4,10-Dibromoanthanthrone as a New Building Block for p-Type, n-Type, and Ambipolar π -Conjugated Materials

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Abstract: New p-type, n-type, and ambipolar molecules were synthesized from commercially available 4,10-dibromoanthanthrone dye. Substitution at the 4,10- and 6,12-positions with different electron-rich and electron-poor units allowed the modulation of the optoelectronic properties of the molecules. A bis(dicyanoviny-lene)-functionalized compound was also prepared with a reduction potential as low as -50 mV versus Ag⁺ with a crystalline two-dimensional lamellar packing arrangement. These characteristics are important prerequisites for air-stable n-type organic field-effect transistor applications.

Introduction

Over the past thirty years, π -conjugated organic molecules have attracted a great deal of attention because of their semiconducting properties. Although the charge mobility for this class of materials is a few orders of magnitude lower than that observed for polycrystalline silicon used in highperformance devices, their ease of synthesis and processability on large surfaces have made them very attractive for specific applications such as light-emitting diodes,^[1] solar cells,^[2] and field-effect transistors.^[3] Consequently, a myriad of new compounds, both polymers and small molecules, have emerged in the aim to improve the physical properties (charge mobility, solubility, light absorption, and so on) of organic semiconductors.

Commercially available dyes and pigments have been underestimated in their capacity as building blocks for organic semiconductors. Many dyes and pigments possess a rigid π conjugated backbone, which explains their optical properties in the visible range. They are often very cheap and have functionalities that allow the introduction of new functional groups to fine-tune their electronic and optical properties.

The best recent example of the use of a commercial dye in organic electronics is diketopyrrolopyrrole (DPP).^[4,5] The success of this dye in building materials for organic electronic applications was nearly instantaneous, and this encouraged us to look for other commercially available dyes that

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could be easily derived through known reactions, especially C-C cross-couplings. We decided to investigate 4,10-dibromanthranthrone, or VAT Orange 3, the structure of which is depicted in Scheme 1 (compound **1**).

This dye has several interesting features. First, the presence of bromine atoms at the 4- and 10-positions allows the introduction of alkyl chains to increase the solubility; conjugated moieties might also be added at those positions to increase the effective conjugation length. Second, the electrophilicity of the carbonyl groups can be used as reactive sites for different nucleophiles to tune the electronic properties. Third, this molecule is symmetrical and is likely to crystallize easily.

Very few reports in which anthanthrone is used as a building block for organic electronics purposes have been published so far.^[6] In most cases, anthanthrone was used as the starting material to prepare the anthanthrene analogue.^[7]

Herein we report the synthesis and optical and electrochemical properties of new derivatives prepared from 4,10dibromoanthanthrone. The aim of this study is to explore the chemistry of this building block to enable the synthesis of new p-type, n-type, and ambipolar conjugated molecules for organic electronics applications.

Results and Discussion

Because 4,10-dibromoanthanthrone is poorly soluble in common organic solvents, solubilizing groups were introduced at the 4- and 10-positions at the beginning of the synthesis to enable further purification steps by column chromatography. The different strategies we explored are depicted in Scheme 1. Rather than using electronically inert, straight alkyl chains to solubilize the anthanthrone derivatives, we decided to attach electroactive moieties, namely, triisopropylsilylethylnyl (TIPS), 5-octylthiophene, and diphenylamine.





Scheme 1. Synthesis of 4,10-substituted soluble anthanthrone derivatives 2-4.

Thiophene and diarylamine were chosen for their electron-donating abilities, which we expected to result in an intramolecular donor-acceptor complex when coupled with the electron-deficient anthanthrone. TIPS has often been used in the synthesis of conjugated materials for organic electronics applications, since, in most cases, it provides oxidative stability to the materials without affecting the electronic properties of π -conjugated molecules in the solid state.^[8]

In this way, a Sonogashira coupling between compound **1** and triisopropylsilylacetylene (TIPSA) under standard conditions at 60 °C gave compound **2** in 70 % yield. On account of the poor solubility of starting material **1**, the reaction is quite slow and a long reaction time (72 h) proved necessary to obtain a good conversion. Compound **2** is highly soluble in chloroform and moderately soluble in CH_2Cl_2 , THF, and toluene.

In parallel, electron-donating 5-octylthiophene units were introduced by using a Stille coupling under standard conditions with 2-tributylstannylthiophene to give soluble compound 3 in 77% yield. Finally, the diarylamines, which are strong electron-donating groups,^[9] can be conveniently installed on 4,10-dibromoanthanthrone by using a Buchwald-Hartwig amination reaction.^[10] In the first attempt, we used potassium tert-butoxide (KOtBu) as a base, but the reaction proved to be unsuccessful. We found that the use of a strong base in the presence of compound 1 produces a dark purple solution that can be ascribed to the formation of the anthanthrone radical anion. By using weaker bases such as Cs₂CO₃, which do not produce the formal diphenylamide anion, we were able to obtain the soluble 4,10-bis(diphenylamine)anthanthrone (compound 4) in 41% yield. Interestingly, the formation of monocoupled product was not observed during the course of Sonogashira, Stille, and Buchwald-Hartwig

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coupling reactions. This can be attributed to the improved solubility of monoadducts that make the addition of the second moiety kinetically favorable. These functionalization strategies are therefore not well suited for the preparation of asymmetric compounds.

To the best of our knowledge, no example of a reaction at the ketone groups of the anthanthrone that keeps the quinoidal structure intact has been reported so far. As first targets, we undertook the preparation of electron-deficient derivatives that possess dicyanovinylene units at the 6and 12-positions. Dicyanovinylene is a strong electron-withdrawing group that is known to significantly decrease the re-

duction potential of conjugated organic materials.^[11] Also, Diederich et al. have demonstrated the usefulness of this functional group to prepare push–pull chromophores based on tetracyanoanthraquinodimethane (TCAQ, anthraquinone analogue).^[12]

Because of the very low reactivity of diarylketones toward nucleophilic attack, we performed a Knoevenagel condensation using Lehnert's reagent (TiCl₄/pyridine).^[13] The reaction between TIPS-appended compound 2 and malononitrile in CH₂Cl₂ under reflux conditions overnight produced monoadduct 6 as the major product (Scheme 2). A second addition of reactant proved necessary to push the conversion toward bis-adduct 5. Mono-adduct 6 and bisadduct 5 were isolated in 7 and 38% yield, respectively. We attempted a Knoevenagel condensation using the same conditions on the more electron-rich compound 3, but the conversion was very low and required an excessive reaction time. To shorten the reaction time and improve the conversion of the starting material, we attempted the reaction in chlorobenzene at 70°C, thereby yielding compound 7 in 11% yield. The higher temperature allowed a complete conversion overnight, which simplified the purification process, but the yield remained practically unchanged.

Application of the same conditions to the even more electron-rich compound **4** afforded emerald-green compound **8** in a poor 7% yield. Conversion of the starting material proved complete in a short reaction time, so the product must be unstable under the conditions used. A possible pathway of decomposition is polymerization through the activated *para* position of the phenylamine unit. It is clear that the donor character of the substituents affects the outcome of the reaction and that diphenylamines might be at the threshold of stability under the present conditions.

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Scheme 2. Synthesis of dicyanovinylene-functionalized dihydroanthanthrenes 5-8.

Interestingly, the 6- and 12-positions that bear the ketone functional groups can also be used to change the anthanthrone moiety into an electron-rich molecule that can be used as a p-type building block in π -conjugated materials. In fact, *p*-quinones can be protected in their *p*-dialkoxy form, usually by means of reduction of the quinone moiety to hydroquinone, followed by an in situ alkylation.

Moreover, the soluble, easy-to-process p-dialkoxy form can be used to protect the p-quinoid form, which can be later recovered by simple oxidation reaction to yield back the n-type material.^[14] The strategy we used to prepare dialkoxyanthanthrene derivatives is depicted in Scheme 3. The



Scheme 3. Bis(octyloxy)anthanthrene derivatives 9 and 10.

reduction–alkylation^[15] sequence on compound **1** was performed with sodium hydrosulfite in aqueous NaOH with an ammonium-based phase-transfer agent; 1,6-bis(octyloxy)-4,10-dibromoanthanthrene (compound **9**) was obtained in 73 % yield. Stille coupling on compound **12** by using 2-tributylstannylthiophene produced compound **10** in 85 % yield.

Another route to the aromatic anthanthrene core is the direct twofold nucleophilic attack of the quinone moiety using a nucleophilic alkyne species followed by reductive aromatization. This represents an attractive method to extend the π conjugation of the structure because it is a single-step

approach that leads to alkynesubstituted acene derivatives that proved to be an efficient class of materials in organic electronics.^[3] Following the procedure used on unsubstituted anthanthrone with lithium TIPS-acetylide followed by SnCl₂ reduction,^[7] we obtained the highly soluble compound 11 in 25% yield (Scheme 4). The reaction was not optimized and the low yield is partly caused by purification problems associated with the low polarity of the desired compound and byproducts.



Scheme 4. Preparation of 4,6,10,12-tetrakis(triisopropylsilylethynyl)an-thanthrene.

Finally, we wanted to explore the possibility of extending the effective conjugation length through the 6- and 12-positions using aromatic and heteroaromatic units, and our attempts are summarized in Scheme 5. The first strategy that we used to synthesize bis(diarylethylene) compound 13 was to prepare the bis(gem-dibromoolefin) by means of a Corey-Fuchs olefination using CBr₄ and PPh₃. Despite numerous attempts to optimize the reaction conditions (longer heating time, higher temperature, addition of reactants), we were unable to obtain the desired product in greater than 10% yield. We observed that the bis(gem-dibromoolefin) decomposed under the reaction conditions, which competed with the desired product formation. We then attempted the Barton-Kellog olefination, a strategy that allowed the expeditious synthesis of hexabenzocoronenes.^[16] The conversion of compound 2 to the dithioquinone with Lawesson's reagent led to the formation of an insoluble material. Dithioquinones, notably dithioanthraquinone, are known to be unstable and form polymeric materials by means of the thioketone reduction to the thiol species, followed by disulfide formation.^[17] Attempts to introduce hydrazone groups on the anthanthrone moiety by using hydrazine at a high temperature did not lead to any conversion, and the addition of ZnCl₂ as a Lewis acid to activate the ketone did not improve the conversion. Direct nucleophilic attack of the

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Scheme 5. Synthetic pathways to diarylethylene compounds.

ketone with lithium diphenylmethane formed a deep blue species, presumably the ketyl radical,^[18] analogous to the benzophenone reduction.

Following these attempts, we returned to the Corey-Fuchs reaction but shifted our attention to the less sterically demanding gem-dichloroolefin. Dichloroolefination reactions are rare in the literature and generally require higher temperatures. By using a modified procedure from the literature,^[19] the reaction of compound 2 in neat carbon tetrachloride in the presence triphenylphosphine in a microwave reactor at 150°C afforded the bis(gem-dichloroolefin) 12 with a good (75%) yield. This proves to be an efficient and rapid method to obtain gem-dichloroolefin compounds from unreactive acenequinones. The chloroalkenes can be functionalized with a broad range of coupling partners such as alkynes and aromatic units by using well-developed palladium-catalyzed reactions. As a proof of concept, we prepared compound 13 from compound 12 through a fourfold Suzuki coupling using phenylboronic acid under classical conditions in an acceptable (42%) yield (approximately 80% yield per coupling step). The use of bulkier dialkylbiphenyl phosphine xPhos and sPhos^[20] was not successful at increasing the reaction yield.

Optical properties: The optical properties of anthanthrone chromophores **2–4** are shown in Figure 1. Solution UV-visible and fluorescence spectra of all the newly prepared molecules were recorded in CH_2Cl_2 and the fluorescence spectrum are indicated by arrows.



Figure 1. UV-visible and fluorescence spectra of anthanthrone-based chromophores **2–4**.

Alkyne-substituted **2** shows an intense absorption band with a maxima at 522 nm with a bandgap of 2.25 eV at the absorption onset. The absorption maximum (λ_{max}) of thiophene-appended compound **3** is redshifted by 13 nm to 535 nm, and the band is broadened with an onset at 605 nm. The electron-rich thiophene lowers the optical bandgap by 0.20 eV at 2.05 eV. The introduction of stronger electron-donating diphenylamines in compound **4** further redshifts the absorption maxima at 640 nm with a low bandgap of 1.69 eV. This significant decrease in the bandgap is the result of a strong intramolecular donor-acceptor interaction that involves the amine and quinone moieties. Compounds **2** and **3** are moderately fluorescent with Stokes shifts of 35 and 108 nm, respectively. Compound **4** emits very weakly in the near-IR region at 795 nm.

Substitution of both ketones on compound 2 with stronger electron-withdrawing dicyanovinylene groups (compound 5) redshifts the maxima by 58 nm to 608 nm (Figure 2). Interestingly, the mono-dicyanovinylene compound 6 is redshifted by 33 nm relative to compound 2, which is about half of the bathochromic shift observed for compound 5. Conversion of a ketone to the dicyanovinylene lowers the bandgap in a linear trend by about 0.14 eV, which is due in part to the increase in the conjugation length. This trend is roughly preserved for compounds 7 and 8 with a respective redshift of 73 and 91 nm. Compound 8 shows a broad absorption spectrum with an onset that reaches 866 nm, which results from the strong intramolecular donor-acceptor interaction between the diphenylamine and the dicyanovinylene moieties. Although solution quantum yields were not measured, it is clear that the fluorescence of dicyanovinylene-functionalized compounds 5-7 is much weaker than that of their qui-

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Figure 2. UV-visible and fluorescence spectra of dicyanovinylene-functionalized compounds **5–8**.

noid analogues owing to the stronger intramolecular donoracceptor interaction. Compound **8** is completely nonfluorescent.

Reduction of the conjugated anthraquinone to the polycyclic aromatic anthanthrene core produces fine vibronic bands that are typical of fused conjugated systems. Compounds 9 and 10 show similar spectra with two sharp transitions at about 433 and 460 nm (Figure 3). The λ_{max} value of thiophene-appended compound 10 is redshifted by only 5 nm although the thiophene units extend the conjugation length. This contrasts with the anthraquinone analogue 3 because no charge-transfer interaction is possible between the electron-donating alkoxy and thiophene unit. The UV-visible spectrum of tetra-alkyne-substituted compound 11 is redshifted by about 40 nm relative to those of compounds 9 and 10. All anthanthrene compounds 9–11 are emissive with very small Stokes shifts between 6 and 15 nm.

Electrochemistry: The redox properties on the anthanthrone derivatives were investigated using cyclic voltammetry in *o*-dichlorobenzene saturated with Bu_4NPF_6 electrolyte using platinum electrodes with an Ag/AgCl reference electrode.



Figure 3. UV-visible and fluorescence spectra of anthanthrene compounds **9–11**.

The potentials are reported at the onset against Ag/Ag⁺. For calculation of the HOMO–LUMO levels, the onset redox potentials were corrected against an external Fc/Fc⁺ reference and 5.39 eV was added to obtain the vacuum levels.^[21] Table 1 (see below) summarizes the optical, electrochemical, and vacuum levels for compounds **2–11**.

The anthanthrone derivatives **2–4** show two well-resolved, reversible one-electron reduction peaks that are about 350 mV apart (Figure 4). Alkyne-substituted compound **2** showed the lowest first reduction potential at -420 mV, whereas compounds **3** and **4** are reduced at similar but more negative potentials (-580 and -570 mV, respectively) since the presence of thiophenes and diarylamines increase the electronic density on the molecule. Diphenylamine-appended compound **4** showed ambipolar character with two poorly resolved reversible oxidation peaks at 1050 and 1310 mV, which correspond to two successive one-electron oxidation processes of the amine functions. A low electrochemical bandgap of 1.62 eV, which is about 0.6 eV lower than regioregular P3HT,^[22] was measured for compound **4**.

Bis(dicyanovinylene) compounds 5, 7, and 8 show a single two-electron reduction step that is typical of TCAQ deriva-

Table 1. Summary of electro-optic and calculated properties for compounds 2-11. [a]

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	Optical properties						Electrochemical properties							Computational		
	λ _{max} [nm]	λ_{onset} [nm]	$rac{arepsilon_{\lambda_{\max}}}{\left[\mathrm{M}^{-1}\mathrm{cm}^{-1} ight]}$	$\lambda_{ m fluo}$ [nm]	E_{g} [eV]	$V_{\rm red}$ [V]		$V_{\rm ox}$ [V]		E_{g} [eV]	$E_{\rm HOMO}$ [eV]	E_{LUMO} [eV]	$E_{\rm HOMO}$ [eV]	E_{LUMO} [eV]	E_{g} [eV]	
2	522	551	14000	557	2.25	-0.42	-0.82	-	_	_	-6.69	-4.44	-5.63	-3.05	2.58	
3	535	605	15000	643	2.05	-0.58	-0.99	_	-	_	-6.33	-4.28	-5.68	-3.07	2.61	
4	640	734	13000	795	1.69	-0.57	-0.97	1.05	1.31	1.62	-5.91	-4.29	-5.03	-2.94	2.09	
5	580	626	25000	598	1.98	-0.05	-	-	-	-	-6.79	-4.81	-5.90	-3.81	2.09	
6	555	594	9000	630	2.09	-0.19	-0.34	-	-	-	-6.76	-4.67	-5.80	-3.46	2.34	
7	608	697	20000	740	1.78	-0.12	-	-	-	-	-6.52	-4.74	-5.85	-3.81	2.04	
8	731	866	11000	-	1.43	-0.14	-	1.04	-	1.18	-5.90	-4.72	-5.25	-3.61	1.64	
9	458	470	53000	470	2.64	-	-	0.95	1.13	-	-5.81	-3.17	-5.06	-2.29	2.77	
10	463	478	50000	478	2.59	_	_	0.80	1.14	_	-5.66	-3.07	-4.78	-2.04	2.74	
11	500	507	106000	506	2.45	-1.05	-	1.08	-	2.13	-5.94	-3.81	-4.65	-2.20	2.45	

[a] V is the onset versus Ag/AgCl, scan rate of 100 mVs⁻¹. Fc/Fc⁺ $E_{1/2}$ measured at 0.53 versus Ag/AgCl and versus SCE. Vacuum levels are determined electrochemically when possible. Otherwise the optical bandgap is used.



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Figure 4. Cyclic voltammograms of compounds 2-4.

tives (Figure 5).^[23] Compound **5** has a very low reduction potential of -50 mV, which corresponds to a very low LUMO level of -4.81 eV. This significant decrease (370 mV) relative to compound **2** can be ascribed to the presence of strong electron-withdrawing dicyanovinylene moieties at the 6- and 12-positions. Compound **6**, which bears both ketone and dicyanoanovinylene groups, shows two reduction peaks at -190 and -340 mV that could be associated to the oneelectron reduction step of the dicyanovinylene and ketone moiety, respectively. Thiophene- and diphenylamine-appended compounds **7** and **8** have similar reduction potentials are slightly negatively shifted by about -80 mV relative to compound **5** since thiophene and diarylamine are more electron-rich than TIPS-protected alkyne.



Figure 5. Cyclic voltammograms of compounds 5–8.

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Unlike other dicyanovinylene derivatives, compound **8** shows ambipolar character with a broad oxidation step with an onset at 1050 mV, similar to the oxidation of compound **4**. The lower electrochemical bandgap of compound **8** (1.18 eV) than compound **4** (1.62 eV) is a result of the lower LUMO of compound **8**, whereas the HOMO levels are virtually identical for both compounds. The anthraquinone and dicyanovinylene derivatives are particularly easy to reduce, because the injection of two electrons in the polycyclic system generates the aromatic anthanthrene unit. The electron count changes from 20 to 22, which respects Huckel's rule for aromaticity with n=5.

Electron-rich and aromatic anthanthrene compounds **9–11** are p-type analogues of the anthraquinone derivatives (Figure 6). Compound **9** shows two poorly resolved, partially reversible oxidation peaks at 950 and 1130 mV. The cyclovoltammogram of compound **10** is well defined with two



Figure 6. Cyclic voltammograms of compounds 9-11.

well-resolved oxidation peaks. Substitution of the bromine atoms by thiophene units make compound **10** more easily oxidized by 150 mV than compound **9**. Although the oxidation processes are reversible, the hystereses are large at about 420 mV. It has been shown that reversibility of otherwise irreversible cyclovoltammogram of anthracene derivatives—more interestingly, 9,10-dimethoxyanthracene—can be achieved by the adjustment of the sweep rate or by the addition of trifluoroacetic acid.^[24] Changes in the experimental conditions were not attempted to assert the reversibility of the oxidations.

The tetra-alkyne anthanthrene compound **11** shows welldefined reversible ambipolar character with a reduction peak at -1050 mV and an oxidation peak at 1080 mV, which correspond to a bandgap of 2.13 eV. The great stability of this compound combined with its ease of functionalization makes it a promising candidate for ambipolar organic fieldeffect transistor (OFET) applications. Substitution at the 4- and 10-positions with electron-donating groups allowed the modulation of the HOMO from -6.69 to -5.90 eV in the anthanthrone series, whereas the electron-withdrawing groups at the 6- and 12-positions govern the position of the LUMO level. Interestingly, the widely used fullerene derivative [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM) has a LUMO level of -4.3 eV,^[25] which make the electronic levels of the anthanthrone **3** and **4** derivatives well suited for use as n-type, small-molecule building materials in organic solar cells.

DFT calculations: DFT calculations were performed on compounds **2–14** to determine the distribution of the HOMO–LUMO frontier orbitals using the B3LYP/6-31G* model.^[26] Representative examples using the thiophene-appended compounds **3**, **7**, **10**, and tetra-alkyne **11** are presented in Figure 7. Compounds **2**, **4–6**, **8**, and **9** are presented in the Supporting Information. The values of the calculated vacuum levels are presented in Table 1. To shorten the calculation time, the alkyl chains of the thiophene units were omitted, and the TIPS and octyl groups were replaced by methyl groups.

For n-type compounds 3 and 7, the HOMO level is delocalized over the thiophene units and is mostly present along the 4,10-axis. As expected, the LUMO level for anthanthrone 3 is present in the two nonaromatic quinoidal rings and is calculated to be -3.07 eV. The LUMO for compound 7 is further delocalized on the dicyanovinylene unit and the calculated LUMO is 0.74 eV lower than that of compound 3; this is in good agreement with the experimental data.

For alkoxy-substituted compound **10**, the HOMO and LUMO levels are delocalized over the aromatic anthanthrene core. The tetra-alkyne **11** presents a similar pattern but the frontier orbitals are more localized on the alkynes of the 6- and 12-positions than on the 4- and 10-positions. This indicates that the 6- and 12-positions might present a better conjugation pathway on the anthanthrene core.

Single-crystal analysis: Since compound **5** represents a potentially interesting material for OFET applications, we devoted our efforts to making crystals out of it to study its packing behavior in the solid state. Single crystals of compound **5** were obtained by recrystallization from acetone, and the structure was resolved by X-ray diffraction.

As shown in Figure 8, compound **5** adopts an *anti*-folded out-of-plane configuration with a dihedral angle of 40° between the vinylene bond and the plane. This *anti* configuration differs from tetracyanoanthraquinodimethane (TCAQ) derivatives that adopt a *syn*-folded saddle-shaped conformation.^[12] This change in conformation is possibly caused by the greater energy required to bend the more rigid polycyclic ring system. In the crystal, the cyano groups point toward the center of the conjugated core of the neighboring molecule with a distance of 3.33 Å (depicted as dashed line in Figure 8).

The crystal packing shows a two-dimensional lamellar stacking pattern (Figure 8) with molecules facing each other.



Figure 7. Calculated HOMO (bottom) and LUMO (top) plots for compounds 3, 7, 10, and 11.

This kind of molecular arrangement is known to give good charge mobility values in organic electronics devices.^[3,27] Because compound **5** exhibits a very low reduction potential and the proper molecular packing arrangement, this molecule represents a very promising candidate for an air-stable n-type OFET.

Conclusion

Commercially available 4,10-dibromoanthanthrone was functionalized at the 4- and 10-positions with a variety of

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Figure 8. Crystallographic structure and molecular packing of compound **5**.

electron-donating groups, producing soluble anthanthronebased opto- and electroactive materials with very interesting properties. The 6- and 12-positions were successfully functionalized to tune the electronic properties of the anthanthrone conjugated core. Knoevenagel condensation afforded dicyanovinylene-based n-type materials with very low reduction potentials of up to -50 mV. The single-crystal study of compound 5 allowed for the determination of an anti-folded conformation in a two-dimensional lamellar packing arrangement. Another benefit was that reduction and alkylation of the quinoid structure generates soluble p-type building blocks that could be well suited for copolymerization with other conjugated moieties. These functionalization pathways allowed for a great flexibility in the modulation of the HOMO-LUMO frontier orbitals and generated structures with tunable properties, of great interest in organic electronics. Our current efforts are devoted to the investigation of the most promising candidates in plastic solar cells and OFET applications.

Experimental Section

Chemical reagents were purchased from Sigma-Aldrich Co. Canada, Alfa Aesar Co. or TCI America Co. and were used as received. 4,10-Dibromoanthanthrone was a courtesy from Heubach GmbH as Monolite Red 316801 product. Solvents used for organic synthesis were purified using a Solvent Purifier System (Vacuum Atmosphere Co., Hawthorne, USA). An Anton Paar Monowave 300 microwave apparatus with glass vial and IR temperature sensor was used for reaction under microwave. NMR spectra were recorded using a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz or an Agilent DD2 500 MHz. Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), and brs (broad singlet), and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm (δ) relative to residual solvent peak or TMS. High-resolution mass spectra (HRMS) were recorded using a Agilent 6210 time-of-flight (TOF) LC-MS apparatus equipped with an APPI ion source (Agilent Technologies, Toronto, Canada). UV-visible absorption spectra were recorded using a Varian diode-array spectrophotometer (Cary 500 model). Fluorescence spectroscopy was performed using a fluorescence spectrophotometer (Cary Eclipse model).

Electrochemical measurements: All cyclic voltammograms were acquired using a three-electrode BAS Epsilon potentiostat (purchased from Bioanalytical Systems). The potential was referenced to a Ag/AgCl saturated KCl electrode (purchased from Bioanalytical Systems) and Pt wire working and counter electrodes. Supporting electrolyte of *o*-dichlorobenzene saturated with Bu_4NPF_6 (<0.1 M) was purged with argon for 5 min prior to electrochemical measurements. For calculation of vacuum levels, the potentials were calibrated against ferrocene/ferrocenium external standard measured at 0.53 V versus Ag/AgCl and the saturated calomel electrode.

Computational methods: DFT calculations were carried out with the Gaussian 03 program suite^[26] at the B3LYP/6-31G* level of theory under vacuum by using the default optimization parameters, and the orbital plots are reported at an isovalue of 0.02.

4,10-Bis[(triisopropylsily])ethynyl]anthanthrone (2): A dry flask under argon was charged with 4,10-dibromoanthanthrone **(1)** (1.00 g, 2.15 mmol), [PdCl₂(PPh₃)₂] (75 mg, 0.11 mmol), CuI (20 mg, 0.10 mmol), triisopropylsilylacetylene (1.44 mL, 1.178 g, 6.46 mmol), diisopropylamine (4 mL, 2.888 g, 28.5 mmol), and dry THF (20 mL). The mixture was degassed with a flow of argon for 10 min and then stirred at 60 °C for 58 h. Once cooled, it was precipitated in MeOH and filtered. The residue was solubilized in CHCl₃ and adsorbed on silica gel. Silica gel column chromatography (CH₂Cl₂/hexanes 40:60 v/v) afforded compound **2** as an orange solid (1.006 g, 70%). M.p. >250 °C; ¹H NMR (400 MHz, CDCl₃): δ =8.58–8.49 (m, 4H), 8.23 (d, *J*=0.9 Hz, 2H), 7.80 (dd, *J*=8.2, 7.3 Hz, 2H), 1.31–1.24 ppm (m, 47H); ¹³C NMR (100 MHz, CDCl₃): δ =181.69, 133.83, 133.73, 131.18, 129.59, 129.09, 128.90, 128.78, 127.07, 126.96, 124.44, 103.73, 100.86, 19.08, 11.67 ppm; HRMS (APPI⁺): *m*/z calcd for C₄₄H₅₁O₂Si₂: 667.3422; found: 667.3423 [*M*]⁺.

4,10-Bis(5-octyl-2-thienyl)anthanthrone (3): 2-Octylthiophene^[28] (845 mg, 4.3 mmol) and dry THF (8 mL) were charged in a dry flask under argon. The mixture was cooled to -78°C, and nBuLi (2.5 M in hexane, 1.72 mL, 4.3 mmol) was added dropwise. The mixture was stirred for 60 min before adding Bu₃SnCl (1.40 g, 1.16 mL, 4.3 mmol) dropwise. The reaction was warmed to room temperature over 2 h. A second dry flask under argon was charged with 1 (500 mg, 1.08 mmol), [PdCl₂(PPh₃)₂] (38 mg, 0.05 mmol), and THF (10 mL). The mixture was degassed with a flow of argon for 10 min, and the stannyl solution was transferred with a syringe. The resulting mixture was heated at 75 °C overnight. The mixture was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (CH2Cl2/hexanes 80:20 v/v) to afford compound ${\bf 3}$ as a pasty purple solid (580 mg, 77 %). $^1\!H$ NMR (500 MHz, CDCl₃): $\delta = 8.51$ (dd, J = 8.3, 1.3 Hz, 2H), 8.11 (dd, J = 7.2, 1.3 Hz, 2H), 7.84 (s, 2H), 7.59 (dd, J=8.3, 7.2 Hz, 2H), 7.12 (d, J=3.4 Hz, 2H), 6.91 (d, J=3.4 Hz, 2H), 2.93 (t, J=7.7 Hz, 4H), 1.86-1.76 (m, 4H), 1.54-1.27 (m, 20H), 0.97–0.89 ppm (m, 6H); 13 C NMR (125 MHz, CDCl₃): $\delta =$ 181.41, 148.17, 137.45, 135.44, 133.69, 132.03, 130.22, 128.87, 128.40,

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128.30, 128.09, 127.24, 125.64, 124.88, 124.78, 31.96, 31.87, 30.36, 29.48, 29.40, 29.37, 22.74, 14.18 ppm; HRMS (APPI⁺): m/z calcd for $C_{46}H_{46}O_2S_2$: 694.2939; found: 694.2944 [M]⁺.

4,10-Bis(diphenylamino)anthanthrone (4): A dry flask under argon was charged with 1 (200 mg, 0.43 mmol), $[PdCl_2(dppf)]$ (15 mg, 0.02 mmol; dppf = 1,1'-bis(diphenylphosphino)ferrocene), Cs₂CO₃ (505 mg, 1.55 mmol), diphenylamine (218 mg, 1.29 mmol), and dry toluene (10 mL). The mixture was degassed with a flow of argon for 10 min and then stirred at 90 $^{\circ}\mathrm{C}$ for 24 h. The cooled mixture was filtered on a silica gel pad and washed with CH2Cl2. The solvent was evaporated and the crude product recrystallized from MeOH to afford compound 4 as a blue solid (115 mg, 41 %). M.p. >250 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 8.67$ (dd, J=7.3, 1.3 Hz, 2H), 8.37 (dd, J=8.4, 1.3 Hz, 2H), 8.25 (s, 2H), 7.66 (dd, J=8.4, 7.3 Hz, 2 H), 7.30-7.21 (m, 8 H), 7.14-7.07 (m, 8 H), 7.06-7.01 ppm (m, 4H); 13 C NMR (101 MHz, CDCl₃): $\delta = 183.10$, 148.45, 147.03, 132.36, 132.24, 130.98, 130.64, 129.91, 129.58, 129.49, 128.83, 125.49, 123.94, 123.14, 122.99 ppm; HRMS (APPI⁺): m/z calcd for $C_{46}H_{29}N_2O_2$: 641.2224; found: 641.2268 [*M*+H]⁺.

 $\label{eq:constraint} 4, 10 - Bis[(triis opropyls ilyl) ethynyl] - 6, 12 - bis(dicyanovinylene) dihydroan-$

thanthrene (5) and 4,10-bis[(triisopropylsilyl)ethynyl]-6-one-12-dicyanovinylenedihydroanthanthrene (6): A dry flask under argon was charged with compound 2 (71 mg, 0.11 mmol), malononitrile (112 mg, 1.70 mmol), and dry CH₂Cl₂ (16 mL). TiCl₄ (1 m in CH₂Cl₂, 0.75 mL, 0.75 mmol) was added dropwise followed by pyridine (176 mg, 0.18 mL, 2.23 mmol), and the resulting mixture heated to reflux for 24 h. A second addition of the same quantities of malononitrile, TiCl4, and pyridine was done in the same order, and the mixture was heated to reflux for 24 h. Once cooled, CH_2Cl_2 was added, and the organic layer was washed with HCl 10% (1× 20 mL) and NaOH 5% (1×20 mL). The organic layer was dried with MgSO₄ and filtered. The solvent was evaporated under reduced pressure, and the crude product was purified by silica gel column chromatography (CH₂Cl₂/hexanes 20:80 to 100:0 v/v) to afford compound 5 as a green solid (31.2 mg, 38%) and 6 as a red solid (5.5 mg, 7%). For 5: M.p. >250 °C; ¹H NMR (500 MHz, CDCl₃): δ = 8.85 (dd, J = 7.6, 1.0 Hz, 2 H), 8.76 (dd, J=8.3, 1.1 Hz, 2H), 8.73 (s, 2H), 7.94 (dd, J=8.3, 7.6 Hz, 2H), 1.24–1.19 ppm (m, 42 H); ¹³C NMR (125 MHz, CDCl₃): δ = 159.80, 133.75, 133.12, 130.83, 129.28, 128.99, 128.93, 128.51, 125.62, 124.83, 124.03, 114.84, 114.25, 103.11, 102.66, 82.29, 18.76, 11.32 ppm; HRMS (APPI⁺): m/z calcd for C₅₀H₅₀N₄Si₂: 762.3569; found: 762.3571 [M]⁺. For 6: M.p. >250 °C; ¹H NMR (500 MHz, CDCl₃): $\delta = 8.85$ (dd, J = 7.6, 1.2 Hz, 1 H), 8.80-8.72 (m, 4H), 8.62 (s, 1H), 8.01-7.88 (m, 2H), 1.34-1.16 ppm (m, 42 H); 13 C NMR (126 MHz, CDCl₃): $\delta = 182.39$, 159.51, 134.62, 133.82, 133.29, 133.16, 131.61, 130.70, 129.69, 129.45, 129.11, 128.83, 128.81, 128.79, 128.70, 128.69, 127.75, 126.68, 125.00, 124.65, 124.60, 124.42, 115.37, 114.69, 103.20, 102.81, 102.57, 101.64, 82.65, 18.79, 18.77, 11.37, 11.34 ppm; HRMS (APPI⁺): *m*/*z* calcd for C₄₇H₅₀N₂OSi₂: 714.3456; found: 714.3431 [M]+

4,10-Bis(5-octyl-2-thienyl)-6,12-bis(dicyanovinylene)dihydroanthanthrene (7): A dry flask under argon was charged with compound 3 (100 mg, 0.143 mmol), malononitrile (95 mg, 1.43 mmol), and dry chlorobenzene (10 mL). TiCl₄ (1 m in CH₂Cl₂, 2.6 mL, 2.61 mmol) was added dropwise, followed by pyridine (296 mg, 0.3 mL, 3.74 mmol). The mixture was heated at 70 °C overnight. CH2Cl2 was added to the mixture, and the organic layer was washed three times with H2O. The organic layer was dried with MgSO4, filtered, and evaporated. Purification by silica gel column chromatography (CH2Cl2/hexanes 50:50 v/v) followed by precipitation in MeOH afforded compound 7 as a green solid (13 mg, 11%). M.p. 164–166 °C; ¹H NMR (500 MHz, CDCl₃): $\delta = 8.71-8.66$ (m, 2H), 8.37-8.31 (m, 2H), 8.14 (s, 2H), 7.62 (t, J=8.0 Hz, 2H), 7.32-7.24 (m, 8H), 7.12–7.05 ppm (m, 12H); ¹³C NMR (125 MHz, CDCl3): $\delta = 160.60$, 149.78, 136.49, 136.32, 133.35, 132.06, 130.51, 129.68, 128.92, 128.33, 128.23, 125.96, 125.32, 124.86, 124.48, 115.13, 114.79, 81.51, 31.88, 31.71, 30.31, 29.35, 29.27, 29.25, 22.68, 14.13 ppm; HRMS (APPI⁺): m/z calcd for C₅₂H₄₆N₄S₂: 790.3158; found: 790.3186 [*M*]⁺.

4,10-Bis(diphenylamino)-6,12-bis(dicyanovinylenedihydro)anthanthrene (8): A dry flask under argon was charged with compound 4 (50 mg, 0.078 mmol), malononitrile (51 mg, 0.78 mmol), and dry chlorobenzene (10 mL). TiCl₄ (1 M in CH₂Cl₂, 1.4 mL, 1.42 mmol) was added dropwise, followed by pyridine (160 mg 0.16 mL, 2.03 mmol), and the mixture was heated at 80 °C for 5 h. Once cooled, CH_2Cl_2 and triethylamine (1 mL) were added, and the mixture was filtered on a silica gel pad and washed with CH_2Cl_2 . The mixture was evaporated under reduced pressure and purified by silica gel column chromatography (CH_2Cl_2). The product was precipitate in MeOH to afford compound **8** as a dark green solid (4 mg, 7%). M.p. > 250 °C. ¹H NMR (500 MHz, $CDCl_3$): δ = 8.71–8.66 (m, 2 H), 8.37–8.31 (m, 2 H), 8.14 (s, 2 H), 7.62 (t, *J* = 8.0 Hz, 2 H), 7.32–7.24 (m, 8H), 7.12–7.05 ppm (m, 12 H); ¹³C NMR (125 MHz, $CDCl_3$): δ = 160.64, 148.21, 146.94, 131.74, 131.28, 130.39, 129.79, 129.45, 129.32, 127.87, 125.71, 124.02, 123.77, 123.74, 123.00, 115.13, 114.40, 81.31 ppm; HRMS (APPI⁺): *m/z* calcd for $C_{s2}H_{28}N_6$: 736.2375; found: 736.2409 [*M*]⁺.

4,10-Dibromo-6,12-bis(octyloxy)anthanthrene (9): A flask under argon was charged with compound 1 (500 mg, 1.08 mmol), aqueous NaOH (0.1 M, 50 mL, 5 mmol), Aliquat 336 (530 mg, 0.6 mL, 1.31 mmol), Na₂S₂O₄ (485 mg, 2.78 mmol), and 1-bromooctane (1.5 mL, 1.66 g, 8.62 mmol). The mixture was degassed with a flow of argon for 10 min heated at 60 °C for 3 h until the mixture turned colorless. The water was decanted and MeOH (30 mL) was added. The crude product was filtered and washed with MeOH. Purification by silica gel column chromatography (CH₂Cl₂/hexanes 50:50 v/v) afforded compound 9 as an orange solid (544 mg, 73 %). M.p. 144–146 °C; ¹H NMR (500 MHz, CDCl₃): $\delta = 8.70$ (dd, J=8.3, 1.0 Hz, 2 H), 8.68 (s, 2 H), 8.57 (dd, J=7.6, 1.0 Hz, 2 H), 8.21-8.09 (m, 2H), 4.30 (t, J=6.5 Hz, 4H), 2.24-2.03 (m, 4H), 1.86-1.70 (m, 4H), 1.56–1.32 (m, 16H), 1.02–0.89 ppm (m, 6H); ¹³C NMR (500 MHz, $CDCl_3$): $\delta = 149.0, 130.4, 126.5, 126.1, 125.6, 125.1, 124.7, 123.6, 122.1,$ 122.0, 119.1, 77.0, 32.2, 30.9, 29.8, 29.6, 26.5, 23.0, 14.4 ppm; HRMS (APPI⁺): m/z calcd for C₅₂H₄₆N₄S₂: 790.3158; found: 790.3186 [M]⁺.

4,10-Bis(2-thienyl)-6,12-bis(octyloxy)anthanthrene (10): A dry flask under argon was charged with compound 9 (102 mg, 0.15 mmol), 2-tributylstannylthiophene (165 mg, 0.14 mL, 0.44 mmol), [PdCl₂(PPh₃)₂] (5 mg, 0.007 mmol), and anhydrous toluene (7 mL). The mixture was degassed with a flow of argon for 10 min and heated at 80°C overnight. Once cooled, the mixture was poured in MeOH. The precipitate was collected by filtration to afford compound 10 as an orange solid (87 mg, 85%). M.p. 140–145°C; ¹H NMR (500 MHz, CDCl₃): $\delta = 8.85$ (dd, J = 8.1, 1.0 Hz, 2 H), 8.63 (dd, J=7.6, 1.1 Hz, 2 H), 8.61 (s, 2 H), 8.18 (dd, J=8.2, 7.6 Hz, 2H), 7.60–7.53 (m, 4H), 7.34 (dd, J=5.1, 3.4 Hz, 2H), 4.42 (t, J= 6.5 Hz, 4H), 1.81-1.74 (m, 4H), 1.54-1.46 (m, 4H), 1.45-1.38 (m, 4H), 1.38–1.31 (m, 12 H), 0.96–0.89 ppm (m, 6 H); ¹³C NMR (126 MHz, $CDCl_3$): $\delta = 149.85$, 142.21, 132.23, 131.10, 127.61, 127.45, 125.94, 125.88, 125.53, 124.63, 124.23, 123.05, 121.44, 120.91, 119.68, 76.65, 31.88, 30.80, 29.62, 29.37, 26.38, 22.72, 14.15 ppm; HRMS (APPI+): m/z calcd for C₄₆H₄₉O₂S₂: 699.3191; found: 699.3213 [*M*+H]⁺.

4,6,10,12-Tetrakis(triisopropylsilylethynyl)anthanthrene (11): In a dry flask under argon, triisopropylsilylacetylene (274 mg, 0.34 mL, 1.50 mmol) was added to dry THF (15 mL) cooled to 0°C. nBuLi (2.5 м in hexanes, 0.54 mL, 1.35 mmol) was added dropwise and the solution was stirred for 1.5 h at 0°C. Compound 2 (100 mg, 0.15 mmol) was added and the mixture was stirred at room temperature overnight. SnCl₂·2H₂O (137 mg, 0.60 mmol) and aqueous HCl 3M (0.7 mL) were added, and the mixture was stirred for an additional 5 h. CH2Cl2 was added, and the organic layer was washed with water. The organic layer was dried with MgSO₄, and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexanes) to afford compound 11 as an orange solid (37 mg, 25%). M.p. >250 °C; ¹H NMR (500 MHz, CDCl₃): $\delta = 9.16$ (dd, J = 8.2, 1.1 Hz, 2 H), 9.13 (s, 2H), 8.85 (dd, J=7.5, 1.2 Hz, 2H), 8.31 (dd, J=8.1, 7.5 Hz, 2H), 1.38–1.30 (m, 35 H), 1.30–1.26 ppm (m, 42 H); $^{13}{\rm C}\,{\rm NMR}$ (125 MHz, $CDCl_3$): $\delta = 132.34$, 131.76, 130.95, 130.55, 127.15, 126.29, 124.75, 122.84, 122.47, 121.09, 117.38, 105.34, 105.06, 103.58, 97.02, 18.97, 18.87, 11.61, 11.48 ppm; HRMS (APPI⁺): *m/z* calcd for C₆₆H₉₃Si₄: 997.6349; found: 997.6418 [M+H]+

$\label{eq:constraint} 4, 10 - Bis (triis opropyl silyle thynyl) - 6, 12 - bis (gem-dichlorovinylene) dihy-$

droanthanthrene (12): A dry microwave flask under argon was charged with compound **2** (350 mg, 0.53 mmol), PPh₃ (1.097 g, 4.19 mmol), and CCl_4 (8.1 g, 5.2 mL, 53 mmol). The mixture was degassed with a flow of argon for 10 min and heated in a microwave apparatus to 150 °C for

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10 min, followed by 10 min at that same temperature. Once cooled, CH_2Cl_2 was added and the crude reaction mixture was filtered on a silica pad and rinsed with CH_2Cl_2 . The solvent was evaporated, and the residue was purified by silica gel column chromatography (CH_2Cl_2 /hexanes 50:50 v/v) to afford compound **12** as an orange solid (320 mg, 70%; the product should be kept in the dark as it darkens under prolonged exposure to ambient light). M.p. 190–195 °C; ¹H NMR (500 MHz, CDCl_3): δ =8.37 (dd, J=8.3, 1.1 Hz, 6H), 8.35 (s, 2H), 8.28 (dd, J=7.5, 1.1 Hz, 2H), 7.66 (d, J=8.3 Hz, 3H), 1.24–1.17 ppm (m, 42H); ¹³C NMR (125 MHz, CDCl_3): δ =131.84, 131.61 (2C), 130.57, 128.85, 128.73, 126.81, 126.69, 126.42, 125.99, 121.00, 120.88, 104.60, 98.03, 18.79, 11.41 ppm; HRMS (APPI⁺): m/z calcd for $C_{46}H_{51}Cl_4Si_2$: 799.2278; found: 799.2277 [M+H]⁺.

4,10-Bis(triisopropylsilylethynyl)-6,12-bis(diphenylvinylene)dihydroanthanthrene (13): A dry flask under argon was charged with compound 12 (50 mg, 0.062 mmol), phenylboronic acid (61 mg, 0.44 mmol), K₃PO₄ (230 mg, 1.00 mmol), [PdCl₂(PPh₃)₂] (4.3 mg, 0.006 mmol), and Bu₄NBr (10 mg, 0.031 mmol). Toluene (6 mL) and H₂O (0.5 mL) were added, then the mixture was degassed with a flow of argon for 10 min and heated at 95°C overnight. Once cooled, water was added and the aqueous layer was extracted twice with toluene. The organic layer was dried over MgSO₄, evaporated, and purified by silica gel column chromatography (CH2Cl2/hexanes 10:90 v/v) to afford compound 13 as a yellow powder (25 mg, 42 %). M.p. >250 °C; ¹H NMR (500 MHz, CDCl₃): $\delta =$ 8.03-7.97 (m, 2H), 7.48 (s, 2H), 7.45 (d, J=6.1 Hz, 4H), 7.38-7.27 (m, 13H), 7.21 (d, J=7.5 Hz, 5H), 7.08 (t, J=7.9 Hz, 2H), 1.12 ppm (s, 42 H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 143.92$, 143.59, 143.44, 133.58, 132.92, 132.31, 131.18, 130.93, 129.58, 128.86, 128.67, 127.73, 127.26, 127.00, 126.64, 125.56, 125.08, 119.29, 105.23, 95.55, 18.79, 11.38 ppm; HRMS (APPI⁺): m/z calcd for $C_{70}H_{71}Si_2$: 969.5134; found: 969.5181 $[M+H]^+$.

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- [1] X.-H. Zhu, J. Peng, Y. Cao, J. Roncali, Chem. Soc. Rev. 2011, 40, 3509–3524.
- [2] P. E. Schwenn, K. Gui, A. Nardes, K. B. Krueger, K. H. Lee, K. Mutkins, H. Rubinstein-Dunlop, P. E. Shaw, N. Kopidakis, P. L. Burn, P. Meredith, *Adv. Eng. Mater.* **2011**, *1*, 73–81.
- [3] C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, Chem. Rev. 2012, 112, 2208–2267.
- [4] D. G. Farnum, G, Mehta, G. G. I. Moore, F. P. Siegel, *Tetrahedron Lett.* 1974, 15, 2549–2552.
- [5] S. Qu, H. Tian, Chem. Commun. 2012, 48, 3039-3051.
- [6] L. Viaene, H. V. Mingroot, P. V. Haver, M. V. der Auweraer, F. C. De Schryver, J. Photochem. Photobiol. A 1992, 66, 1-13; S.-H. Yi, S. Ohashi, K. Ogino, H. Sato, H. Nomori, Synth. Met. 1993, 61, 247–251; M. Irimia-Vladu, P. A. Troshin, M. Reisinger, G. Schwabegger, M. Ullah, R. Schwoediauer, A. Mumyatov, M. Bodea, J. W. Fergus, V. F. Razumov, H. Sitter, S. Bauer, N. S. Sariciftci, Org. Electron. 2010, 11, 1974–1990.
- [7] L. Zhang, B. Walker, F. Liu, N. S. Colella, S. C. B. Mannsfeld, J. J. Watkins, T.-Q. Nguyen, A. Briseno, *J. Mater. Chem.* **2012**, 22, 4266–4268; B. K. Shah, D. C. Neckers, J. Shi, E. W. Forsythe, D. Morton, *J. Phys. Chem. A* **2005**, *109*, 7681.

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- [8] O. Lobanova Griffith, N. E. Gruhn, J. E. Anthony, B. Purushothaman, D. L. Lichtenberger, *J. Phys. Chem. C* 2008, *112*, 20518–20524;
 O. L. Griffith, A. G. Jones, J. E. Anthony, D. L. Lichtenberger, *J. Phys. Chem. C* 2010, *114*, 13838–13845; H. Qu, C. Chi, *Org. Lett.* 2010, *12*, 3360–3363.
- [9] M. Xu, D. Zhou, N. Cai, J. Liu, R. Li, P. Wang, *Energy Environ. Sci.* 2011, 4, 4735–4742.
- [10] M. S. Driver, J. F. Hartwig, J. Am. Chem. Soc. 1996, 118, 7217-7218.
- [11] Y. Ie, K. Nishida, M. Karakawa, H. Tada, Y. Aso, J. Org. Chem. 2011, 76, 6604–6610; H. Usta, C. Risko, Z. Wang, H. Huang, M. K. Deliomeroglu, A. Zhukhovitskiy, A. Facchetti, T. J. Marks, J. Am. Chem. Soc. 2009, 131, 5586–5608.
- [12] F. Bureš, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, *Eur. J. Org. Chem.* 2008, 6, 994–1004.
- [13] W. Lehnert, Tetrahedron Lett. 1970, 11, 4723-4724.
- [14] T. Yakura, Y. Yamauchi, Y. Tian, M. Omoto, *Chem. Pharm. Bull.* 2008, 56, 1632–1634.
- [15] G. A. Kraus, T. O. Man, Synth. Commun. 1986, 16, 1037–1042.
- [16] K. N. Plunkett, K. Godula, C. Nuckolls, N. Tremblay, A. C. Whalley, S. Xiao, Org. Lett. 2009, 11, 2225–2228.
- [17] M. V. Lakshmikantham, M. Levinson, M. Menachery, M. P. Cava, J. Org. Chem. 1986, 51, 411–412.
- [18] I. G. Lopp, J. D. Buhler, E. C. Ashby, J. Am. Chem. Soc. 1975, 97, 4966–4970.
- [19] P. Hodge, E. Khoshdel, React. Polym. 1985, 3, 143-150.
- [20] R. Martin, S. L. Buchwald, Acc. Chem. Res. 2008, 41, 1461-1473.
- [21] C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, Adv. Mater. 2011, 23, 2367–2371.
- [22] M. Heeney, W. Zhang, D. J. Crouch, M. L. Chabinyc, S. Gordeyev, R. Hamilton, S. J. Higgins, I. McCulloch, P. J. Skabara, D. Sparrowea, S. Tierneya, *Chem. Commun.* 2007, 5061–5063.
- [23] N. Martin, J. L. Segura, C. Seoane, P. de La Cruz, F. Langa, E. Orti, P. M. Viruela, R. Viruela, J. Org. Chem. 1995, 60, 4077–4084.
- [24] J. M. Masnovi, E. A. Seddon, J. K. Kochi, Can. J. Chem. 1984, 62, 2552–2559.
- [25] M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec, *Adv. Mater.* 2006, *18*, 789–794.
- [26] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [27] C. Wang, H. Dong, H. Li, H. Zhao, Q. Meng, W. Hu, Cryst. Growth Des. 2010, 10, 4155–4160; J. E. Anthony, J. S. Brooks, D. L. Eaton, S. R. Parkin, J. Am. Chem. Soc. 2001, 123, 9482–9483.
- [28] P. Wilson, D. Lacey, S. Sharma, B. Worthington, Mol. Cryst. Liq. Cryst. 2001, 38, 279–292.

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