stirred overnight at 80 °C. The solvent was removed in vacuo, avoiding contact with air, and the resulting solid was redispersed in dry toluene (100 L), stirred 20 min at 100 °C and cooled down. After filtration and washing with toluene, the pure octathiophene **18** was obtained as a red microcrystalline powder (5.21 g, 80%). M.p.: > 400 °C; ^{1}H NMR (400.13 MHz, [D$_2$]TCE, 120 °C): $\delta = 3.03$ (t, $J = 7.6$ Hz, 4H, 2 CH_2C(O)), 3.33 (t, $J = 7.6$ Hz, 4H, 2 CH_2-Ar), 4.00 (s, 4H, 4 C*H*), 6.86 (m, 2H, Ar-*H*), 7.03–720 ppm (m, 14H, Ar-*H*); UV/Vis (THF): λ_{max} (ε) = 438 nm (42 500 L mol^{-1} cm^{-1}). HRMS (APPI): *m/z* calcd for $C_{58}H_{29}Cl_{12}N_2O_8S_8$: 1538.5870 $[M+H]^+$; found: 1538.5870; elemental analysis calcd (%) for $C_{56}H_{28}Cl_{12}N2O_8S_8$: C 43.71; H 1.83; N 1.82; found: C 43.70; H 2.05; N 1.93.

Perylene-3,4:9,10-tetracarboximide-*N*,*N*′-di(ethan-2-oic acid) di(*tert*-butyl ester) (19): Perylene-3,4:9,10-tetracarboxylic dianhydride (4.0 g, 10 mmol), glycine *tert*-butylester hydrochloride (6.8 g, 40 mmol), and [Zn(OAc)$_2$] (1.9 g, 10 mmol) were suspended in quinoline (200 mL). The reaction mixture was stirred at 80 °C for 3 d. Most of the quinoline was removed in vacuo, and the residue was diluted with CH_2Cl_2. The resulting mixture washed three times with 1 M HCl and evaporated to dryness. The crude product was purified by flash column chromatography (SiO_2; CH_2Cl_2/MeOH 10:1) to obtain pure **19** as a red solid (4.6 g, 73%). R_f (CH_2Cl_2/MeOH 20:1): 0.9; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.54$ (s, 18H, C(CH_3)$_3$) 4.88 (s, 4H, 2 CH_2N), 8.42 (d, $J = 8.1$ Hz, 4H, Ar-*H*), 8.55 ppm (d, $J = 8.0$ Hz, 4H, Ar-*H*); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 28.28$, 42.31, 82.70, 122.76, 123.02, 125.95, 129.11, 131.46, 134.35, 162.86, 167.21 ppm; HRMS (MALDI): *m/z* calcd for $C_{36}H_{30}N_2O_8Na$: 641.1894 $[M+Na]^+$; found: 641.1739.

Perylene-3,4:9,10-tetracarboximide-*N*,*N*′-di(ethan-2-oic acid) di(chlorendylimidyl ester) (20): Compound **19** (13.0 g, 21 mmol) was suspended in $CHCl_3$ (500 mL). TFA (48 mL, 630 mmol) was added, and the reaction mixture was heated to reflux and stirred for 5 h. The volatiles were removed by the repeated addition of $CHCl_3$ followed by evaporation in vacuo. The crude product was suspended in 1 M HCl (500 mL), filtered and dried at 80 °C under reduced pressure to give the corresponding dicarboxylic acid derivative as red solid (10.6 g, 99%), which was used for the subsequent esterification without further purification. The crude dicarboxylic acid derivative (1.25 g, 2.5 mmol) and chlorendic hydroxylimide **9** were suspended in dry DMF (150 mL), and diisopropylcarbodiimide (2.3 mL, 14.8 mmol) was added. The reaction mixture was stirred for 24 h at 40 °C resulting in a dark-red solution. DMF was removed by distillation, and the residue was redissolved in dry THF (80 mL) and precipitated into vigorously stirred diisopropyl ether (2 L). After stirring for 1 h, the precipitate was filtered over a G4 glass filter, then dried in high vacuum to obtain the pure **20** as red microcrystalline powder (2.85 g, 93%). R_f (CH_2Cl_2/MeOH 20:1): 0.6; ^{1}H NMR

(400.13 MHz, $[D_2]CH_2Cl_2$): $\delta = 4.01$ (s, 4H, 2 C*H*), 5.26 (s, 4H, 2 CH_2N), 8.71 ppm (m, 8H, Ar-*H*); ^{13}C NMR (151 MHz, [D$_6$]DMSO): $\delta =$ ^{13}C NMR 39.52, 49.56, 78.51, 103.76, 120.87, 123.50, 124.32, 127.42, 130.81, 130.87, 133.31, 161.52, 163.31, 163.62 ppm; UV/Vis (THF): λ (ε) = 523 (77700), 487 (48700), 457 nm (18000 L mol^{-1} cm^{-1}); HRMS (MALDI): *m/z* calcd for $C_{46}H_{16}N_4O_{12}Cl_{12}$: 1235.7027 $[M]^+$; found: 1235.7009.

5,5‴-Bis(2-acetamidoethyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quaterthiophene (21): The quaterthiophene dihydrochloride **27** (300 mg, 0.61 mmol; see below) was suspended in DMSO (20 mL), and triethylamine (5 mL, 67.9 mmol) as well as acetic anhydride (10 mL, 90.1 mmol) were added. The mixture was heated to 120 °C for 30 min, then cooled to 100 °C, and stirred overnight. The reaction mixture was diluted with MeOH and then evaporated to dryness. The resulting solid was suspended in H_2O, filtered and subsequently washed with MeOH, Et_2O, and finally CH_2Cl_2. The residue was dried to afford the pure product (297 mg, 97%) as a yellow powder. R_f (CH_2Cl_2/MeOH 9:1): 0.46; M.p. (DSC in N_2): 272–274 °C; ^{1}H NMR (400.13 MHz, [D$_6$]DMSO): $\delta = 1.81$ (s, 6H, 2 CH_3), 2.91 (t, $J = 6.9$ Hz, 4H, 2 CH_2), 3.28 (m, 4H, 2 CH_2), 6.85 (d, $J = 3.5$ Hz, 2H, Ar-*H*), 7.17 (d, $J = 3.5$ Hz, 2H, Ar-*H*), 7.20 (d, $J = 3.8$ Hz, 2H, Ar-*H*), 7.27 (d, $J = 3.7$ Hz, 2H, Ar-*H*), 8.02 ppm (t, $J = 5.5$ Hz, 2H, 2 N*H*); ^{13}C NMR (100.62 MHz, [D$_6$]DMSO): $\delta = 22.6$, 29.5, 40.0, 124.1, 124.4, 125.0, 126.5, 134.0, 134.3, 135.7, 141.9, 169.2 ppm; HRMS (ESI): *m/z* calcd for $C_{24}H_{24}N_2O_2S_4^+$ 501.0793 $[M+H]^+$; found: 501.0785; elemental analysis calcd (%) for $C_{24}H_{24}N_2O_2S_4$: C 49.07; H 4.53; N 5.72; found: C 48.15; H 4.28; N 6.11.

2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗″-Sexithiophene-5,5⁗′-di(propan-3-oic acid) di(polyisobutyl-L-alanyl-L-alanyl amide) (22): PIB-Ala$_2$-NH$_2$[42] (1.23 g, 0.84 mmol) was dissolved in THF (600 mL), and compound **16** (550 mg, 0.40 mmol) was added. The reaction mixture was stirred overnight at room temperature. After reducing the volume of the solution in vacuo to about 300 mL, the crude product was precipitated by dropwise addition of the solution into methanol (3.2 L) and stirring of the resulting slurry overnight. The precipitate was collected by filtration, taken up in THF (200 mL), and reprecipitated into methanol (3 L), to afford **22** as a sticky solid (1.2 g, 86%). ^{1}H NMR (400.13 MHz, [D$_2$]TCE, 120 °C): $\delta = 0.75$–1.75 (m, 449H, aliphatic *H*), 2.65 (t, $J = 7.2$ Hz, 4H, CH_2C(O)), 3.23 (t, $J = 7.2$ Hz, 4H, CH_2-Ar), 3.27–3.40 (m, 4H, CH_2-NHC(O)), 4.34–4.52 (m, 4H, C**H*), 5.72–5.87 (m, 4H, N*H*), 6.33–6.41 (m, 2H, N*H*), 6.81 (d, $J = 3.2$ Hz, 2H, Ar-*H*), 7.04–7.20 ppm (m, 10H, Ar-*H*); MS (MALDI): *m/z* calcd for $C_{228}H_{416}N_6O_6S_6$: 3527.0756 $[M]^+$; found: 3531.3691.

2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗″:5⁗″2⁗‴-Octathiophene-5,5⁗‴-di(propan-3-oic acid) di(polyisobutyl-L-alanyl-L-alanyl amide) (23): PIB-Ala$_2$-NH$_2$[42] (673 mg, 0.46 mmol) was dissolved in THF (300 mL), and 18 (345 mg, 0.22 mmol) was added. The red suspension was sonicated for 5 min and stirred for 45 h at room temperature. After reducing the volume of the solution in vacuo to about 100 mL, the crude product was precipitated by dropwise addition of the solution into methanol (1 L) and stirring of the resulting slurry for 2 h. The precipitate was collected by filtration, taken up in THF (120 mL), and reprecipitated into methanol (1.2 L), to afford **23** as a sticky red-brown solid (751 mg, 91%). ^{1}H NMR (400.13 MHz, [D$_2$]TCE, 130 °C): $\delta = 0.80$–1.80 (m, 440H, aliphatic *H*), 2.65 (t, $J = 7.2$ Hz, 4H, CH_2C(O)), 3.24 (t, $J = 7.2$ Hz, 4H, CH_2-Ar), 3.28–3.41 (m, 4H, CH_2-NHC(O)), 4.34–4.52 (m, 4H, C**H*), 5.72–5.87 (m, 4H, N*H*), 6.31–6.39 (m, 2H, N*H*), 6.82 (m, 2H, Ar-*H*), 7.05–7.21 ppm (m, 14H, Ar-*H*).

Perylene-3,4:9,10-tetracarboximide *N*,*N*′-di(ethan-2-oic acid) di(2,2,3,3,4,4,4-heptafluorobutyl amide) (24): Compound **20** (2.8 g, 2.3 mmol) was dissolved in DMSO (80 mL), and 2,2,3,3,4,4,4-heptafluorobutylamine (0.9 mL, 6.8 mmol) was added. The reaction mixture was stirred for 2 h and precipitated into vigorously stirred MeOH (1.2 L). After stirring for 1 h, the precipitate was filtered over a G4 glass filter, and then dried in high vacuum to obtain pure **24** as dark-red solid (1.85 g, 94%). ^{1}H NMR (400.13 MHz, [D$_6$]DMSO, 120 °C): $\delta = 4.04$ (td, $J = 16.2$, 6.0 Hz, 4H, CF_2CH_2NH), 4.86 (s, 4H, CH_2N(CO)$_2$), 8.40 (m, 1H, N*H*), 8.62 (d, $J = 7.8$ Hz, 4H, Ar-*H*), 8.91 ppm (d, $J = 7.8$ Hz, 4H, Ar-*H*); ^{19}F NMR (376 MHz, [D$_6$]DMSO + [D$_1$]TFA): $\delta = -82.98$, −120.36, −130.19 ppm; HRMS (MALDI): *m/z* calcd for $C_{38}H_{18}N_4O_6F_{14}Na$: 891.0895 $[M+Na]^+$; found: 891.1123.

5-Tributylstannyl-2,2′-bithiophene (25): Bithiophene (13.5 g, 81.4 mmol) and tetramethylethylenediamine (TMEDA, 12.3 mL, 81.4 mmol) were dissolved in THF (600 mL) in 1 L pre-dried Schlenk flask. The mixture was cooled to −78 °C before slowly adding *n*-BuLi (34.2 mL, 85.5 mmol). The mixture was then stirred for 30 min at a temperature of −78 °C, and for 45 min at room temperature. The dark-green slurry was cooled again to −78 °C, and Bu_3SnCl (24.3 mL, 89.6 mmol) was added slowly. The clear orange solution was stirred over 3 d at room temperature, and solvents were removed in vacuo afterwards. The black oil was finally purified by distillation (10^{-3} mbar, side product < 150 °C, product > 170 °C) to afford the product as a clear slightly yellowish oil (28.1 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 7.2$ Hz, 9H, CH_3), 1.02–1.21 (m, 6H, CH_2), 1.29–1.41 (m, 6H, CH_2), 1.47–1.69 (m, 6H, CH_2), 6.98–7.11 (m, 2H, Ar*H*), 7.15–7.25 (m, 2H, Ar*H*), 7.30 ppm (d, $J = 3.2$ Hz, 1H, Ar*H*). ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 11.1$, 13.8, 27.4, 29.1, 123.6, 124.1, 125.1, 127.9, 136.2 ppm.

5,5′-Bis(tributylstannyl)-2,2′-bithiophene (26): Bithiophene (16.0 g, 96,2 mmol) and tetramethylethylenediamine (TMEDA, 29.1 mL, 192 mmol) were dissolved in THF (600 mL) in 1 L dried Schlenk flask. The mixture was cooled to −78 °C before slowly adding *n*-BuLi (78.9 mL, 197 mmol). The mixture was then stirred for 30 min at a temperature of −78 °C, and for 1.5 h at room temperature. The white slurry was cooled again to −78 °C, and Bu_3SnCl (54.8 mL, 202 mmol) was added slowly. The clear brown solution was stirred over 4 d at room temperature. Then, heptane was added, and the solution was washed three times with aqueous 5 wt% Na_2CO_3 solution, once with water, and finally with brine. The organic phase was dried over $MgSO_4$, filtered, and the solvents were removed in vacuo to yield the product as a brown oil (74.3 g). The product was pure enough to be used in the following reactions and was used immediately. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.91 (t, $J = 7.2$ Hz, 18H, CH_3), 1.03–1.21 (m, 12H, CH_2), 1.29–1.41 (m, 12H, CH_2), 1.45–1.70 (m, 12H, CH_2), 7.06 ppm (d, $J = 3.2$ Hz, 2H, Ar*H*), 7.30 ppm (d, $J = 3.2$ Hz, 2H, Ar*H*); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 11.0$, 13.8, 27.4, 29.1, 124.8, 136.2, 136.2, 143.16 ppm; HRMS (APCI): *m/z* calcd for $C_{32}H_{58}S_2Sn_2$: 746.2018 $[M]^+$; found: 746.2098.

5–5‴-Bis(2-amino-ethyl)-2,2′:5′,2″:5″,2‴-quaterthiophene dihydrochloride (27): The quaterthiophene chlorendylimide **7** (4.50 g, 4.01 mmol) was dissolved in THF (100 mL) and hydrazine monohydrate (10 mL, 193 mmol) was added. The mixture was heated at reflux for 72 h before the solvent was removed in vacuo. 1 M HCl was added to the residue, and the mixture was evaporated to dryness. The resulting solid was suspended in H_2O, filtered, and subsequently washed with acetone, MeOH, EtOAc, and CH_2Cl_2. The residue was dried in vacuo to yield the pure product (1.38 g, 70%) as a yellow powder. ^{1}H NMR (400.13 MHz, [D$_6$]DMSO, 120 °C): $\delta = 3.10$ (m, 8H, 2 CH_2), 6.97 (d, $J = 3.4$ Hz, 2H, Ar-*H*), 7.23 (m, 4H, Ar-*H*), 7.29 (d, $J = 3.7$ Hz, 2H, Ar-*H*), 8.02 ppm (s_b, 6H, 2 NH_3); ^{13}C NMR (100.62 MHz, [D$_6$]DMSO, 120 °C): $\delta = 27.4$, 39.5 (under DMSO signal), 124.4, 124.8, 125.2, 127.5, 134.5, 134.6, 135.5, 139.0 ppm; HRMS (ESI): *m/z* calcd for $C_{20}H_{21}N_2S_4^+$: 417.0582 $[M-H-2Cl]^+$); found: 417.0587.

X-ray Crystallography

Crystallographic information files (CIF) for compounds **2** (CCDC 949892), **3** (CCDC 949900), **4** (CCDC 949893), **5** (CCDC 949894), **6** (CCDC 949895), **7** (CCDC 949896 and CCDC 949897), **8** (CCDC 949898), **9** (CCDC 949909), **10** (CCDC 949904), **11** (CCDC 949905 and CCDC 949906), **12** (CCDC 949907), and **13** (CCDC 949908) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors would like to thank Dr. Shawn Koppenhoefer for his help with photography. Funding from the European Research Council (ERC Grant 239831, "OrgElNanoCarbMater"; ERC "Proof of Concept" Grant 310357, "WHITELIGHT"), the Swiss National Science Foundation (SNF Grants 200020–121812 and 200020–144417), and the Verband der Chemischen Industrie (Chemiefonds-Stipendium Jan Gebers) is gratefully acknowledged.

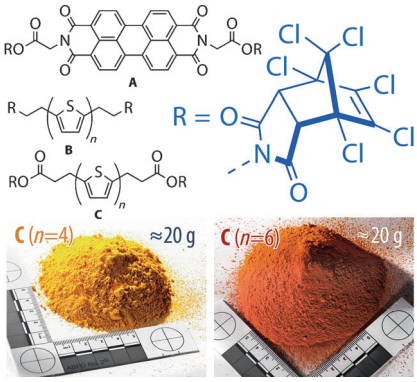
Keywords: functional molecules · polymers · protecting groups · supramolecular chemistry · synthetic methods

[1] D. Braga, G. Horowitz, *Adv. Mater.* **2009**, *21*, 1473.
[2] C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.* **2011**, *111*, 2208.
[3] A. Facchetti, *Chem. Mater.* **2011**, *23*, 733.
[4] M. C. Gather, A. Kohnen, K. Meerholz, *Adv. Mater.* **2011**, *23*, 233.
[5] P. Lin, F. Yan, *Adv. Mater.* **2012**, *24*, 34.
[6] Y. Guo, G. Yu, Y. Liu, *Adv. Mater.* **2010**, *22*, 4427.
[7] A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066.
[8] C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.* **2012**, *112*, 2208.
[9] A. Mishra, C.-Q. Ma, P. Bäuerle, *Chem. Rev.* **2009**, *109*, 1141.
[10] T. Lei, J.-Y. Wang, J. Pei, *Chem. Mater.* **2013**, *25*, 2991.
[11] B. J. Jung, N. J. Tremblay, M.-L. Yeh, H. E. Katz, *Chem. Mater.* **2011**, *23*, 568.
[12] X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, *Adv. Mater.* **2011**, *23*, 268.
[13] A. Kreyes, A. Mourran, Z. Hong, J. Wang, M. Möller, F. Gholamrezaie, W. S. C. Roelofs, D. M. de Leeuw, U. Ziener, *Chem. Mater.* **2013**, *25*, 2128.
[14] S. Ellinger, U. Ziener, U. Thewalt, K. Landfester, M. Möller, *Chem. Mater.* **2007**, *19*, 1070.
[15] A. Kreyes, M. Amirkhani, I. Lieberwirth, R. Mauer, F. Laquai, K. Landfester, U. Ziener, *Chem. Mater.* **2010**, *22*, 6453.
[16] D. González-Rodríguez, A. P. H. J. Schenning, *Chem. Mater.* **2011**, *23*, 310.
[17] G. S. Vadehra, B. D. Wall, S. R. Diegelmann, J. D. Tovar, *Chem. Commun.* **2010**, *46*, 3947.
[18] D. A. Stone, L. Hsu, S. I. Stupp, *Soft Matter* **2009**, *5*, 1990.
[19] S.-i. Kawano, N. Fujita, S. Shinkai, *Chem. Eur. J.* **2005**, *11*, 4735.
[20] H.-A. Klok, A. Rösler, G. Götz, E. Mena-Osteritz, P. Bäuerle, *Org. Biomol. Chem.* **2004**, *2*, 3541.
[21] E.-K. Schillinger, E. Mena-Osteritz, J. Hentschel, H. G. Börner, P. Bäuerle, *Adv. Mater.* **2009**, *21*, 1562.
[22] J. Hernando, P. A. J. de Witte, E. M. H. P. van Dijk, J. Korterik, R. J. M. Nolte, A. E. Rowan, M. F. Garcia-Parajo, N. F. van Hulst, *Angew. Chem. Int. Ed.* **2004**, *43*, 4045; *Angew. Chem.* **2004**, *116*, 4137.
[23] S. Yagai, T. Seki, T. Karatsu, A. Kitamura, F. Würthner, *Angew. Chem. Int. Ed.* **2008**, *47*, 3367; *Angew. Chem.* **2008**, *120*, 3415.
[24] A. R. Murphy, P. C. Chang, P. VanDyke, J. S. Liu, J. M. J. Fréchet, V. Subramanian, D. M. DeLongchamp, S. Sambasivan, D. A. Fischer, E. K. Lin, *Chem. Mater.* **2005**, *17*, 6033.
[25] G. L. Nelson, P. L. Kinson, C. B. Quinn, *Annu. Rev. Mater. Sci.* **1974**, *4*, 391.
[26] H. E. Ungnade, E. T. McBee, *Chem. Rev.* **1958**, *58*, 249.
[27] B. D. Wall, S. R. Diegelmann, S. Zhang, T. J. Dawidczyk, W. L. Wilson, H. E. Katz, H.-Q. Mao, J. D. Tovar, *Adv. Mater.* **2011**, *23*, 5009.
[28] L. Tian, R. Szilluweit, R. Marty, L. Bertschi, M. Zerson, E.-C. Spitzner, R. Magerle, H. Frauenrath, *Chem. Sci.* **2012**, *3*, 1512.
[29] E.-C. Spitzner, C. Riesch, R. Szilluweit, L. Tian, H. Frauenrath, R. Magerle, *ACS Macro Lett.* **2012**, *1*, 380.
[30] R. Marty, R. Szilluweit, A. Sánchez-Ferrer, S. Bolisetty, J. Adamcik, R. Mezzenga, E.-C. Spitzner, M. Feifer, S. N. Steinmann, C. Corminboeuf, H. Frauenrath, *ACS Nano* **2013**, *7*, 8498.
[31] E. D. Glowacki, M. Irimia-Vladu, S. Bauer, N. S. Sariciftci, *J. Mater. Chem. B* **2013**, *1*, 3742.
[32] K. Masui, H. Ikegami, A. Mori, *J. Am. Chem. Soc.* **2004**, *126*, 5074.
[33] M. Takahashi, K. Masui, H. Sekiguchi, N. Kobayashi, A. Mori, M. Funahashi, N. Tamaoki, *J. Am. Chem. Soc.* **2006**, *128*, 10930.
[34] J. S. Moore, S. I. Stupp, *Macromolecules* **1990**, *23*, 65.
[35] E. E. Havinga, I. Rotte, E. W. Meijer, W. T. Hoeve, H. Wynberg, *Synth. Met.* **1991**, *41*, 473.
[36] P. Bäuerle, *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, Weinheim, **2007**, pp. 89 – 181.
[37] T. Siegrist, C. Kloc, R. A. Laudise, H. E. Katz, R. C. Haddon, *Adv. Mater.* **1998**, *10*, 379.
[38] R. S. Becker, M. S. de, A. L. Macanita, F. Elisei, *Pure Appl. Chem.* **1995**, *67*, 9.
[39] A. Rademacher, S. Märkle, H. Langhals, *Chem. Ber.* **1982**, *115*, 2927.
[40] J. Gebers, L. Hartmann, M. Schaer, S. Suàrez, P. Bugnon, H.-G. Steinrück, O. Konovalov, A. Magerl, M. Brinkmann, R. Petraglia, C. Corminboeuf, H. Frauenrath, *A Hydrogen-Bonded Quaterthiophene with Dense Packing and Improved OFET Performance*, submitted.
[41] B. A. Jones, M. J. Ahrens, M. H. Yoon, A. Facchetti, T. J. Marks, M. R. Wasielewski, *Angew. Chem. Int. Ed.* **2004**, *43*, 6363; *Angew. Chem.* **2004**, *116*, 6523.
[42] R. Marty, R. Nigon, D. Leite, H. Frauenrath, *J. Am. Chem. Soc.* **2014**, *136*, 3919 – 3927.

Received: May 21, 2014
Published online on ■■ ■■, 2014

FULL PAPER

Solubility and crystallizability: The use of chlorendylimides as protecting groups for carboxylic acid and amine functionalities significantly facilitates the synthesis of end-substituted π-conjugated compounds, including octathiophene and perylene bisimide derivatives, by providing high solubility and crystallizability at the same time. The obtained compounds can then be readily converted to functional π-conjugated compounds (see figure).



Functional Molecules

*J. Gebers, D. Rolland, R. Marty, S. Suàrez, L. Cervini, R. Scopelliti, J. C. Brauer, H. Frauenrath**

■■ – ■■

Solubility and Crystallizability: Facile Access to Functionalized π-Conjugated Compounds with Chlorendylimide Protecting Groups