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## COMMUNICATION

# Isoindigo-based polymer field-effect transistors: effects of selenophene-substitution toward high charge carrier mobility

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**We show that selenophene-substitution can be an efficient synthetic strategy toward high charge carrier mobility of isoindigo (IID)-based copolymers when their side chains are optimized. High mobility of 5.8 cm<sup>2</sup>/Vs is demonstrated by a strategically designed IID-based polymer, with both side-chain adjustment and selenophene-substitution:**

## Introduction

Donor–acceptor-based copolymers have attracted great attention in the field of polymer field-effect transistors (PFETs) due to their unprecedented high charge carrier mobility, despite having apparently less-oriented microstructures.<sup>1–3</sup> In addition to their own merits, such as flexibility, ruggedness, and mechanical strength, such high mobility now makes these polymer semiconductors the key materials for next-generation optoelectronic devices.<sup>4</sup> The successes basically originate from the development of a smart design strategy of polymeric semiconductors that involves: enhancing intramolecular charge transport 1) via strong donor–acceptor charge delocalization, mostly using diketopyrrolopyrrole (DPP) or isoindigo (IID) as an electron acceptor,<sup>5</sup> 2) via “molecular docking”, by using small-sized donor moieties, particularly those with centrosymmetry,<sup>6,7</sup> and 3) by moving the branching point of branched side chains away from the polymer backbone.<sup>8,9</sup> By adopting these design strategies, great successes have been reported in the field. The peak mobility value now exceeds 10 cm<sup>2</sup>/Vs,<sup>4,9–12</sup> that is compatible with a realistic minimum requirement for driving FETs of commercial organic light-emitting diodes.<sup>13</sup>

Among polymer semiconductors, IID-based polymers have been less studied compared to DPP-based polymers, presumably due to their relatively lower charge carrier mobility. One can find many reports on mobilities >5 cm<sup>2</sup>/Vs for DPP-based polymers, while the mobilities of IID-based polymers reach a plateau near 1–3 cm<sup>2</sup>/Vs.<sup>4,5,9,10,12</sup> Therefore, it would be meaningful to develop a more efficient donor moiety to achieve higher mobility.

Here we demonstrate new IID-based copolymers employing thiophene–vinylene–thiophene (TVT) and selenophene–vinylene–selenophene (SVS) as centrosymmetric donor moieties. According to previous research, substitution of selenophene for thiophene generally leads to higher charge carrier mobility due to better intermolecular interaction.<sup>14</sup> However, this theory has not been

thoroughly confirmed in the case of IID-based polymers. Although some reports have tried to combine IID with Se-moieties, the resulting mobility values were only comparable to those of S-analogues.<sup>6</sup> Here we demonstrate for the first time that selenophene-substitution can clearly lead to a higher crystalline order, as well as a high charge carrier mobility in IID-polymers. Furthermore, we tried to adjust the branching position of IID-TVT and IID-SVS: P-24-IID-TVT and P-24-IID-SVS have branched alkyl chains whose branching points are a single-carbon distance from the polymer backbone, whereas P-29-IID-TVT and P-29-IID-SVS have branched alkyl chains with 6-carbon alkyl spacer between the branching point and backbone. As a result, we can expect that P-29-IID-SVS has 1) enhanced intramolecular charge transport via strong donor (IID)–acceptor (SVS) charge delocalization, 2) enhanced intermolecular charge transport via “molecular docking” of the centrosymmetric SVS unit to the adjacent IID unit, and 3) highly aligned crystalline ordering due to an adjusted branching point of the branched side chains away from the polymer backbone. In particular, we show that the selenophene-substitution strategy effectively works only on P-29s, in which the side chains are optimized. The systematic studies based on photo-physical, structural, and morphological analyses fully supported the above-described arguments. We show that the charge carrier mobility of P-29-IID-SVS reaches 5.83 cm<sup>2</sup>/Vs, which is the highest among those for previously reported IID-derivatives.

Figure 1 shows the UV-Vis absorption spectra of all polymers in their dilute solution, thin film, and annealed thin film states. Notably, the absorption peaks of all polymers as thin films do not shift with respect to those in solution, implying planarity of the polymer backbone, even in solution. Typical dual-band absorption spectra are obtained in all of the prepared samples: band I (500–800 nm) and band II (300–500 nm). In band I, three vibrational peaks are observed, 0–0, 0–1, and 0–2, corresponding to the charge-transfer absorption by the IID unit from the donor. When the polymer state is changed from solution to solid film, the 0–0 absorption peak intensity tends to

increase while the 0–1 absorption peak intensity decreases, implying a rearrangement of the polymer conformation. This relative growth of the 0–0 peak intensity compared to the 0–1 peak intensity by tuning from solution to film, becomes very pronounced in the case of P-29-IID-SVS. Therefore, one can expect P-29-IID-SVS to have the most efficient intermolecular interactions in the thin film state. When comparing the absorption spectra of P-24s and P-29s we can observe a distinct red shift by 20–30 nm in the P-29s, meaning that the P-29s have more planar backbone structures. Similar effects were reported by the previous side chain engineering technique.<sup>8,9</sup> The comparison between P-TVTs and P-SVSs enables us to elucidate the effect of selenophene-substitution. In both P-24s and P-29s, we can see that the absorption spectra of P-SVSs are red-shifted by ~15 nm, meaning that selenophene substitution results in stronger donor–acceptor charge delocalization.

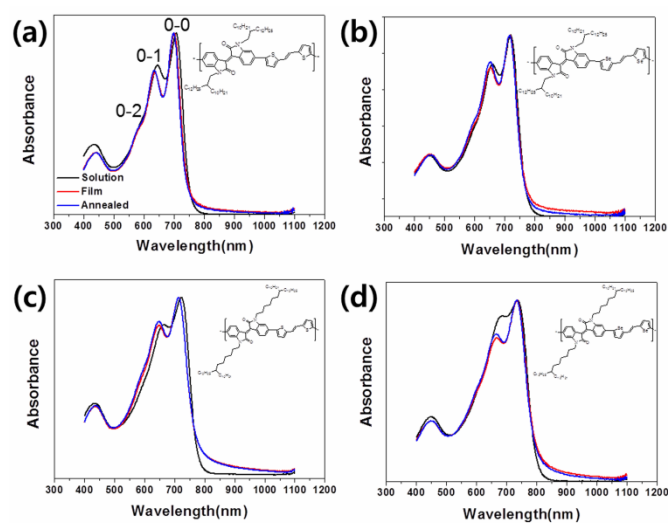


Figure 1. UV-Vis absorption spectra of (a) P-24-IID-TVT, (b) P-24-IID-SVS, (c) P-29-IID-TVT, and (d) P-29-IID-SVS. The chemical structures of each polymer are also presented as insets.

Collectively, according to the UV-Vis absorption spectra, we can say that P-29-IID-SVS, with both a farther branching point and a selenophene-substitution, has the most planar backbone, as well as the strongest intermolecular interactions. Energies of molecular orbitals were calculated based on oxidation/reduction potentials of polymers (versus Ag/Ag<sup>+</sup>) measured from cyclic voltammetry (Figure S1 in ESI). Consistent with the UV-Vis absorption spectra, P-29s with an alkyl spacer between the branching point and the polymer backbone show higher HOMO levels of 5.25 and 5.22 for P-29-IID-TVT and P-29-IID-SVS, respectively, compared to those of the P-24s (5.3 and 5.29 for P-24-IID-TVT and P-24-IID-SVS, respectively). The peak positions of the absorption spectra, together with the electrochemical information, are fully summarized in Table S1 and S2. Structural analyses were conducted on all polymers by employing Grazing Incident X-ray Diffraction (GIXD) tools in 3C beamline of Pohang accelerator laboratory. Since none of the polymers show changes to the absorption peaks of thin films after thermal annealing, GIXD studies were conducted only on the annealed films. As shown in Figure 2 and Figure S2, all polymers reveal typical lamellar packing structures with well-developed out-of-plane Bragg peaks up to (003)

in the case of P-24s, and up to (004) in the case of P-29s, indicating that all of the polymers have a long-range ordered edge-on structure. Based on the peak position of (001), we can estimate the d-spacing of each lamellar structure of polymers to be 21.8 Å and 27.6 Å for P-24s and P-29s, respectively, attributed to the different alkyl chain lengths. At the same time, the more developed Bragg peaks of the P-29s along the out-of-plane direction imply a longer range of crystalline order of the polymers with an alkyl spacer, compared to P-24s without an alkyl spacer. Actually, compared with P-24s, P-29s show remarkably narrower diffraction peaks (smaller full-width at half-maximum), as highlighted in Figure S3, which can be correlated with the larger crystalline domain size of the P-29s. In addition, P-29s reveal (010) diffraction peaks in the GIXD pattern along the  $q_{xy}$  direction, while no diffraction peaks are observed along the  $q_{xy}$  axis in the case of P-24s. To elucidate the crystalline orientation of polymer films further, we conducted pole figure analyses, as presented in Figure 2(e). For the pole figure analysis, we analyzed the distribution of (200) orientations to avoid the surface scattering effects resulting from the substrate. The pole figure shows that all of the polymer films adopt a preferential edge-on orientation. In particular, most crystals in the P-29-IID-SVS-based film are preferentially oriented within the narrowest degree near zero. After careful scrutiny of the GIXD results, it is obvious that the farther branching position has a dramatic effect on enhancing the intermolecular interactions, consistent with previous observations from the absorption spectra. More importantly, we found selenophene-substitution further enhanced intermolecular interactions, resulting in P-29-IID-SVS having the most highly edge-on oriented structure, as well as the shortest  $\pi$ - $\pi$  stacking distance.

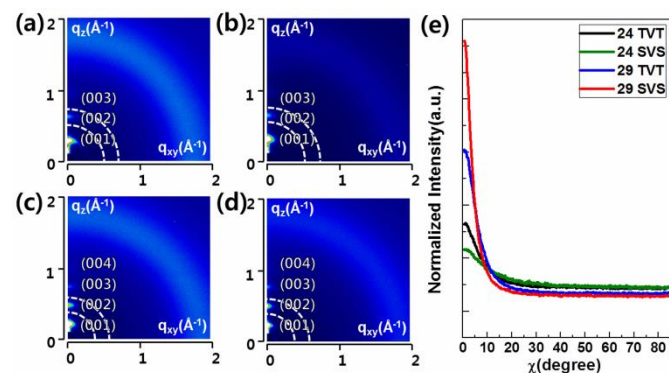


Figure 2. GIXD patterns of (a) P-24-IID-TVT, (b) P-24-IID-SVS, (c) P-29-IID-TVT, and (d) P-29-IID-SVS. Pole figures for the polymers are summarized in (e).

To investigate the morphologies of all polymers, tapping-mode atomic force microscopy was employed and the resulting height images are summarized in Figure S4 (ESI). According to the root-mean-square (rms) analyses of height images, all the polymer films have a very smooth morphology with rms roughness of ~ 1 nm. Nonetheless, in the case of P-29-IID-SVS, one can clearly see the existence of fibrillary nanostructures, while all other films have much less pronounced features. Overall, both structural and morphological analyses indicate that P-29-IID-SVS has the most favorable charge transport pathway in thin films.

Finally, to confirm the effect of selenophene substitution in IID-based polymers, we fabricated FETs based on all of the polymers using

conventional OTS-modified SiO<sub>2</sub>/Si substrates. The corresponding transfer and output characteristics are summarized in Figure 3. The field-effect mobility values of the polymers, measured from the maximum slope of the ( $I_{DS}$ )<sup>1/2</sup>-V<sub>G</sub>, are summarized in Table 1. One can see that the mobility values generally follow our previous expectation based on structural and morphological analyses except that P-24-IID-SVS does not have higher mobility compared to P-24-IID-TVT. Actually, previous studies also noticed such unexpected results of selenophene-substitution in IID-based copolymers.<sup>6,7</sup> Nonetheless, P-29-IIDSVS shows dramatically increased mobility compared to P-29-IID-TVT, reaching the maximum mobility of 5.83 cm<sup>2</sup>/Vs, which is the highest value among all other previously reported IID-based polymers. Together with the observations from UV-Vis absorption, GIXS, and AFM, this result strongly suggests that selenophene substitution in IID-based polymers can still be an attractive synthetic strategy once the side chain is optimized.

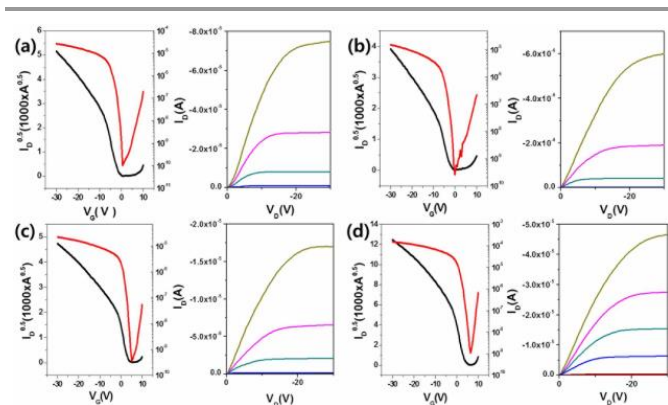


Figure 3. Transfer (left) and output (right) characteristics of (a) P-24-IID-TVT, (b) P-24-IID-SVS, (c) P-29-IID-TVT, and (d) P-29-IID-SVS. In the output curves, each trace has an interval of V<sub>GS</sub> = -6 V.

Table 1. The summary on transistor parameters

Polymer	$\mu$ (cm <sup>2</sup> /vs)			V <sub>th</sub> (V)	I <sub>on</sub> /I <sub>off</sub>
	Ave.*	STD**	Max.		
P-24-IID-TVT	0.86	0.16	1.11	-2	10 <sup>5</sup>
P-24-IID-SVS	0.47	0.11	0.72	-8	10 <sup>5</sup>
P-29-IID-TVT	1.69	0.18	2.13	10	10 <sup>5</sup>
P-29-IID-SVS	5.10	0.54	5.83	14	10 <sup>5</sup>

\*The average values were calculated from fifteen independent transistors.

\*\*Standard Deviation

## Conclusions

In summary, compared to DPP-based polymers, which continue to show gradually increasing charge carrier mobilities over time, the development of IID-based polymers has somehow recently stagnated. Compared to all other semiconducting polymers, there has been no meaningful success on selenophene substitution in IID-based polymers. To elucidate this issue, we designed and synthesized

four different IID-based copolymers: P-24-IIDTVT, P-24-IIDSVS, P-29-IIDTVT, and P-29-IIDSVS. From photophysical and structural analyses, combined with electrical characterization, we found that selenophene substitution could enhance intermolecular interaction as well as charge carrier mobility, only when the side chain is optimized.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: details of the polymer synthesis, structural/morphological characterization, and the device fabrication process. See DOI: 10.1039/c000000x/

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- D. Venkateshvaran, M. Nikolka, A. Sadhanala, V. Lemaure, M. Zelazny, M. Kepa, M. Hurhangee, A. J. Kronemeijer, V. Pecunia, I. Nasrallah, I. Romanov, K. Broch, I. McCulloch, D. Emin, Y. Olivier, J. Cornil, D. Beljonne, H. Sirringhaus, *Nature*, 2014, **515**, 384.
- X. Zhang, H. Bronstein, A. J. Kronemeijer, J. Smith, Y. Kim, R. J. Kline, L. J. Richter, T. D. Anthopoulos, H. Sirringhaus, K. Song, M. Heeney, W. Zhang, I. McCulloch, D. M. Delongchamp, *Nature Commun.* 2013, **4**, 2238.
- R. Noriega, J. Rivnay, K. Vandewal, F. P. V. Koch, N. Stingelin, P. Smith, M. F. Toney, A. Salleo, *Nature Mater.* 2013, **12**, 1038.
- J. Li, Y. Zhao, H. S. Tan, Y. Guo, C.-A. Di, G. Yu, Y. Liu, M. Lin, S. H. Lim, Y. Zhou, H. Su, B. S. Ong, *Sci. Rep.* 2012, **2**, 754.
- L. Biniek, B. C. Schroeder, C. B. Nielsen, I. J. McCulloch, *Mater. Chem.* 2012, **22**, 14803.
- T. Lei, Y. Cao, X. Zhou, Y. Peng, J. Bian, J. Pei, *Chem. Mater.* 2012, **24**, 1762.
- T. Lei, J.-Y. Wang, J. Pei, *Acc. Chem. Res.* 2014, **47**, 1117.
- T. Lei, J.-H. Dou, J. Pei, *Adv. Mater.* 2012, **24**, 6457.
- I. Kang, H.-J. Yun, D. S. Chung, S.-K. Kwon, Y.-H. Kim, *J. Am. Chem. Soc.* 2013, **135**, 14896.
- H.-R. Tseng, H. Phan, C. Luo, M. Wang, L. A. Perez, S. N. Patel, L. Ying, E. J. Kramer, T.-Q. Nguyen, G. C. Bazan, A. J. Heeger,
- G. Kim, S.-J. Kang, G. K. Dutta, Y.-K. Han, T. J. Shin, Y.-Y. Noh, C. Yang, *J. Am. Chem. Soc.* 2014, **136**, 9477.
- A.-R. Han, G. K. Dutta, J. Lee, H. R. Lee, S. M. Lee, H. Ahn, T. J. Shin, J. H. Oh, C. Yang, *Adv. Func. Mater.* DOI: 10.1002/adfm.201403020.
- H. Sirringhaus, *Adv. Mater.* 2014, **26**, 1319.

- 14 I. Kang, T. K. An, J. Hong, H.-J. Yun, R. Kim, D. S. Chung, C. E. Park, Y.-H. Kim, S.-K. Kwon, *Adv. mater.* 2013, **25**, 4.