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PAPER

Thiophene-functionalized isoindigo dyes bearing electron donor substituents with absorptions approaching the near infrared region†

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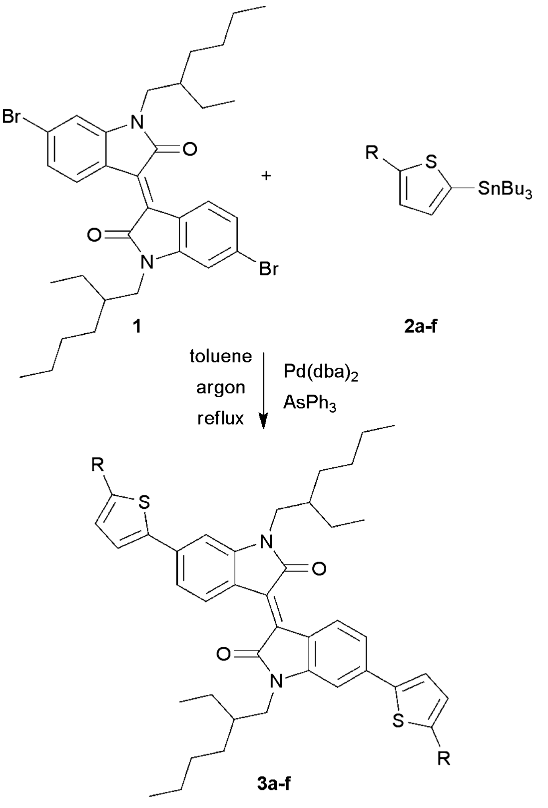
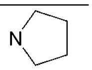
A series of six new, highly soluble *N*,*N*′-dialkylated isoindigo derivatives bearing different electron donating thiophene units at the 6,6′-positions were synthesized by Stille cross-coupling reaction. The optical and electrochemical properties of these dyes were studied by UV-vis spectroscopy and cyclic voltammetry, revealing a good tunability of their electronic properties by peripheral substituents with amino groups leading to strong absorption reaching the NIR region. The DFT calculations of the frontier molecular orbitals of these dyes corroborate the observed substituent effect on absorption and redox properties.

Introduction

The search for new dyes with high absorptivity in the visible and near infrared (NIR) spectral region is still a crucial synthetic task for developing high- performance electronic materials, in particular for organic photovoltaics based on small molecules.[1,2] In this context chemical modification of traditional dyes and pigments has been shown to be a promising approach as derivatives of phthalocyanines,[2] perylene bisimides,[3] acenes,[4] merocyanines,[5] squaraines,[6] borondipyrromethenes,[7] and diketopyrrolopyrroles[8] have been successfully used in organic solar cells. Although isoindigo, a constitutional isomer of the most prominent industrial colorant indigo, has been known for a very long time,[9] only recently isoindigo derivatives[10] became in focus as organic materials.[11–14] In a patent of 2009 on ketopyrroles as organic semiconductors, the synthesis of molecular and polymeric isoindigos containing thiophene substituents was reported.[11] More importantly, Reynolds and coworkers have recently introduced bithiophene-functionalized isoindigos as donor materials in bulk-heterojunction (BHJ) solar cells.[12] Isoindigo-based conjugated donor–acceptor polymers have also been synthesized and their potential as photovoltaic materials has been described.[13] Nevertheless, to the best of our knowledge there is no report on the influence of peripheral substituents on the optical and electrochemical properties of isoindigo dyes. Herein we report the synthesis of a series of six new *N*,*N*′-dialkylated isoindigo derivatives **3a–f** (Scheme 1) bearing different electron-donating thiophene groups at the 6,6′-positions of isoindigo core and show that optical and electronic properties of isoindigo dyes can be tuned by peripheral substituents.



	3a	3b	3c	3d	3e	3f
R	H	Me	SMe	OMe	NMe$_2$	
yield (%)	95	41	45	31	16	16

Scheme 1 Synthesis of isoindigo derivatives **3a–f** by Stille cross-coupling reaction.

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† Electronic supplementary information (ESI) available: Computational details, cyclic voltammograms, ^{1}H NMR and ^{13}C NMR spectra. See DOI: 10.1039/c1ob05508a

Results and discussion

Synthesis

The isoindigo derivatives **3a–f** were synthesized according to the route shown in Scheme 1. The starting compound 6,6′-dibromoisoindigo **1**[12] functionalized with the solubilizing 2-ethylhexyl groups at the lactam nitrogen atoms was reacted in a palladium-catalyzed Stille cross-coupling reaction with 2-[tri(n-butyl)-stannyl]-thiophenes **2a–f**[15–18] comprising different substituents (R) at the 5-position (Scheme 1). The cross-coupling reactions were carried out in freshly dried toluene under reflux in an argon atmosphere. We have used Pd(dba)$_2$ and AsPh$_3$ as a catalytic system for these reactions as this system can be handled under ambient conditions, thus no glove box is required for this purpose. The reference compound **3a** without substituent (R = H) at thiophene was obtained in an excellent yield of 95% and the derivatives **3b–f** with electron donor substituents were obtained in 45–16% yields. The good solubility of these compounds facilitated their purification by simple silica gel column chromatography. These new isoindigo derivatives were characterized by ^{1}H, ^{13}C NMR and high resolution mass spectrometry (for details see Experimental section).

Optical and electrochemical properties

The optical properties of the newly synthesized isoindigos **3a–f** were studied by UV-vis spectroscopy. The absorption spectra are shown in Fig. 1 and the optical data are collected in Table 1.

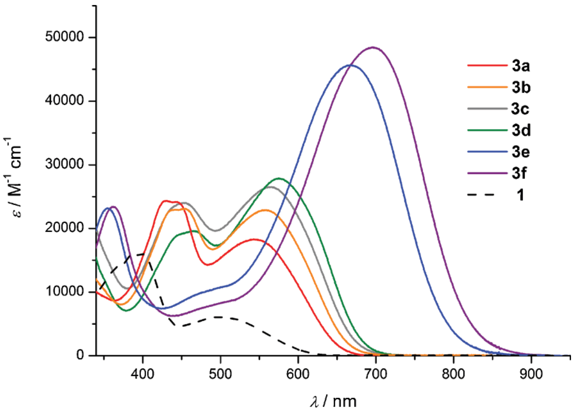

Fig. 1 Absorption spectra of 6,6′-dithiophene-functionalized isoindigos **3a–f** in dichloromethane. The spectrum of 6,6′-dibromoisoindigo **1** is shown for comparison.

For the derivatives **3a–d** (R = H, Me, SMe, OMe) broad absorption bands with two maxima around 450 nm and 560 nm are observed. The introduction of thiophene groups at isoindigo core evokes a red-shift as well as more intense absorption maxima for **3a–d** compared to the dibrominated precursor **1**. Whereas for compound **1** the blue-shifted band with the absorption maximum at 400 nm is more intense than the broad charge-transfer band with a maximum at about 500 nm, the intensity ratio of these two bands changes considerably for the thiophene-substituted derivatives **3a–d** with a decrease of the low-wavelength absorption in favour of an increase of the CT band at higher wavelength, particularly for **3c,d** (R = SMe, OMe). Moreover, compared to **3a** (R = H), a bathochromic shift of the main absorption band is observed for compounds **3b–d**. For the amino-substituted derivatives **3e** and **3f** the situation is dramatically different as for each of these dyes in the visible spectral range only one broad and very intense CT absorption band extended into the NIR region up to 900 nm was observed with maxima at 668 and 696 nm, respectively, along with a weak shoulder between 450 and 510 nm. Consequently, the optical bandgap that was calculated from the absorption maximum decreases with increasing electron-donating property of the substituents R (see Table 1). Since all these compounds are very weakly fluorescent, their emission properties are not discussed here.

The electrochemical properties of **3a–f** have been investigated by cyclic voltammetry (CV) in dichloromethane with ferrocene as an internal standard and their redox properties are summarized in Table 1, while representative cyclic voltammograms are shown in Fig. 2 (for CVs of all compounds see ESI†). For each of these six isoindigo derivatives **3a–f** two reduction waves are observed. While the first one is fully reversible, for the second reduction wave an increase of the peak-to-peak separation with increasing scan rate is observed. Obviously the reductions are only marginally sensitive to the peripheral substituents R at the thiophene unit, indicating that the LUMO is localized at the isoindigo core. Except for the methylthio-substituted derivative **3c** (R = SMe), which exhibits the least negative values (−1.67 and −1.27 V) of all six compounds, reduction is slightly hampered with increasing electron-donating property of the substituents R within the series **3a–f** with a maximal potential difference of 0.11 V for the first and 0.10 V for the second reduction potential observed for the amino-substituted derivative **3f** (R = pyrrolidinyl) compared with those of the reference **3a** (R = H). On the other hand, the oxidation is strongly influenced by the electron donor character of the substituents. For **3a** one irreversible oxidation with a peak potential of 0.89 V is observed and a shoulder at higher potential

Table 1 Optical and electronic properties of isoindigo derivatives **3a–f**

	Color[a]	λ_{max}/nm	ε/M^{-1} cm^{-1}	Optical bandgap[b]/eV	$E_{1/2}^{red}$/V	$E_{1/2}^{ox}$/V	HOMO[c]/eV
3a	Orange	544	18400	2.28	−1.69, −1.29	0.89[d], *ca.* 1.20[d]	−5.69
3b	Red	559	22800	2.22	−1.72, −1.32	0.75[e]	−5.55
3c	Red	565	26600	2.21	−1.67, −1.27	0.59[e]	−5.39
3d	Violet	575	28300	2.15	−1.75, −1.34	0.52[e]	−5.32
3e[f]	Blue	668	45500	1.86	−1.75, −1.38	−0.03[e]	−4.77
3f[f]	Blue	696	47900	1.78	−1.79, −1.40	−0.09[e]	−4.71

[a] In CH$_2$Cl$_2$ solution. [b] Calculated from λ_{max}. [c] Calculated from $E_{1/2}^{ox}$ using 4.8 eV as potential for ferrocene. [d] Peak potential. [e] Two electrons are involved in the process. [f] Since the oxidation wave overlaps with the Fc/Fc$^+$ wave, the measurement was performed against decamethylferrocene and calculated back to ferrocene.

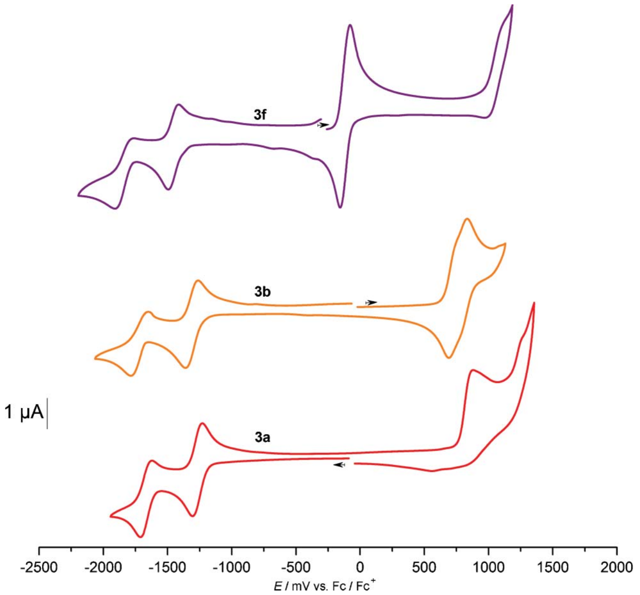

Fig. 2 Cyclic voltammograms of **3a**, **3b** and **3f** in dry dichloromethane (10^{-4} M); scan rate 100 mV s^{-1}; supporting electrolyte: tetrabutylammonium hexafluorophosphate (NBu_4PF_6, 0.1 M).

indicates a second oxidation at *ca.* 1.20 V. The observed shoulder in the oxidation wave of **3b** suggests two single-electron oxidations, which are not resolved due to a small difference between the peak potentials. For compounds **3d–f** only one reversible oxidation wave of each with a peak-to-peak separation of about 70 mV is observed. The peak current, however, is approximately doubled compared to the corresponding first reduction wave, and hence the recorded waves can be related to a two electron process.[19] This observation might be attributed to two subsequent oxidations, which are not resolved due to a small difference in potential. From the cyclic voltammetry data the energy levels of the highest occupied molecular orbitals (HOMO) of **3a–f** are estimated (see Table 1) by applying the most commonly used ionization potential for ferrocene (4.8 eV).[20]

In order to shed more light on the observed substituent effects on optical and redox properties of these isoindigo dyes, their HOMO and LUMO energy levels were calculated by DFT method (Table 2 and Fig. 3).[21] For computational details and the frontier molecular orbitals (FMO) of all compounds **3a–f** see ESI†. The calculated HOMO energy levels (Table 2) increase within this series from **3a** to **3f** which is in accordance with the experimental values (see Table 1, last column). The computation of the HOMO energy levels led to an overestimation of about 0.2–0.4 eV compared to the experimental values determined by CV, which can be explained by neglected solvent effects in calculations. In contrast to the CV data, however, where the reduction potentials did not increase significantly within the series **3a–f**, the calculated LUMO energies rise with increasing electron donating character of substituents R with a maximum increase of 0.53 eV for amino-substituted derivative **3f** compared to the reference **3a** (R = H). The calculated transition energy, which relates to the excitation energy from the ground state into the first excited state, shows the same trend as the optical gap. The FMOs depicted in Fig. 3 reveal that the LUMO is rather localized at the isoindigo core, which is a clear indication for the marginal influence of electron-donating substituents on the reduction potentials as discussed before. On the other hand, the HOMO is extended over the entire π-system with high coefficients at the donating heteroatoms in derivatives **3c–f** (for FMOs of **3b–e** see ESI†). When comparing the transition densities of the reference **3a** and the amino-substituted derivative **3f** qualitatively (Fig. 3), it is apparent that in the latter case the electron-donating pyrrolidinyl substituent at the thiophene unit is strongly involved in the first optical transition. Furthermore, it evokes a substantial participation of the thiophene units in this process, which is much smaller for **3a** (R = H). The features of FMOs of the present isoindigos corroborate the observed strong absorption with bathochromic shift for the amino-functionalized isoindigo derivatives **3e,f**.

Table 2 DFT calculated energy levels and the transition energy derived by coupled cluster method

	HOMO[a]/eV	LUMO[a]/eV	HOMO–LUMO gap/eV	Transition energy[b]/eV
3a	−5.49	−2.97	2.52	2.49
3b	−5.27	−2.83	2.44	2.48
3c	−5.10	−2.84	2.26	2.40
3d	−5.05	−2.73	2.31	2.41
3e	−4.68	−2.57	2.11	2.22
3f	−4.47	−2.44	2.03	2.11

[a] DFT (B3-LYP) calculation. [b] Coupled cluster calculation.

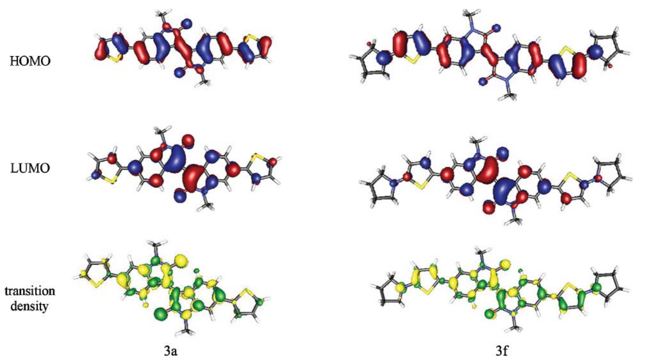

Fig. 3 HOMO, LUMO according to DFT (B3-LYP) calculations and transition density (CC2 level) of **3a** (left) and **3f** (right).

Conclusions

In summary, the successful synthesis of a series of six new thiophene-functionalized isoindigos with different electron-donating groups at the thiophene units enabled a systematic study on structure-electronic properties relationship of this class of dyes currently in focus as photovoltaic materials. Our investigations have shown that the optical and electrochemical properties of these dyes can be tuned by peripheral substituents. The introduction of stronger donor substituents such as dimethylamino and pyrrolidinyl at the thiophene units leads to a significant red-shift of the absorption approaching the NIR region. Thus, the new isoindigo dyes **3e,f** possess potential as donor materials in organic solar cells.

Experimental section

General

The isoindigo precursor **1** was prepared according to the literature procedure.[12] 2-[Tri(n-butyl)-stannyl]-thiophene **2a** is commercially available. Methyl-5-[tri(n-butyl)-stannyl]-thiophene **2b**,[15] 2-(methylthio)-5-[tri(n-butyl)-stannyl]-thiophene **2c**[16] were prepared by a subsequent deprotonation-transmetalation reaction of the corresponding thiophenes with n-butyllithium and tributyltinchloride according to known literature procedures. 2-Pyrrolidino-thiophene and 2-dimethylamino-thiophene were prepared according to the procedure described in the literature.[22] All other reagents and solvents were obtained from commercial suppliers and purified and dried according to standard procedures.[23] Column chromatography was performed on silica gel (Merck Silica 60, particle size 0.040–0.063 mm). Solvents for spectroscopic studies were of spectroscopic grade and used as received. Elemental analyses were performed on a CHNS 932 analyzer. ^1H and ^{13}C NMR spectra were recorded in CD_2Cl_2 on a Bruker Avance 400 or DMX 600 spectrometer. Residual undeuterated solvent was used as internal standard (5.32 ppm for ^1H, 53.84 ppm for ^{13}C). High-resolution ESI-TOF mass spectrometry was carried out on a microTOF focus instrument (Bruker Daltronik GmbH). UV-vis measurements were performed in CH_2Cl_2 (10^{-4} M) in a conventional quartz cell (light pass 10 mm) on a Perkin-Elmer Lambda 950 spectrometer. For cyclic voltammetry a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three electrode single-compartment cell was used. Dichloromethane (HPLC grade) was dried over calcium hydride under argon and degassed before using. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared according to the literature,[24] and recrystallized from ethanol/water. Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively. The measurements were carried out in dichloromethane at a concentration of about 10^{-4} M with ferrocene (Fc) as an internal standard for the calibration of the potential. Due to an overlap of the oxidation waves of **3e** or **3f** with the Fc/Fc^+ wave, these measurements were performed against decamethylferrocene (–0.55 V *vs.* Fc/Fc^+) and afterwards calculated back against ferrocene.

Synthesis

2-Tributylstannylthiophenes (2d–f). 2-Methoxy-5-[tri(n-butyl)-stannyl]-thiophene **2d**[25], dimethylamino-5-[tri(n-butyl)-stannyl]-thiophene **2e**[17,18] and 2-pyrrolidino-5-[tri(n-butyl)-stannyl]-thiophene **2f**[18] were prepared in analogy to the literature reported procedures for similar trimethylstannylthiophenes.

2-Methoxy-5-[tri(n-butyl)-stannyl]-thiophene (2d). 2-Methoxythiophene (2.63 g, 23.1 mmol) was placed under argon in dry THF (10 mL) at −78 °C and a solution of n-butyllithium in hexane (2.5 M, 12.4 mL, 31.0 mmol) was added dropwise. The suspension was stirred for 80 min until the temperature reached –10 °C and then cooled down again to –78 °C. Tributyltinchloride (7.56 g, 23.2 mmol) was added and the reaction mixture was allowed to warm up to room temperature within 2 h and stirred for further 19 h. The mixture was poured into water (30 mL) and extracted with diethylether (3 × 15 mL), and the organic phase was dried over sodium sulfate. The solvent was removed under reduced pressure affording a brownish oil (7.78 g, 84%). The product was used without further purification in the coupling reaction.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.77 (d, ^3J(H,H) = 3.5 Hz, 1H), 6.33 (d, ^3J(H,H) = 3.5 Hz, 1H), 3.89 (s, 3H), 1.66–1.51 (m, 6H), 1.39–1.16 (m, 6H), 1.16–0.96 (m, 6H), 0.94–0.84 (m, 9H) ppm.

MS (EI): *m/z* 404.1 $[M]^+$, 347.1 $[M\text{-}Bu]^+$.

2-Dimethylamino-5-[tri(n-butyl)-stannyl]-thiophene (2e). 2-Dimethylamino-thiophene (950 mg, 7.48 mmol) was placed under argon in dry THF (7 mL). The mixture was cooled to −78 °C and n-butyllithium in hexane (2.5 M, 3.90 mL, 9.75 mmol) was added dropwise. The mixture was allowed to warm up to −20 °C, the mixture was cooled down to −78 °C again and tributyltinchloride (2.52 g, 7.73 mmol) was added. The reaction was allowed to warm up to room temperature within 2 h and stirred for further 1.5 h. The mixture was poured into water (40 mL) and extracted with diethylether (3 × 30 mL) and the organic phase was dried over sodium sulfate. After removal of the solvent, **2e** was obtained as an oil which was pure enough for the further reaction (1.52 g, 49%).

^1H NMR (400 MHz, CD_2Cl_2): δ = 6.80 (d, ^3J(H,H) = 3.5 Hz, 1H), 6.02 (d, ^3J(H,H) = 3.4 Hz, 1H), 2.89 (s, 6H), 1.62–1.50 (m, 6H), 1.40–1.28 (m, 6H), 1.14–0.96 (m, 6H), 0.89 (t, ^3J(H,H) = 7.3 Hz, 9H) ppm. MS (EI): *m/z* 417.1 $[M]^+$, 361.0 $[M - Bu]^+$.

2-Pyrrolidino-5-[tri(n-butyl)-stannyl]-thiophene (2f). 1-(Thiophen-2-yl)pyrrolidine (4.3 g, 28.1 mmol) was placed under argon in dry THF (53 mL). The mixture was cooled to −78 °C and n-butyllithium in n-hexane (2.5 M, 14.6 mL, 36.5 mmol) was added dropwise. After 1 h, during this time the temperature was maintained below –10 °C, the mixture was cooled to −78 °C again and a solution of tributyltinchloride (11.9 g, 10 mL, 36.5 mmol) in THF (8 mL) was added. The reaction was stirred at −78 °C for 4 h and after removal of the cooling bath for additional 16 h. The mixture was poured into water and extracted with diethylether. The solvent was removed under reduced pressure. After distillation (80 °C, 0.33 mbar) the starting compounds were removed and a brownish oil was obtained which was pure enough for the further reaction (12.3 g, >95%).

^1H NMR (400 MHz, $CDCl_3$): δ = 6.86 (d, ^3J(H,H) = 3.4 Hz, 1H), 5.93 (d, ^3J(H,H) = 3.4 Hz, 1H), 3.33–3.24 (m, 4H), 2.05–1.97 (m, 4H), 1.68–1.46 (m, 6H), 1.42–1.26 (m, 6H), 1.16–0.96 (m, 6H), 0.91 (t, ^3J(H,H) = 3.4 Hz, 12H). HRMS (ESI, pos. mode, acetonitrile/chloroform): *m/z* 443.1666 $[M^+]$ (calcd. for $C_{20}H_{37}NSSn$ 443.1669).

6,6′-Dithiophen-2-yl-*N*,*N*′-(2-ethylhexyl)-isoindigo (3a). 6,6′-Dibromo-*N*,*N*′-(2-ethylhexyl)-isoindigo **1** (76.4 mg, 0.119 mmol), $Pd(dba)_2$ (6.10 mg, 10.6 μmol), $AsPh_3$ (3.21 mg, 10.5 μmol) and 2-[tri(n-butyl)-stannyl]-thiophene **2a** (201 mg, 0.539 mmol) were placed in a flask under argon. Dry and degassed toluene (19 mL) was added and the mixture was refluxed for 15 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (n-pentane/dichloromethane 9: 2) yielding **3a** as a dark solid (73.6 mg, 95%). mp 175 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 9.18 (d, ^3J(H,H) = 8.5 Hz, 2H), 7.47 (dd, ^3J = 3.6 Hz, ^4J(H,H) = 1.1 Hz, 2H), 7.40 (dd,

^3J(H,H) = 5.0 Hz, ^4J(H,H) = 1.1 Hz, 2H), 7.31 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.8 Hz, 2H), 7.15 (dd, ^3J(H,H) = 5.0 Hz, ^4J(H,H) = 3.6 Hz, 2H), 7.04 (d, ^4J(H,H) = 1.7 Hz, 2H), 3.78–3.66 (m, 4H), 1.93–1.87 (m, 2H), 1.49–1.28 (m, 16H), 1.03–0.81 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 168.9, 146.3, 144.4, 138.1, 132.3, 130.6, 128.8, 126.6, 124.7, 121.5, 119.3, 105.4, 44.4, 38.2, 31.3, 29.3, 24.7, 23.5, 14.3, 11.0. HRMS (ESI, pos. mode, acetonitrile/chloroform): *m/z* found 651.3077 [M+H]$^+$ (calcd. for $C_{40}H_{47}N_2O_2S_2$ 651.3074). Elemental Anal. Found: C, 73.61; H, 7.09; N, 4.10; S, 9.83. Calc. for $C_{40}H_{46}N_2O_2S_2$: C, 73.81; H, 7.12; N, 4.30; S, 9.85. UV-vis (CH_2Cl_2): λ_{max}/nm (ε_{max} M^{-1} cm^{-1}) = 309 (29000), 431 (24400), 445 (24200), 544 (18400). CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc$^+$): E_{red} (X^-/X^{2-}) = −1.69 V, E_{red} (X/X^-) = −1.29 V, E_{ox} (X/X^+) = 0.89 V, E_{ox} (X^+/X^{2+}) > 1.20 V.

6,6′-Bis(5-methylthiophen-2-yl)-*N*,*N*′-(2-ethylhexyl)-isoindigo (3b). 6,6′-Dibromo-*N*,*N*′-(2-ethylhexyl)-isoindig **1** (97.6 mg, 0.152 mmol), $Pd(dba)_2$ (9.70 mg, 16.8 μmol), $AsPh_3$ (5.20 mg, 17.0 μmol) and methyl-5-[tri(n-butyl)-stannyl]-thiophene **2b** (233 mg, 0.602 mmol) were placed in a flask under argon. Dry and degassed toluene (10 mL) was added and the mixture was refluxed for 18 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (n-pentane/dichloromethane 12: 5) yielding **3b** as a dark solid (42.1 mg, 41%). mp 192–194 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.14 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.27 (d, ^3J(H,H) = 3.6 Hz, 2H), 7.24 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.7 Hz, 2H), 6.98 (d, ^4J(H,H) = 1.8 Hz, 2H), 6.81 (dd, ^3J(H,H) = 3.5 Hz, ^4J(H,H) = 1.2 Hz, 2H), 3.80–3.62 (m, 4H), 2.54 (d, ^4J(H,H) = 0.8 Hz, 6 H), 1.95–1.83 (m, 2 H), 1.48–1.25 (m, 16H), 0.97–0.90 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 169.0, 146.2, 142.0, 141.8, 138.3, 132.0, 130.5, 127.1, 124.7, 121.1, 118.7, 104.9, 44.4, 38.21, 31.3, 29.3, 24.7, 23.5, 15.7, 14.3, 11.0. HRMS (ESI, pos. mode, acetonitrile/chloroform): *m/z* found 701.3208 [M+Na]$^+$ (calcd for $C_{42}H_{50}N_2NaO_2S_2$ 701.3206), Elemental Anal. Found: C, 73.91; H, 7.06; N, 3.92; S, 9.05. Calc. for $C_{42}H_{50}N_2O_2S_2$: C, 74.29; H, 7.42; N, 4.13; S, 9.44. UV-vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}) = 316 (27300), 455 (23000), 559 (22800). CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc$^+$): E_{red} (X^-/X^{2-}) = −1.72 V, E_{red} (X/X^-) = −1.32 V, E_{ox} (X/X^+) = 0.72 V, E_{ox} (X^+/X^{2+}) = 0.79 V.

6,6′-Bis(5-methylthiothiophen-2-yl)-*N*,*N*′-(2- ethylhexyl)-isoindigo (3c). 6,6′-Dibromo-*N*,*N*′-(2-ethylhexyl)-isoindigo **1** (78.6 mg, 0.122 mmol), $Pd(dba)_2$ (16.0 mg, 27.8 μmol), $AsPh_3$ (8.56 mg, 28.0 μmol) and 2-(methylthio)-5-[tri(n-butyl)-stannyl]-thiophene **2c** (286 mg, 0.683 mmol) were placed in a flask under argon. Dry and degassed toluene (15 mL) was added and the mixture was refluxed for 15 h. After further addition of **2c** (187 mg, 0.446 mmol) the mixture was refluxed for further 15 h and the solvent was removed under reduced pressure. After purification by column chromatography (n-pentane/dichloromethane 4 : 1) product **3c** was obtained as a dark solid (40.6 mg, 45%). mp 171–173 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.17 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.32 (d, ^3J(H,H) = 3.8 Hz, 2H), 7.24 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.7 Hz, 2H), 7.07 (d, ^3J(H,H) = 3.8 Hz, 2H), 6.97 (d, ^4J(H,H) = 1.6 Hz, 2H), 3.82–3.61 (m, 4H), 2.57 (s, 6H), 1.97–1.80 (m, 2H), 1.49–1.21 (m, 16H), 1.03–0.81 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 168.9, 146.3, 145.7, 139.5, 137.6, 132.1, 131.6, 130.6, 125.0, 121.5, 118.9, 104.9, 44.4, 38.2, 31.3, 29.3, 24.7, 23.5, 21.8, 14.3, 11.0. HRMS (ESI, pos. mode, acetonitrile/chloroform): *m/z* found 743.2826 [M+H]$^+$ (calcd for $C_{42}H_{51}N_2O_2S_4$ 743.2828). Elemental Anal. Found: C, 67.64; H, 6.92; N, 3.62; S, 17.29. Calc. for $C_{42}H_{50}N_2O_2S_4$: C, 67.88; H, 6.78; N, 3.77; S, 17.26. UV-vis (CH_2Cl_2): λ_{max}/nm (ε_{max} M^{-1} cm^{-1}) = 321 (25200), 455 (24000), 565 (26600). CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc$^+$): E_{red} (X^-/X^{2-}) = −1.67 V, E_{red} (X/X^-) = −1.27 V, E_{ox} (X^+/X^{2+}) = 0.59 V.

6,6′-Bis(5-methoxythiophen-2-yl)-*N*,*N*′-(2-ethylhexyl)-isoindigo (3d). 6,6′-Dibromo-*N*,*N*′-(2-ethylhexyl)-isoindigo **1** (79.2 mg, 0.123 mmol), $Pd(dba)_2$ (14.6 mg, 25.4 μmol), $AsPh_3$ (8.10 mg, 26.5 μmol) and 2-methoxy-5-[tri(n-butyl)-stannyl]-thiophene **2d** (248 mg, 0.615 mmol) were placed in a flask under argon. Dry and degassed toluene (10 mL) was added and the mixture was refluxed for 20 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (n-pentane/dichloromethane 3 : 1) yielding **3d** as a dark solid (26.8 mg, 31%). mp 181–183 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.11 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.17–7.12 (m, 4H), 6.89 (d, ^4J(H,H) = 1.8 Hz, 2H), 6.26 (d, ^3J(H,H) = 4.0 Hz, 2H), 3.95 (s, 6H), 3.77–3.63 (m, 4H), 1.94–1.83 (m, 2H), 1.48–1.27 (m, 16H), 0.98–0.90 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 169.1, 167.8, 146.2, 138.4, 131.7, 130.4, 130.2, 122.9, 120.7, 117.9, 105.6, 104.1, 60.75, 44.3, 38.2, 31.3, 29.3, 24.7, 23.5, 14.3, 11.0. HRMS (ESI, pos. mode, acetonitrile/chloroform): *m/z* 710.3195 [M$^+$] (calcd for $C_{42}H_{50}N_2O_4S_2$ 710.3207). Elemental Anal. Found: C, 70.44; H, 7.04; N, 3.81; S, 8.73. Calc. for: C, 70.95; H, 7.09; N, 3.94; S, 9.02. UV-vis (CH_2Cl_2): λ_{max}/nm (ε_{max} M^{-1} cm^{-1}) = 323 (24200), 467 (19900), 575 (28300). CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc$^+$): E_{red} (X^-/X^{2-}) = −1.75 V, E_{red} (X/X^-) = −1.34 V, E_{ox} (X/X^{2+}) = 0.52 V.

6,6′-Bis(5-dimethylaminothiophen-2-yl)-*N*,*N*′-(2-ethylhexyl)-isoindigo (3e). 6,6′-Dibromo-*N*,*N*′-(2-ethylhexyl)-isoindigo **1** (90.0 mg, 0.140 mmol), $Pd(dba)_2$ (8.10 mg, 14.1 μmol), $AsPh_3$ (4.80 mg, 15.7 μmol) and dimethylamino-5-[tri(n-butyl)-stannyl]-thiophene **2e** (189 mg, 0.454 mmol) were placed in a flask under argon. Dry and degassed toluene (10 mL) was added and the mixture was refluxed for 15 h. After addition of a second batch of **2e** (154 mg, 0.370 mmol) the mixture was refluxed for further 15 h and the solvent was removed under reduced pressure. After purification by column chromatography (n-pentane/dichloromethane 3 : 2) the product **3e** was obtained as a dark solid (16.9 mg, 16%). mp 249–251 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.04 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.23 (d, ^3J(H,H) = 4.2 Hz, 2H), 7.08 (d, ^3J(H,H) = 8.1 Hz, 2H), 6.85 (d, ^4J(H,H) = 1.4 Hz, 2H), 5.90 (d, ^3J(H,H) = 3.8 Hz, 2H), 3.76–3.63 (m, 4H), 3.01 (s, 12H), 1.98–1.80 (m, 2 H), 1.48–1.27 (m, 16H), 1.03–0.83 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 169.4, 160.9, 146.0, 138.7, 130.6, 130.1, 127.7, 125.7, 119.7, 116.8, 103.5, 103.1, 44.3, 42.7, 38.3, 31.3, 29.4, 24.7, 23.5, 14.3, 11.0. HRMS (ESI, pos. mode, acetonitrile/chloroform): *m/z* 736.38401 [M$^+$] (calcd. for $C_{44}H_{56}N_4O_2S_2$ 736.3839). UV-vis (CH_2Cl_2): λ_{max}/nm (ε_{max} M^{-1} cm^{-1}) = 355 (23200), 668 (45500). CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc$^+$): E_{red} (X^-/X^{2-}) = −1.75 V, E_{red} (X/X^-) = −1.38 V, E_{ox} (X/X^{2+}) = −0.03 V.

6,6′-Bis(5-pyrrolidinothiophen-2-yl)-*N*,*N*′-(2-ethylhexyl)-isoindigo (3f). 6,6′-Dibromo-*N*,*N*′-(2-ethylhexyl)-isoindigo **1** (79.2 mg, 0.123 mmol), $Pd(dba)_2$ (7.38 mg, 12.8 μmol), $AsPh_3$ (3.87 mg, 12.6 µmol) and 2-pyrrolidino-5-[tri(n-butyl)-stannyl]-thiophene **2f** (144 mg, 0.326 mmol) were placed in a flask under argon. Dry and degassed toluene (16 mL) was added and the mixture was refluxed for 23 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (n-pentane/dichloromethane 12 : 5) yielding **3f** as a dark solid (15.6 mg, 16%). mp 242–243 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 9.02$ (d, ^3J(H,H) = 8.5 Hz, 2H), 7.25 (d, ^3J(H,H) = 4.0 Hz, 2H), 7.06 (d, ^3J(H,H) = 8.3 Hz, 2H), 6.84 (d, ^4J(H,H) = 1.4 Hz, 2H), 5.79 (d, ^3J(H,H) = 3.2 Hz, H), 3.76–3.62 (m, 4H), 3.45–3.25 (m, 8H), 2.00–2.15 (m, 8H), 1.92–1.86 (m, 2H), 1.48–1.22 (m, 16H), 0.96–0.91 (m, 12H). ^{13}C NMR (151 MHz, CD_2Cl_2): $\delta = 169.5$, 157.2, 145.8, 138.8, 130.1, 129.9, 126.0, 125.9, 119.3, 116.4, 102.7, 101.7, 51.1, 44.1. 38.2, 31.2, 29.3, 26.2, 24.6, 23.5, 14.3, 11.0. HRMS (ESI, pos. mode, acetonitrile/chloroform): m/z 788.4150 [M+] (calcd. for $C_{48}H60N_4O_2S_2$ 788.1452). UV-vis (CH_2Cl_2): λ_{max}/nm (ε_{max} M^{-1} cm^{-1}) = 362 (23300), 696 (47900). CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc^+): E_{red} (X^-/X^{2-}) = −1.79 V, E_{red} (X/X^-) = −1.40 V, E_{ox} (X/X^{2+}) = 0.09 V.

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