Chemical Science

RSCPublishing

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2013, **4**, 2447

Chlorination as a useful method to modulate conjugated polymers: balanced and ambient-stable ambipolar high-performance field-effect transistors and inverters based on chlorinated isoindigo polymers†

Ting Lei,[a] Jin-Hu Dou,[a] Zhi-Jun Ma,[b] Chen-Jiang Liu,*[b] Jie-Yu Wang*[a] and Jian Pei*[a]

Received 28th January 2013
Accepted 28th February 2013

DOI: 10.1039/c3sc50245g

www.rsc.org/chemicalscience

For the first time, ambient-stable and balanced carrier transport is achieved in polymer ambipolar field-effect transistors (FETs) and inverters with high performance. With chlorinated isoindigo polymers, FETs fabricated in ambient conditions show hole mobilities up to 0.81 cm^2 V^{-1} s^{-1} and dramatically increased electron mobilities from 10^{-2} to 0.66 cm^2 V^{-1} s^{-1}. Hence, chlorination is effective to modulate electronic properties and improve the device performance of conjugated polymers.

Introduction

Solution-processable semiconducting polymers are important for flexible, large-area, and low-cost plastic electronics.[1] For instance, ambipolar polymer field-effect transistors (FETs) have potential applications in complementary-like circuits and in organic light-emitting transistors,[2–4] and their development largely relies on new polymers. Electron-deficient building blocks, such as diketopyrrolopyrrole (DPP),[5] naphthalene diimide (NDI),[6] and benzobisthiadiazole (BBT),[7] have been widely used to prepare ambipolar polymers. Nonetheless, only few of these polymers can be operated in ambient conditions,[8] and fewer show balanced carrier transport.[9] To our knowledge, none offer both balanced carrier transport and transport in ambient conditions—criteria for an ideal ambipolar material that can significantly simplify circuit design and minimize patterning and fabrication processes.[2,8–10]

Fluorine is strongly electron-withdrawing and small in size. As a popular approach for material modification, fluorination of organic small molecules or polymers can lower their LUMO levels without harmful steric effects, thus improving device stability or performance.[11,12] We recently demonstrated that fluorination of the isoindigo unit can increase electron mobility from 10^{-2} to 0.43 cm^2 V^{-1} s^{-1}.[13] By contrast, chlorination of small molecules has been investigated less, although the precursors are more readily available[11] and chlorinated molecules have shown comparable or better performances than their fluorinated counterparts.[14] Moreover, chlorination of conjugated polymers has never been reported, presumably due to the larger atom size of chlorine and thereby steric hindrance effects.

Herein, we chlorinate isoindigo-based polymers through an efficient chlorination reaction. Balanced charge carrier transport with hole mobilities up to 0.81 cm^2 V^{-1} s^{-1} and electron mobilities up to 0.66 cm^2 V^{-1} s^{-1} are obtained for devices fabricated in ambient conditions using these polymers. These mobilities are among the highest for ambipolar polymer FETs. Therefore, our work represents the first chlorination of semiconducting polymers, and our chlorinated isoindigo polymers are the first ambipolar polymers that can offer both balanced carrier transport and transport in ambient conditions.

Results and discussion

Design and synthesis

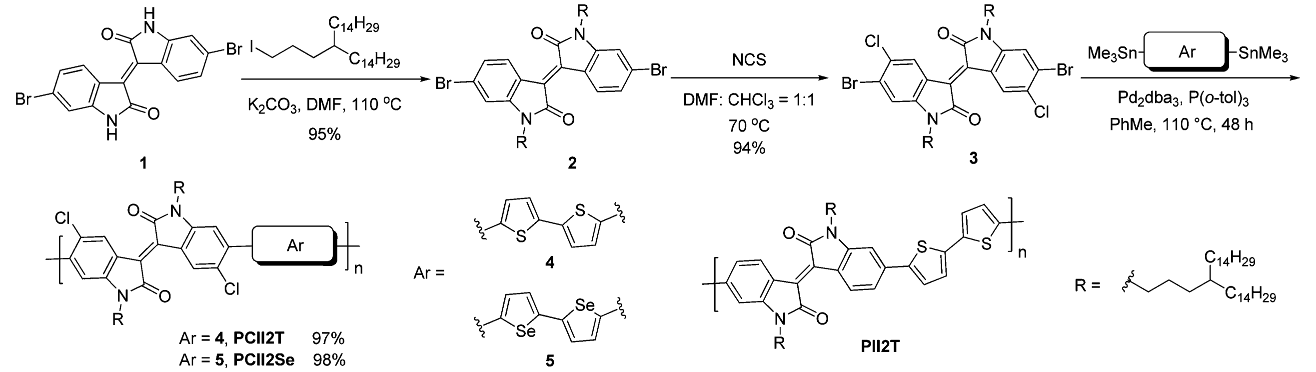
4-Tetradecyloctadecyl groups were used as side chains because a farther branching point can increase the mobility of isoindigo-based polymers.[15] Besides 2,2′-bithiophene, 2,2′-biselenophene was also chosen as the donor unit because recent studies showed that replacing thiophene with selenophene increases mobility in polymer FETs.[16] As illustrated in Scheme 1, the synthesis of chlorinated isoindigo polymers started from the alkylation of commercially available 6,6′-dibromoisoindigo (**1**) with K_2CO_3, giving **2** in 95% yield. Direct chlorination of the isoindigo core with *N*-chlorosuccinimide (NCS) provided 5,5′-dichloro-6,6′-dibromoisoindigo (**3**) in high yield (94%) with high regioselectivity. **3** was then subjected to a Stille coupling polymerization with 5,5′-bis(trimethylstannyl)-2,2′-bithiophene to give chlorinated

---

[a] *Beijing National Laboratory for Molecular Sciences, The Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. E-mail: jianpei@pku.edu.cn; jieyuwang@pku.edu.cn; Fax: +86-10-62758145*

[b] *Physics and Chemistry Detecting Center, The Key Laboratory of Oil & Gas Fine Chemicals of Ministry of Education, School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China. E-mail: pxylcj@126.com*

† Electronic supplementary information (ESI) available: Experimental details and characterization data. See DOI: 10.1039/c3sc50245g



Scheme 1 Synthesis of chlorinated isoindigo polymers **PCII2T** and **PCII2Se**, and the reference isoindigo polymer **PII2T**.

polymer **PCII2T** in 97% yield, and with 5,5′-bis(trimethylstannyl)-2,2′-biselenophene to give chlorinated polymer **PCII2Se** in 98% yield. A reference polymer **PII2T** was also prepared to show the chlorination effect. All polymers were purified by adding a coordinating ligand to remove residual palladium catalyst,[17] and Soxhlet extraction was then performed to remove oligomers and other impurities. Molecular weights of all polymers were evaluated by high temperature gel permeation chromatography (GPC) using 1,2,4-trichlorobenzene (TCB) as eluent at 140 °C. Both chlorinated polymers showed similarly high molecular weight with M_n around 60 kDa and PDI around 2.1. The reference polymer **PII2T** exhibited a slightly higher molecular weight of 72.8 kDa and a PDI of 1.93. Note that the fluorinated isoindigo polymer needs 6 steps with only 21% total yield,[13] whereas the chlorinated polymer **PCII2T** needs only 3 steps with 87% total yield. All polymers displayed high thermal stability with decomposition temperatures over 390 °C, and no phase transition was observed for any polymers in the range of 25 to 330 °C.[18]

Photophysical and electrochemical properties

Fig. 1a illustrates a comparison of the absorption spectra of chlorinated polymer **PCII2T** and the reference **PII2T** both in solution and in thin film. Both polymers show similar dual band absorption spectra. **PCII2T** displays a lowered bandgap (1.53 eV) than **PII2T** (1.57 eV) but broadened Band I and blue-shifted Band II absorptions. **PCII2T** only reveals a 0–1 vibrational absorption peak in solution, and the 0–0 vibrational absorption rises as a shoulder peak in film. In contrast, **PII2T** exhibits a stronger 0–0 vibrational peak both in solution and in film. The increase of the 0–0 peak indicates that the polymer backbones may become more planar in film. Computational analysis of the polymer fragment reveals that the introduction of chlorine atoms increases the dihedral angle of the phenyl–thienyl connection from 22.2° to 34.2° (Fig. 1d), significantly larger than those of fluorinated polymers (17.1°).[13] The Cl–H distance (2.74 Å) is shorter than the sum of their van der Waals radii (2.95 Å),[19] indicating the existence of Cl–H interactions. Thus the decreased 0–0 peak in **PCII2T** may be attributed to the larger dihedral angle caused by the steric hindrance of chlorine atoms.[20] Changing the donors to biselenophene units further lowers the polymer bandgap to 1.51 eV, due to the stronger electron-donating properties of 2,2′-biselenophene (Fig. 1b).[16a]

The electrochemical behaviors of the polymers were evaluated by cyclic voltammetry (CV). All polymers show one order of magnitude stronger oxidative peaks than their reductive ones (Fig. 1c). The HOMO/LUMO levels of **PCII2T** (−5.64/−3.86 eV) are lower than those of **PII2T** (−5.42/−3.70 eV), and close to those of the fluorinated isoindigo polymers (−5.60/−3.88 eV),[13] indicating that chlorination has a similar electrochemical effect to fluorination. When electron-rich biselenophene is used as donor, the HOMO/LUMO levels of **PCII2Se** increase to −5.57/−3.84 eV. These results agree with our previous findings that changing the donor units can hardly affect the LUMO levels of polymers,[21] because their LUMOs are mostly localized on isoindigo cores (Fig. 1e). However, the HOMOs are well delocalized along the polymer backbone, thus direct modification of the isoindigo cores with electron-deficient chlorine atoms can lower both LUMO levels and HOMO levels. The CV results are also consistent with the energy levels calculated from the photoelectron spectroscopy (PES) and the optical bandgap, as summarized in Table S1.†

Field-effect transistors and complementary inverters

Polymer FETs with top-gate/bottom-contact (TG/BC) configuration were fabricated by spin-coating the polymer solution in 1,2-dichlorobenzene (DCB) (6 mg mL^{-1}) onto solvent-cleaned gold electrode (source–drain)/SiO$_2$/Si substrates. After thermal annealing the polymer film at optimized temperature (180 °C) for 10 min, a fluoropolymer (Cytop™) solution was spin-coated on top of the polymer film as the dielectric layer, and an aluminum layer was thermally evaporated as the gate electrode. Devices were fabricated both in a glovebox and in ambient conditions (R_H = 50–60%) to compare their device performances. The reference polymer **PII2T** showed high hole mobility up to 0.76 cm^2 V^{-1} s^{-1} and a low electron mobility of 0.07 cm^2 V^{-1} s^{-1} in a glovebox (Table 1). Upon exposure to air, the hole mobility further increased to 1.27 cm^2 V^{-1} s^{-1}, but the electron mobility decreased drastically to 10^{-3} to 10^{-2} cm^2 V^{-1} s^{-1}. In contrast, **PCII2T** showed balanced hole and

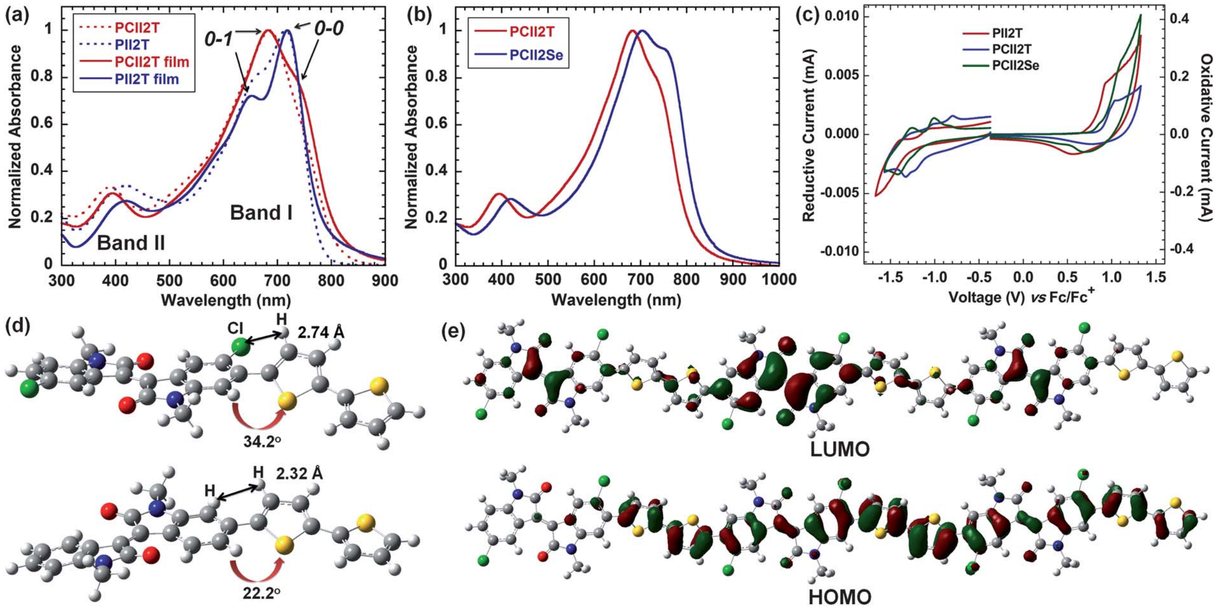


Fig. 1 (a) Normalized absorption spectra of **PCII2T** and **PII2T** in $CHCl_3$ (1×10^{-5} M, dotted line) and in film (solid line). (b) Normalized absorption spectra of **PCII2T** and **PCII2Se** in film. (c) Cyclic voltammograms of polymers in thin films drop-cast on a glassy carbon electrode. (d) Comparison of the phenyl–thienyl dihedral angles of **PCII2T** and **PII2T**. **PCII2T** displays a larger dihedral angle (34.2°) than **PII2T** (22.2°) after introducing the chlorine atoms. (e) Calculated molecular orbitals of the trimer of **PCII2T** (B3LYP/6-31G (d)).

electron transport. For devices fabricated in a glovebox, hole mobilities up to 0.50 $cm^2 V^{-1} s^{-1}$ and electron mobilities up to 0.62 $cm^2 V^{-1} s^{-1}$ were observed; for those fabricated in ambient conditions, the hole mobility slightly increased to 0.54 $cm^2 V^{-1} s^{-1}$ and the electron mobility slightly decreased to 0.48 $cm^2 V^{-1} s^{-1}$. Hence, the introduction of the chlorine atoms obviously improved the electron transport and ambient stability of the isoindigo polymers. In contrast, although fluorinated isoindigo-based polymers showed remarkably high hole mobility (1.85 $cm^2 V^{-1} s^{-1}$), the carrier transport was not balanced because the electron mobility (0.43 $cm^2 V^{-1} s^{-1}$) was relatively low.[13]

With **PCII2Se**, devices fabricated in a glovebox and in ambient conditions showed increased hole and electron mobilities while maintaining balanced transport upon substituting sulfur atoms with selenium atoms in the polymer. High hole and electron mobilities up to 1.05 $cm^2 V^{-1} s^{-1}$ and 0.72 $cm^2 V^{-1} s^{-1}$ were obtained for devices fabricated in a glovebox, and in ambient conditions the hole mobility (0.81 $cm^2 V^{-1} s^{-1}$) and electron mobility (0.66 $cm^2 V^{-1} s^{-1}$) decreased only slightly (Fig. 2a and b). Our chlorinated isoindigo polymers are the first ambipolar polymers that can be operated in ambient conditions and with the transport carriers in balance, and their mobilities are among the highest of ambipolar polymer FETs.[3–9]

An inverter is the most fundamental logic gate,[22] thus ambient fabrication of inverters is significant for large-area and low-cost applications of polymers in digital circuits. Hence, we used chlorinated isoindigo polymers to fabricate complementary-like inverters on a common substrate without patterning the organic semiconductor (Fig. 2c). The inverters consisted of two connected TG/BC ambipolar transistors with a common

Table 1 Summary of molecular weights, OFET device performances, and GIXD results of all polymers

									d^f (Å)	
Polymers	M_w/M_n (kDa)	PDI	$\mu_{hole}{}^a$ ($cm^2 V^{-1} s^{-1}$)	V_T (V)	$\log(I_{on}/I_{off})^d$	$\mu_{electron}{}^a$ ($cm^2 V^{-1} s^{-1}$)	V_T (V)	$\log(I_{on}/I_{off})^e$	L	π
PII2T	141.9/72.8	1.95	0.76 (0.66)^b	−35	4–5	0.07 (0.06)^b	+25	2–3	28.8	3.56
			1.27 (1.44)^c	−14	5–6	0.01 (0.004)^c	+36	1–2		
PCII2T	127.2/60.3	2.11	0.50 (0.38)^b	−70	4–5	0.62 (0.47)^b	+29	4–5	28.8	3.57
			0.54 (0.51)^c	−26	4–5	0.48 (0.42)^c	+36	4–5		
PCII2Se	124.8/58.6	2.13	1.05 (0.85)^b	−68	5–6	0.72 (0.62)^b	+27	5–6	29.0	3.56
			0.81 (0.74)^c	−38	5–6	0.66 (0.58)^c	+47	5–6		

[a] Measured under ambient conditions (R_H = 50–60%). Maximum mobilities and averages are in parentheses (over 20 devices). [b] Devices fabricated in glovebox. [c] Device fabricated in ambient conditions. [d] Evaluated at $V_D = -20$ V. [e] Evaluated at $V_D = +20$ V. [f] Lamellar (L) and π–π stacking (π) distances determined by GIXD experiments.

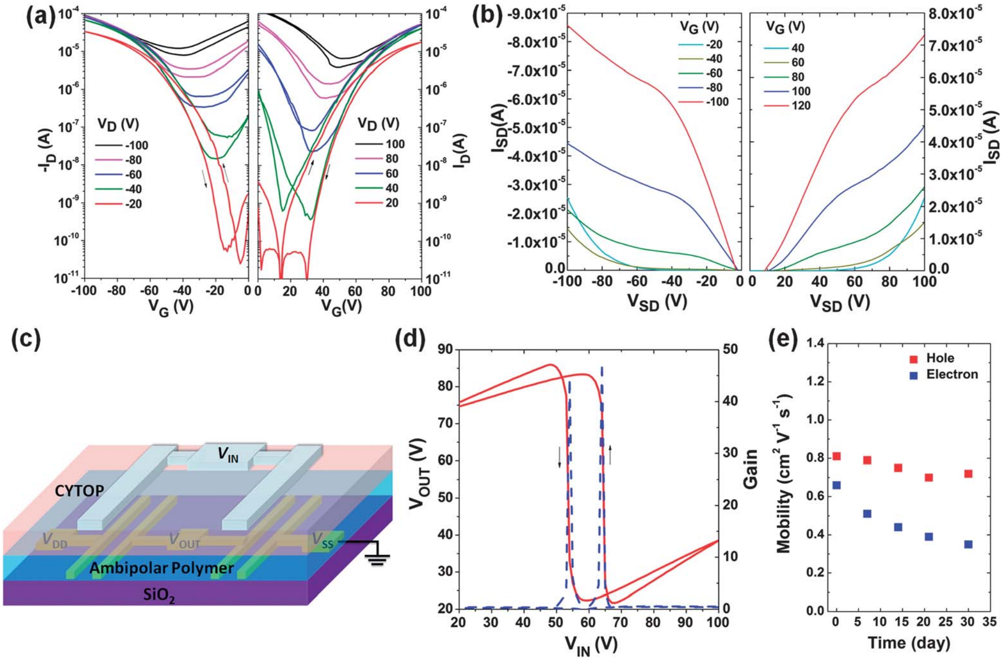


Fig. 2 (a) The transfer and (b) output characteristics of **PCII2Se** devices fabricated and tested in ambient conditions ($L = 50$ μm, $W = 1$ mm, $C = 3.7$ nF cm^{-2}). (c) Schematic diagram of an inverter device consisting of two connected TG/BC ambipolar transistors. (d) The VTC characteristic and gain of a complementary-like inverter fabricated with **PCII2Se** in ambient conditions ($V_{DD} = 100$ V, $L = 50$ μm, $W = 4$ mm). (e) Time-dependent decay of device performance of **PCII2Se** under ambient conditions.

gate as input (V_{IN}) and a common drain as output (V_{OUT}) and were fabricated both in a glovebox and in ambient conditions. Obvious inverting functionality was observed for both chlorinated polymers when the input voltage and the supply voltage (V_{DD}) were both positively or negatively biased (Fig. S8–S11 in the ESI†). The static voltage transfer characteristic (VTC) and gain of the inverter fabricated with **PCII2Se** in ambient conditions are shown in Fig. 2d. Both chlorinated polymers showed high gain values in the range of 40 to 50. For inverters fabricated in ambient conditions, **PCII2T** showed high gains up to 46, and **PCII2Se** showed higher gains up to 48. Note that the hysteresis of the ambient-fabricated devices becomes obviously smaller than those of devices fabricated in nitrogen (Fig. S9 in the ESI†), presumably due to the more balanced threshold voltages in both p- and n-channel modes after exposing to air.[22] To our knowledge, these are the first ambient-fabricated inverters based on ambipolar polymers, and their gain values are the second highest.[3b]

Time-dependent decay of both polymer devices was also assessed by storing the devices under ambient conditions. For both polymers, we observed very good stability of hole transport and a slow roll-off of electron mobility over 30 days (Fig. 2e and S12†). The decay of the electron mobility may be caused by the further diffusion of the oxygen and water into the semiconductors. Although the devices are not long-term stable in ambient conditions, the polymers can be fabricated and tested in ambient conditions, and the stability is also outstanding amongst ambipolar polymers—very few ambipolar polymers can be fabricated and tested in ambient conditions and fewer are reported with stability data.[8]

Thin film microstructure and morphology

Grazing incident X-ray diffraction (GIXD) and tapping-mode atomic force microscopy (AFM) were used to investigate the thin film microstructures and morphology (Fig. 3). All polymers displayed strong out-of-plane (*h*00) diffraction, indicating that typical lamellar packing was formed in polymer films.[23] Peaks attributed to π–π stacking distances were observed for all polymers. **PII2T** showed a much stronger out-of-plane (010) peak and weaker (*h*00) peaks, whereas **PCII2T** showed a stronger in-plane (010) peak. For **PCII2Se**, only an in-plane (010) peak was observed. These observations suggest that the thin film packings for the three polymers are distinct. **PII2T** preferred to form face-on packing in film. However, after introducing chlorine atoms, both edge-on and face-on packings were found in **PCII2T**, and no face-on packing was observed in **PCII2Se** on further changing the donor unit to biselenophene (Fig. 3g–i). Although the packings in thin film are different, all polymers exhibited almost the same lamellar packing and π-stacking distances (Table 1), due to their similar polymer backbones and identical side chains. AFM height images of the polymers displayed fiber-like intercalating networks with obviously crystallized zones, similar to other high-performance polymer FET materials.[24] Root-mean-square (RMS) analysis of the height images showed that **PCII2Se** displayed the largest roughness, presumably due to its stronger crystallinity. Therefore, the introduction of chlorine atoms and the replacement of thiophene by selenophene not only modulate the polymer energy levels, but also affect the interchain interactions, thereby leading to different polymer packing in the solid state.

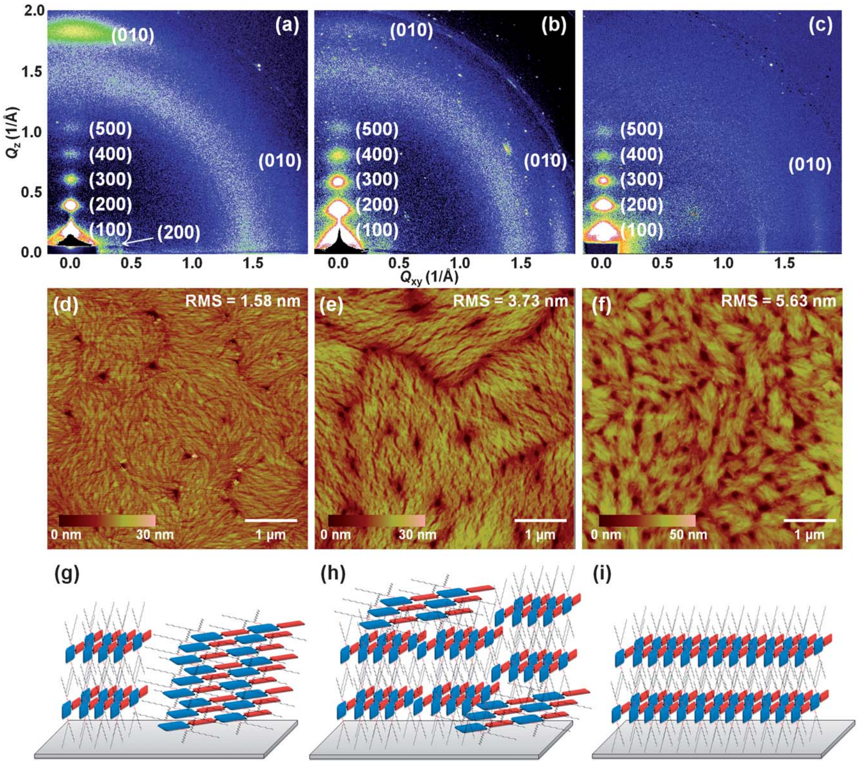


Fig. 3 2D-GIXD patterns, AFM height images and cartoon illustrations of the proposed packing models of (a, d, and g) **PII2T**, (b, e, and h) **PCII2T** and (c, f, and i) **PCII2Se** films. Films were prepared by spin-coating from the DCB solutions of the polymers (6 mg mL^{-1}) and annealed at 180 °C.

Conclusions

In summary, we have developed an efficient chlorination reaction to engineer the isoindigo core of isoindigo-based polymers. Ambipolar FETs using these chlorinated conjugated polymers show significantly increased electron mobilities and ambient stability, as well as high and balanced ambipolar charge carrier transport. Using **PCII2Se**, FETs fabricated in ambient conditions show high hole mobilities up to 0.81 $cm^2\ V^{-1}\ s^{-1}$ and balanced electron mobilities up to 0.66 $cm^2\ V^{-1}\ s^{-1}$. For the first time both good ambient-stability and balanced carrier transport are fulfilled in ambipolar polymers. In addition, complementary-like inverters based on these polymers show a sharp signal switching with high gains up to 48. Endowing isoindigo polymers with new properties that are useful for applications in large-area and more complex complementary-like logic circuits, chlorination has proved to be an effective alternative to modulate properties and improve performances of conjugated polymers.

Acknowledgements

This work was supported by the Major State Basic Research Development Program (no. 2009CB623601 and 2013CB933501) from the Ministry of Science and Technology, and National Natural Science Foundation of China. The authors thank beamline BL14B1 (Shanghai Synchrotron Radiation Facility) for providing the beam time.

Notes and references

1 (*a*) P. F. Moonen, I. Yakimets and J. Huskens, *Adv. Mater.*, 2012, **24**, 5526; (*b*) H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Doltz, M. Kestler and A. Facchetti, *Nature*, 2009, **457**, 679; (*c*) H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu and E. P. Woo, *Science*, 2000, **290**, 2123.

2 (*a*) J. Zaumseil and H. Sirringhaus, *Chem. Rev.*, 2007, **107**, 1296; (*b*) Y. Guo, G. Yu and Y. Liu, *Adv. Mater.*, 2010, **22**, 4427.

3 (*a*) A. J. Kronemeijer, E. Gili, M. Shahid, J. Rivnay, A. Salleo, M. Heeney and H. Sirringhaus, *Adv. Mater.*, 2012, **24**, 1558; (*b*) Z. Chen, H. Lemke, S. Albert-Seifried, M. Caironi, M. M. Nielsen, M. Heeney, W. Zhang, I. McCulloch and H. Sirringhaus, *Adv. Mater.*, 2010, **22**, 2371.

4 (*a*) J. Zaumseil, R. H. Friend and H. Sirringhaus, *Nature Mater.*, 2006, **5**, 69; (*b*) L. Bürgi, M. Turbiez, R. Pfeiffer, F. Bienewald, H.-J. Kirner and C. Winnewisser, *Adv. Mater.*, 2008, **20**, 2217.

5 (*a*) C. B. Nielsen, M. Turbiez and I. McCulloch, *Adv. Mater.*, DOI: 10.1002/adma.201201795; (*b*) J. Lee, A.-R. Han, J. Kim, Y. Kim, J. H. Oh and C. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 20713; (*c*) J. C. Bijleveld, A. P. Zoombelt, S. G. J. Mathijssen, M. M. Wienk, M. Turbiez, D. M. de Leeuw and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2009, **131**, 16616.

6 K.-J. Baeg, D. Khim, S.-W. Jung, M. Kang, I.-K. You, D.-Y. Kim, A. Facchetti and Y.-Y. Noh, *Adv. Mater.*, 2012, **24**, 5433.

7 (*a*) J. D. Yuen and F. Wudl, *Energy Environ. Sci.*, 2013, **6**, 392; (*b*) J. Fan, J. D. Yuen, M. Wang, J. Seifter, J.-H. Seo, A. R. Mohebbi, D. Zakhidov, A. Heeger and F. Wudl, *Adv. Mater.*, 2012, **24**, 2186; (*c*) J. D. Yuen, J. Fan, J. Seifter, B. Lim, R. Hufschmid, A. J. Heeger and F. Wudl, *J. Am. Chem. Soc.*, 2011, **133**, 20799.

8 H. Usta, C. Newman, Z. Chen and A. Facchetti, *Adv. Mater.*, 2012, **24**, 3678.

9 (*a*) Z. Chen, M. J. Lee, R. S. Ashraf, Y. Gu, S. Albert-Seifried, M. M. Nielsen, B. Schroeder, T. D. Anthopoulos, M. Heeney, I. McCulloch and H. Sirringhaus, *Adv. Mater.*, 2012, **24**, 647; (*b*) M. Shahid, T. McCarthy-Ward, J. Labram, S. Rossbauer, E. B. Domingo, S. E. Watkins, N. Stingelin, T. D. Anthopoulos and M. Heeney, *Chem. Sci.*, 2012, **3**, 181.

10 (*a*) H. Jiang, *Macromol. Rapid Commun.*, 2010, **31**, 2007; (*b*) Y.-Y. Liu, C.-L. Song, W.-J. Zeng, K.-G. Zhou, Z.-F. Shi, C.-B. Ma, F. Yang, H.-L. Zhang and X. Gong, *J. Am. Chem. Soc.*, 2010, **132**, 16349.

11 M. L. Tang and Z. Bao, *Chem. Mater.*, 2011, **23**, 446.

12 (*a*) H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angew. Chem., Int. Ed.*, 2011, **50**, 2995; (*b*) S. C. Price, A. C. Stuart, L. Yang, H. Zhou and W. You, *J. Am. Chem. Soc.*, 2011, **133**, 4625; (*c*) H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nature Photon.*, 2009, **3**, 649; (*d*) Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792.

13 T. Lei, J.-H. Dou, Z.-J. Ma, C.-H. Yao, C.-J. Liu and J. Pei, *J. Am. Chem. Soc.*, 2012, **134**, 20025.

14 (*a*) M. L. Tang, J. H. Oh, A. D. Reichardt and Z. Bao, *J. Am. Chem. Soc.*, 2009, **131**, 3733; (*b*) M. Gsänger, J. H. Oh, M. Könemann, H. W. Höffken, A.-M. Krause, Z. Bao and F. Würthner, *Angew. Chem., Int. Ed.*, 2010, **49**, 740.

15 (*a*) T. Lei, J.-H. Dou and J. Pei, *Adv. Mater.*, 2012, **24**, 6457; (*b*) J. Mei, D. H. Kim, A. L. Ayzner, M. F. Toney and Z. Bao, *J. Am. Chem. Soc.*, 2011, **133**, 20130.

16 (*a*) I. Kang, T. K. An, J.-a. Hong, H.-J. Yun, R. Kim, D. S. Chung, C. E. Park, Y.-H. Kim and S.-K. Kwon, *Adv. Mater.*, 2013, **25**, 524; (*b*) J. S. Ha, K. H. Kim and D. H. Choi, *J. Am. Chem. Soc.*, 2011, **133**, 10364.

17 K. T. Nielsen, K. Bechgaard and F. C. Krebs, *Macromolecules*, 2005, **38**, 658.

18 Note that a phase transition around 0 °C is observed for all these polymers, which is attributed to the melting of the long alkyl chains. We observed that the transition temperature is mainly determined by the type of the alkyl side chain regardless of the polymer backbone, and longer alkyl chains lead to higher transition temperatures.

19 (*a*) A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441; (*b*) R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384.

20 The corresponding fluorinated polymer **PFII2T** showed a stronger 0–0 peak than 0–1 peak, similar to **PII2T**. Thus, the vibrational peak variations are attributed to steric hindrance caused by chlorine atoms rather than electronic effects.

21 (*a*) T. Lei, Y. Cao, X. Zhou, Y. Peng, J. Bian and J. Pei, *Chem. Mater.*, 2012, **24**, 1762; (*b*) T. Lei, Y. Cao, Y. Fan, C.-J. Liu, S.-C. Yuan and J. Pei, *J. Am.Chem. Soc.*, 2011, **133**, 6099.

22 S.-M. Kang and Y. Leblebici, *CMOS Digital Integrated Circuits: Analysis and Design*, McGraw-Hill, New York, 3rd edn, 2003.

23 (*a*) J. Rivnay, S. C. B. Mannsfeld, C. E. Miller, A. Salleo and M. F. Toney, *Chem. Rev.*, 2012, **112**, 5488; (*b*) Y. Wen, Y. Liu, Y. Guo, G. Yu and W. Hu, *Chem. Rev.*, 2011, **111**, 3358.

24 (*a*) H. Chen, Y. Guo, G. Yu, Y. Zhao, J. Zhang, D. Gao, H. Liu and Y. Liu, *Adv. Mater.*, 2012, **24**, 4618; (*b*) I. Osaka, M. Shimawaki, H. Mori, I. Doi, E. Miyazaki, T. Koganezawa and K. Takimiya, *J. Am. Chem. Soc.*, 2012, **134**, 3498; (*c*) H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. S. Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeney and I. McCulloch, *J. Am. Chem. Soc.*, 2011, **133**, 3272; (*d*) Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. van Meurs and J. Tan, *J. Am. Chem. Soc.*, 2011, **133**, 2198.