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# Effect of Chalcogen Atom on the Properties of Naphthobischalcogenadiazole-Based $\pi$ -Conjugated Polymers

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## Abstract

We here discuss the effect of chalcogen atom on the properties of  $\pi$ -conjugated polymers based on electron deficient fused  $\pi$ -electron systems, naphtho[1,2-c:5,6-c']bis[1,2,5]oxadiazole (NOz), naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz), and naphtho[1,2-c:5,6-c']bis[1,2,5]selenadiazole (NSz). We synthesize new donor-acceptor polymers having NOz and NSz combined with quaterthiophene donor unit, namely PNOz4T and PNSz4T, respectively. Physicochemical properties, structures, and charge transport properties of PNOz4T and PNSz4T in comparison with the sulfur analogue (PNTz4T) are discussed. As both NOz and NSz have higher electron deficient nature than NTz. PNOz4T and PNSz4T are found to possess deeper frontier orbital energy levels. In particular, PNOz4T have a sufficiently deep LUMO energy level which allows for ambient ambipolar behavior in transistor devices. Interestingly, whereas PNSz4T is mostly amorphous in the thin film, PNOz4T forms highly crystalline structure that is similar to PNTz4T. This is probably due to the difference of the atomic size, where large selenium may cause larger steric repulsion between NSz and the adjacenet thiophene ring, resulting in a larger defect in the polymer backbone than the others. As a result, whereas PNSz4T exhibited p-channel behavior with modest hole mobilities of the order of  $10^{-2}$  cm<sup>2</sup>/Vs. PNOz4T demonstrated p-channel behavior with high hole mobilities of  $\sim 1 \text{ cm}^2/\text{Vs}$  and ambipolar behavior with balanced hole and electron mobilities of  $\sim 0.5 \text{ cm}^2/\text{Vs}$  and  $\sim 0.3 \text{ cm}^2/\text{Vs}$  depending on the surfactant used for the devices. These results show clear correlations between the chalcogen atom and the properties of the naphthobischalcogenadiazole-based polymers. Overall, in addition to NTz, NOz is found to be another fascinating acceptor unit for  $\pi$ -conjugated polymers.

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## Introduction

 $\pi$ -Conjugated polymers have been widely used in organic electronics due to the advantage in solutionprocessability as well as the good electrical properties in spite of the low crystallinity compared with  $\pi$ conjugated molecular systems.<sup>1-3</sup> Organic field-effect transistors (OFETs)<sup>4</sup> and organic photovoltaics  $(OPVs)^5$  are important devices for the application of  $\pi$ -conjugated polymers, which a great number of research has been conducted in the past decades. One of the most important physical phenomena of  $\pi$ conjugated polymers is the charge transport in thin films, which is strongly dependent on the ordering structure and the electronic structure. High coplanarity of the polymer backbone and strong intermolecular interaction between the backbones are necessary to have highly ordered structure.<sup>6</sup> The molecular orbital should be highly overlaped between the backbones and thus the geometry of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is a key parameter. The energy levels also largely affect the charge carrier polarity.<sup>4</sup> Therefore, the HOMO and LUMO energy levels must be tuned to match the work function of the electrode of the devices for efficient charge injection. In order to realize highly ordered structures and appropriate electronic structures, sulfur-containing  $\pi$ -extended fused heteroaromatic rings, *e.g.*, thiophene-based acenes.<sup>7-11</sup> thiazole-fused systems,<sup>12-18</sup> and thiadiazole-fused systems,<sup>19-23</sup> are often incorporated into the polymer backbone. In the meantime, other chalcogen atoms such as oxygen and selenium have also been used as alternatives to sulfur for the above-mentioned heteroaromatic rings.<sup>10, 24</sup>

2,1,3-Benzothiadiazole (BTz) is one of the most widely used heteroaromatic rings for semiconducting polymers (Figure 1).<sup>19</sup> Due to the high electron deficiency, BTz acts as an acceptor unit for so-called donor–acceptor (D–A) polymers, and largely deepens the energy levels of the polymers. The oxygen and selenium analogues of BTz, *i.e.*, 2,1,3-benzoxadiazole (BOz)<sup>25</sup> and 2,1,3-benzoselenadiazole (BSz)<sup>26</sup> (Figure 1), have also been used as an acceptor unit for D–A polymers. It has been reported that although the crystallinity of the resulting polymers were similar, the replacement of BTz by BOz or BSz altered the electronic structure. Whereas the replacement of BTz by BOz further deepened the energy levels of the polymers, replacement by BSz shallowed the energy levels.

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Naphtho [1,2-c:5,6-c'] bis [1,2,5] thiadiazole (NTz, Figure 1) is a tetracyclic heteroaromatic where two BTz rings are fused. With its high planarity and high electron deficiency,<sup>27</sup> NTz is a fascinating acceptor unit for D-A polymers.<sup>28-33</sup> Independently from other groups, we have been focusing on NTz-based polymers.<sup>28, 30, 31, 34</sup> We revealed that the NTz-based polymers form high crystalline structures and exhibit high hole mobilities of around 0.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in OFETs.<sup>28</sup> NTz polymers also showed quite high power conversion efficiencies when used as the p-type material for the bulk heterojunction solar cells.<sup>28, 30, 31, 35</sup> These results indicated that NTz is promising building unit for D-A polymers. Replacement of the sulfur atom of NTz by the oxygen and selenium atoms, resulting in naphtho[1,2c:5,6-c']bis[1,2,5]oxadiazole (NOz) and naphtho[1,2-c:5,6-c']bis[1,2,5]selenadiazole (NSz) (Figure 1), is expected to alter the electronic structure of the corresponding polymers. As seen from the computation of model compounds, where benzodichalcogenadiazoles (BXz) and naphthobischalcogenadiazoles (NXz) are sandwiched with methylthiophenes, the effect of the chalcogen atom seems to be even larger than in the case of BXz (Figure 2). In particular NOz is expected to bring the corresponding polymers quite deep LUMO energy levels as well as deep HOMO energy levels. which is important in terms of providing n-channel (or ambipolar) behavior in OFETs and high opencircuit voltage ( $V_{0C}$ ) in OPVs. In fact, during the course of our study, Zhang and co-workers reported on an NOz-based D-A semiconducting polymer incorporating a ladder-type heptacyclic arene as the donor unit, which exhibits power conversion efficiencies of ~8.4% with high  $V_{OC}$  of ~0.9 V in OPV devices.<sup>36</sup> Herein, we synthesize NOz and NSz, and the new polymers based on these building units. The

chemical structure of the polymers used here is composed of quaterthiophene as the donor units and NXz as the acceptor units (PNOz4T, PNTz4T and PNSz4T, Figure 3). The use of the simple quaterthiophene unit allows us to better understand the nature of the NXz units. We describe the synthesis, characterization, and structures of PNOz4T and PNSz4T, as well as the corresponding monomeric compounds, in comparison with the NTz analogues. We specifically focus on the charge carrier transport properties of the polymers evaluated by OFET devices, and discuss the effects of chalcogen atoms and the correlations with the electronic structure and the ordering structure.

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Figure 1. Chemical structure of benzochalcogenadiazoles (BXz) and naphthobischalcogenadiazoles (NXz). BOz = 2,1,3-benzothiadiazole, BTz = 2,1,3-benzoxadiazole, BSz = 2,1,3-benzoselenadiazole, NOz = naphtho[1,2-c:5,6-c']bis[1,2,5]oxadiazole, NTz = naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole, NSz = naphtho[1,2-c:5,6-c']bis[1,2,5]selenadiazole.



Figure 2. Calculated HOMOs and LUMOs of the model compounds for BXz (BOz2T, BTz2T, and BSz2T) and NXz (NOz2T, NTz2T, and NSz2T) using the DFT method at the B3LYP/6-31G(d) level.



Figure 3. Chemical structures of the polymers based on NOz, NTz, and NSz studied in this work.

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## **Results and discussion**

# Synthesis and properties.

Synthesis of NOz and NSz is shown in Scheme 1. NOz was synthesized as follows. An oxidation of 1,5-dinitro-2,6-diaminonaphtalene (1) by sodium hypochlorite and potassium hydroxide gave three isomers of NOz N-oxides (2a-c), which were then reduced by hydroxylamine in the presence of potassium hydroxide, giving NOz in a 53% yield with two steps. For NSz, a reduction of 1 by Raney nickel gave 1,2,5,6-tetraaminonaphthalene<sup>37</sup> in a 70% yield, which was cyclized by using seleninyl chloride to afford NSz in a 68% yield. Synthesis of monomers and polymers is shown in Scheme 2. Both NOz and NSz were dibrominated at the 5,10 position to give 4 and 5, respectively. These were crosscoupled with 4-(2-decyltetradecyl)-2-(trimethylstannyl)thiophene (6) via the Stille coupling reaction to afford NOz2T-DT (DT = 2-decyltetradecyl) and NSz2T-DT, which were then dibrominated with Nbromosuccinimide (NBS) to yield the corresponding monomers (7 and 8). The monomers were copolymerized with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (9) via the Stille coupling reaction associated with microwave to give PNOz4T and PNSz4T, respectively. While PNOz4T was synthesized at 140 °C, PNSz4T was synthesized at 180 °C. The lower polymerization temperature for PNOz4T is to avoid "over-polymerization". In fact, when PNOz4T was synthesized at 180 °C, more than 80 wt% of the resulted polymer sample was insoluble. Both PNOz4T and PNSz4T synthesized at 140 °C and 180 °C, respectively, were soluble in hot chlorobenzene (CB) and o-dichlorobenzene (DCB). Although it is difficult to quantify the solubility, both polymers had less solubility than PNTz4T. The number average molecular weight  $(M_n)$  and weight average molecular weight  $(M_w)$  were evaluated by hightemperature gel-permeation chromatography (GPC) using DCB (140 °C) as the eluent.  $M_n$  and  $M_w$  were 49.7 kDa and 240.8 kDa with the polydispersity index (PDI) of 4.8, and 28.7 kDa and 60.6 kDa with PDI of 2.1 for PNOz4T and PNSz4T, respectively (Table 1). As the comparison, PNTz4T was also synthesized by the reported procedure, where the polymerization was carried out at 180 °C ( $M_{\rm p} = 52.9$ kDa,  $M_{\rm w} = 113.5$  kDa, PDI = 2.1). It is noted that the chromatogram of PNOz4T exhibited bimodal distributions, resulting in a high PDI of 4.8. We assume that this is due to the strong aggregation, as

sometimes seen in D–A semiconducting polymers.<sup>38, 39</sup> This implies that PNOz4T has stronger aggregation tendency than PNTz4T and PNSz4T.

Thermal properties of the polymers were evaluated by the differential scanning calorimetry (DSC) (Figure S27) and thermogravimetry (TG) (Figure S28). While the DSC curve of PNTz4T and PNSz4T showed a melting point ( $T_{\rm m}$ ) at 321 °C and 221 °C, respectively, in the heating process (302 °C and 120 °C in the cooling process), that of PNOz4T showed no transition peaks below 350 °C. The DSC results suggest that rigidity or the backbone is in order of PNOz4T > PNTz4T > PNSz4T. The temperatures of 5% weight loss ( $T_{\rm d5}$ ) were 368 °C, 439, and 368 for PNOz4T, PNTz4T, and PNSz4T, respectively.

Scheme 1. Synthesis of NOz and NSz.



Scheme 2. Synthesis of the monomers and polymers. (TBAB = tetrabutylammonium bromide)



Polymer	$M_{\rm n}  {\rm (kDa)}^{\rm a}$	$M_{ m w}( m kDa)^{ m a}$	PDI <sup>a</sup>	DP <sub>n</sub> <sup>b</sup>	$T_{\rm m}$ (°C) <sup>c</sup> heating/cooling	$T_{d5} (^{\circ}\mathrm{C})^{\mathrm{d}}$
PNOz4T	49.7	240.8	4.8	41.0	_	368
PNTz4T	52.9	113.5	2.1	42.5	321/302	439
PNSz4T	28.7	60.6	2.1	21.5	221/120	368

Table 1. Polymerization results and polymer properties.

<sup>a</sup>Determined by GPC using polystyrene standard and DCB as the eluent at 140 °C. <sup>b</sup>Based on the repeating unit. <sup>c</sup>Melting point determined by DSC measurements at a scan rate of 10 °C/min. <sup>d</sup> Temperature of 5% weight loss.

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## Properties and structures of the monomers

We evaluated the electrochemical and optical properties of the NXz-based compounds, *i.e.*, NO22T-DT, NTz2T-DT and NSz2T-DT, by using cyclic voltammetry, UV-vis absorption and photoluminescence (PL) spectroscopies. Figure 4a shows the cyclic voltammograms of the monomers and the corresponding parameters are summarized in Table 2. Whereas the oxidation onset of NO22T-DT (1.40 V) was higher than that of NTz2T-DT (1.18 V), that of NSz2T-DT (1.09 V) was lower. These onset potentials for NO22T-DT, NTz2T-DT, and NSz2T-DT correspond to the HOMO energy levels  $(E_{\rm H}^{\rm CV})$  of -5.76 eV, -5.54 eV, and -5.45 eV, respectively (Table 2, Figure 5). The reduction onset was higher for both NO22T-DT (-0.78 V) and NSz2T-DT (-0.98 V) than for NTz2T-DT (-1.08 V). Accordingly, the LUMO energy levels  $(E_{\rm L}^{\rm CV})$  were -3.58 eV, -3.28 eV, and -3.38 eV for NO22T-DT, NTz2T-DT, and NSz2T-DT, respectively (Table 2, Figure 5). These  $E_{\rm H}^{\rm CV}$ s were in good agreement with the computation by the DFT method at the B3LYP/6-31g(d) level (Table 2), in which NO22T, NTz2T, and NSz2T with the methyl group were used instead of the DT group to simplify the calculation. The computation also revealed that whereas HOMOs are delocalized over the molecule, LUMOs are relatively localized on the NXz unit in all cases (Figure 2).

It is noted that the order of  $E_{\rm H}^{\rm CV}$  of the present system follows the general trend observed in many chalcogenophene-fused aromatic systems. such benzodichalcogenophenes. as naphthodichalcogenophenes, and anthradichalcogenophenes, where it rises in the order of oxygen, sulfur, and selenium.<sup>40, 41</sup> On the other hand,  $E_{\rm L}^{\rm CV}$  does not follow the trend observed in the above chalcogenophene-fused aromatic systems, where it falls in the same order. In contrast,  $E_{\rm L}^{\rm CV}$  of NOz2T-DT was lower than that of NTz2T-DT, although  $E_{\rm L}^{\rm CV}$  of NSz2T-DT was accordingly lower than that of NTz2T-DT, as shown above. This could be explained by taking into account the difference in aromaticity of chalcogenadiazoles and electron negativity of chalcogens.<sup>42</sup> Judging from the reported nucleus-independent chemical shifts (NICS) of 1,2,5-oxadiazole (-11.11 ppm, NICS(0)), 1,2,5thiadiazole (-13.63 ppm), and 1,2,5-selenadiazole (-12.48 ppm),<sup>43</sup> aromaticity of the oxadiazole ring is markedly smaller than those of the thia- and selena-diazole rings,<sup>44</sup> which implies that the local atomic

effect of oxygen is pronounced. In other words, the higher electronegativity of oxygen (3.44) than sulfur (2.58) and selenium (2.55) should be a dominant factor for determining the energy level of the frontier orbitals, in particular, LUMO.

UV-vis absorption and PL spectra of the compounds are displayed in Figures 4b and 4c, respectively, and the properties are summarized in Table 3. NOz2T-DT and NTz2T-DT showed similar spectra for both absorption and PL with the absorption maxima ( $\lambda_{max}$ ) at around 500 nm and for emission maxima (PL<sub>max</sub>) at around 580 nm. In contrast, NSz2T-DT showed a bathochromic shift for both the absorption and PL spectra by roughly 50 nm compared with NOz2T-DT and NTz2T-DT. The difference is mostly consistent with the computation. To better understand the fact that NOz2T-DT and NTz2T-DT provide similar absorption spectra and NSz2T-DT provides slightly bathochromically shifted absorption spectrum, TD-DFT calculations were carried out to simulate the electronic transistion using NOz2T, NTz2T, and NSz2T (Figure S23). For all the compounds, the absorption bands mainly contributed by the HOMO–LUMO transition and appear in the visible region with  $\lambda_{max}$  of 547, 575, and 626 nm for NO22T, NT22T, and NS22T, respectively. These values are somewhat larger than the experimental values. This is probably due to the overestimation of the coplanarity of the compounds in the calculations. The actual molecules have various molecular motions including rotation around the aromatic rings in solution at rt, which may reduce the orbital overlap between the adjacent rings. It is also noted that the difference between experimental and theoretical  $\lambda_{max}$ s become larger with the heavier chalcogen atoms, implying that the ring-size expansion with the heavier chalocogen atom can reduce the coplanarity, as will be discussed below, giving rise to the reduction of the  $\pi$ -electron delocalization in the actual molecules.

A higher PL quantum yield was observed for the oxygen analogue, NOz2T-DT, as similar to the other  $\pi$ -systems.<sup>40, 41</sup> Whereas in the chloroform solution, the quantum yields of NOz2T-DT and NTz2T-DT were similar with 95% and 97%, respectively, in powder, that of NOz2T-DT was 30% which is about three times higher than that of NTz2T-DT (12%). The quantum yield of selenium analogue, NSz2T-DT, was much lower in both solution (52%) and powder ( $\approx 0\%$ ), most likely due to the heavy atom effect.

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We also investigated in depth the molecular structure of NOz2T, NTz2T,<sup>28</sup> and NSz2T by means of single crystal X-ray analysis. Note that these molecules have the methyl groups instead of the DT groups on the flanking thiophene rings (see supporting information for the synthesis). As depicted in Figure 6, the molecules were almost coplanar in all cases. It is also noted that the sulfur atom of the thiophene ring points to the benzene substructure of NXz, resulting in the *anti* arrangement of the thiophene rings. Inspection of bond lengths in the compounds indicates that they have basically similar bond length alternation, representing the formal naphtho[1,2-c:5,6-c']bis[1,2,5]chalcogenadiazole structure. Subtle but potentially important differences in the molecular structure are the N-X distance in the chalcogenadiazole substructure (Figure 6). As the chalcogen atom becomes heavier from oxygen to sulfur and selenium, the N-X distance increases from 1.38 Å (NOz2T) to 1.61 Å (NTz2T) and 1.79 Å (NSz2T). This increase apparently pushes out the nitrogen atom out of the chalcogenadiazole substructure toward the adjacent thiophene ring, which is evident by the fact that  $\theta$  becomes smaller from 129.3° to 125.2°, as it goes from NOz2T to NSz2T (Figure 6). This suggests that the steric repulsion between the NXz core and the thiophene rings becomes larger as the chalcogen atom becomes heavier, although all the molecules remain coplanar in the single crystal: it is often the case and wellknown that the molecular structure is largely affected by the packing motif in the single crystal, which can overcome the local steric repulsion. In parallel,  $\alpha$  is smaller in NTz2T and NSz2T than in NOz2T. This implies that the thiophene ring slightly bends toward the benzene substructure, which suggests that NTz and NSz can cause more steric repulsion than NOz. In addition, the computation by the density functional theory (DFT) method predictied that the energy barrier of the rotation around the NOz core and flanking thiophene rings is largest among the NXz2T (Figure S25), indicating that NOz2T is energetically favorable to take the coplanar structure than others. With these structural features in the single crystal and computation, overall steric repulsion likely increases in the order of NOz2T < NTz2T < NSz2T. Thus, it is speculated that with the addition of the effect of the bulky side chains NXz2T-DT can lose the coplanarity as the chalcogen atom becomes heavier in the solution, which can rationalize the trend in the difference between the experimental and theoretical  $\lambda_{max}$ s as discussed above.



Figure 4. Cyclic voltammograms (a), UV–vis. absorption spectra (b), and photoluminescence spectra (c) of NOz2T-DT, NTz2T-DT, and NSz2T-DT in the solution. The cyclic voltammetry were carried out in dichloromethane, and the absorption and photoluminescence spectroscopies were carried out in chloroform.



Figure 5. HOMO and LUMO energy levels of the monomers and polymers evaluated by cyclic voltammetry.



Figure 6. Molecular structures of NOz2T, NTz2T, and NSz2T determined by the single crystal X-ray structural analysis.

Compounds	Eox	$E_{\rm red}$	$E_{\rm H}^{\rm CV}$	$E_{\rm L}^{\rm CV}$	$E_{\rm H}^{\rm PESA}$	$E_{\rm L}^{\rm opt}$	$E_{\mathrm{H}}^{\mathrm{DFT}}$	$E_{\rm L}^{\rm DFT}$
	$(V)^{a}$	$(V)^{a}$	(eV) <sup>b</sup>	(eV) <sup>b</sup>	(eV) <sup>c</sup>	$(eV)^d$	(eV) <sup>e</sup>	(eV) <sup>e</sup>
NOz2T-DT	1.40	-0.78	-5.76	-3.58	_	_	-5.64	-3.13
NTz2T-DT	1.18	-1.08	-5.54	-3.28	_	-	-5.35	-2.88
NSz2T-DT	1.09	-0.98	-5.45	-3.38	_	_	-5.25	-2.93
PNOz4T	1.13	-0.70	-5.48	-3.65	-5.50	-3.98	_	_
PNTz4T	0.79	-0.89	-5.14	-3.46	-5.15	-3.59	_	_
PNSz4T	0.87	-0.80	-5.22	-3.55	-5.25	-3.69	_	_

Table 2. Electrochemical properties and molecular orbital energy levels of the monomers and polymers.

a) Onset oxidation  $(E_{ox})$  and reduction  $(E_{red})$  potentials observed in cyclic voltammograms. The monomers and polymers were measured in solution and film, respectively. b) HOMO  $(E_H^{CV})$  and LUMO  $(E_L^{CV})$  energy levels evaluated using  $E_{ox}$  and  $E_{red}$ , respectively. c) HOMO energy level  $(E_H^{PESA})$  evaluated by photoelectron spectroscopy in air. d) LUMO energy level  $(E_L^{opt})$  calculated by the addition of the optical band gap  $(E_g)$  to  $E_H^{PESA}$ . e) HOMO  $(E_H^{DFT})$  and LUMO  $(E_L^{DFT})$  energy levels calculated by the B3LYP/6-31g(d) level. Note that the DT group of the side chain was replaced with the methyl group.

Table 3. Optical properties of the monomer and polymers.

Compounds	$\lambda_{\max} (nm)^a$		$\lambda_{edge} (nm)^{b}$		$E_{g} (eV)^{c}$		$PL_{max} (nm)^{d}$		$\Phi_{\mathrm{PL}}\left(\% ight)^{\mathrm{e}}$	
	solution	film	solution	film	solution	film	solution	solid	solution	solid
NOz2T-DT	504	—	557	—	2.23	_	585	648	95	30
NTz2T-DT	490	_	547	_	2.27	_	579	643	97	12
NSz2T-DT	538	_	606	_	2.05	_	648	_	52	<1
PNOz4T	749, 685	749, 680	798	815	1.55	1.52	_	_	_	_
PNTz4T	717, 660sh	721, 658	784	793	1.58	1.56	_	_	_	_
PNSz4T	686	706	796	792	1.56	1.56	-	_	_	_

a) absorption maximum, b) absorption onset, c) optical band gap calculated by using  $\lambda_{edge}$ , d) emission maximum, e) photoluminescence quantum yield.

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# Physicochemical properties of the polymers

 $E_{\rm H}^{\rm CV}$ s and  $E_{\rm L}^{\rm CV}$ s of the polymers were evaluated using the thin films. Figure 7a depicts the cyclic voltammograms of the polymer thin films, in which all polymers showed clear oxidation and reduction signals. The onset oxidation and reduction potentials and  $E_{\rm H}^{\rm CV}$  and  $E_{\rm L}^{\rm CV}$  calculated from these potentials are summarized in Table 2.  $E_{\rm H}^{\rm CV}$ s of PNOz4T and PNSz4T was -5.48 eV and -5.22 eV, respectively, both of which were deeper than that of PNTz4T (-5.14 eV) by 0.34 eV and 0.08 eV (Table 2, Figure 5).  $E_{\rm L}^{\rm CV}$ s of PNOz4T and PNSz4T were -3.65 eV and -3.55 eV, respectively, which were deeper by 0.19 eV and 0.09 eV than that of PNTz4T (-3.46 eV) (Table 2, Figure 5). It is noted that whereas the trend of  $E_{\rm L}^{\rm CV}$  in the polymers was similar to that in NXz2T-DTs, the trend of  $E_{\rm H}^{\rm CV}$  in the polymers was different from that in NXz2T-DT. Whereas  $E_{\rm H}^{\rm CV}$  of NSz2T-DT was shallower than that of NTz2T-DT,  $E_{\rm H}^{\rm CV}$  of PNSz4T was deeper than that of PNTz4T. A plausible explanation is that the large steric repulsion between NXz and the adjacent thiophene rings in the NSz2T-DT moiety compared with the NTz2T-DT moiety, as discussed above, can lead to further large defect of the backbone in the polymer system and thereby the packing structure of PNSz4T compared with PNTz4T. This may result in the reduction of the effective  $\pi$ -conjugation and wider bandgap, which in turn gives rise to the deeper  $E_{\rm H}^{\rm CV}$  in PNSz4T than in PNTz4T. This explantion is consistent with the fact that  $\lambda_{max}$  of PNSz4T was slightly hypsochromically shifted compared to that of PNTz4T as shown below. Photoelectron spectroscopy in air (PESA) was also carried out using the polymer thin films to evaluate the HOMO energy levels  $(E_{\rm H}^{\rm PESA})$  of the polymers (Figure S26).  $E_{\rm H}^{\rm PESA}$  of PNOz4T, PNTz4T, and PNSz4T were -5.50 eV, -5.15 eV, and -5.25 eV, respectively, which were mostly similar to  $E_{\rm H}^{\rm CV}$ . LUMO energy levels ( $E_{\rm L}^{\rm opt}$ ) were calculated by the addition of optical band gap ( $E_g$ ) to  $E_H^{PESA}$ , which were -3.98 eV, -3.59 eV, and -3.69 eV for PNOz4T, PNTz4T, and PNSz4T, respectively. The difference between  $E_L^{\text{CV}}$  and  $E_L^{\text{opt}}$  can be ascribed to the exciton binding energy.<sup>45</sup>

UV-vis absorption spectra of the polymers in thin film and in CB solution are shown in Figures 7b and 8, respectively. In the thin film, PNOz4T gave  $\lambda_{max}$  at 749 nm, which was bathochromically shifted by ca. 30 nm compared with PNTz4T ( $\lambda_{max} = 721$  nm).  $E_g$  of PNOz4T was calculated to be 1.52 eV from the

absorption edge ( $\lambda_{edge} = 815$  nm), which was slightly narrower than that of PNTz4T ( $E_g = 1.56$  eV,  $\lambda_{edge}$ = 793 nm).  $\lambda_{\text{max}}$  of PNSz4T (706 nm) was hypsochromically shifted by 15 nm compared with that of PNTz4T, although  $\lambda_{edge}$  (793 nm) and  $E_g$  (1.56 eV) was similar due to the blunt absorption signal. It is noted that while the bathochromic shift of PNOz4T against PNTz4T is consistent with that observed in NXz2T, the hypsochromic shift of PNSz4T against PNTz4T does not follow the trend in NXz2T-DT. We speculate that the larger steric repulsion in the NSz2T-DT moiety than in the NTz2T-DT moiety may give rise to a further large defect of the backbone structure in PNSz4T than in PNTz4T, which in turn gives rise to the reduction of the effective  $\pi$ -conjugation. In the solution, all the polymers exhibited mostly identical spectrum to that in the film, implying the partial aggregation. The absorption coefficient of the absorption band at 500-800 nm was lower for the polymers with heavier chalcogen atoms. This is consistent with the trend observed in NXz2T-DT and the computation. The polymer solutions were heated up to 110 °C. In PNTz4T, the spectrum became structure-less upon heating, and  $\lambda_{max}$  showed large hypsochromic shift to 597 nm, suggesting the disaggregation as well as the destruction of coplanarity due to the molecular motion (Figure 8b). In PNOz4T, on the contrary,  $\lambda_{max}$  did not show a hypsochromic shift (Figure 8a). This is most likely due to the higher rigidigy and thus the stronger intermolecular interaction of the PNOz4T backbone than PNTz4T, likely originating in the less steric repulsion in the NOz2T-DT moiety than the NTz2T-DT moiety, as described above. Furthermore, the large atom size in the heavier chalcogen can reduce the  $\pi$ - $\pi$  interaction between the polymer backbones. which also contributes to the difference in the aggregation behavior seen in the solution absorption spectra. The spectrum of PNSz4T also became structure-less upon heating and hypsochromically shifted, but the shift of  $\lambda_{max}$  ( $\lambda_{max}$  = 633 nm at 110 °C) was smaller than that in PNTz4T (Figure 8c). The smaller hypsochromic shift is beause  $\lambda_{max}$  of PNSz4T is already located at the slightly shorter wavelength region at rt than that of PNTz4T.



Figure 7. Cyclic voltammograms (a) and UV-vis. absorption spectra (b) of the polymers in thin films.



Figure 8. UV-vis. absorption spectra of the polymers in chlorobenzene. (a) PNOz4T, (b) PNTz4T, and (c) PNSz4T.

# Thin film structure and morphology of the polymers

The grazing incidence wide-angle X-ray diffraction (GIXD) studies were carried out using the polymer thin films.<sup>46</sup> Figure 9 shows the two-dimensional (2D) GIXD patterns of the polymer thin films on the ODTS-treated Si/SiO<sub>2</sub> substrate. The 2D GIXD patterns of the polymers on the FDTS-treated substrate were almost the same as that on the ODTS-treated substrate (Figure S29). In PNOz4T, diffractions assignable to the lamellar ( $q_z \approx 0.28 \text{ Å}^{-1}$ ) and the  $\pi-\pi$  stacking structures ( $q_{xy} \approx 1.8 \text{ Å}^{-1}$ ) mainly appeared on the  $q_z$  and  $q_{xy}$  axes, respectively, indicating the predominant edge-on orientation on the substrate surface as similar to PNTz4T, though some fraction of face-on orientation also exist as the lamellar and  $\pi$ - $\pi$  stacking diffraction also but weakly appeared on the  $q_{xy}$  and  $q_z$  axes, respectively. The  $\pi$ - $\pi$ -stacking distance ( $d_{\pi}$ ) of PNOz4T was determined to be 3.5 Å, which was comparable to that of PNTz4T. Crsytallinity of PNOz4T and PNTz4T was almost the same as the crystallite coherence length, calculated by the Scherrer equation using the full-width-at-half-maximum of the lamellar peak in the  $q_z$ axis and the  $\pi$ - $\pi$  stacking peak in the  $q_{xy}$  axis, showed similar values (Table S2).<sup>47, 48</sup> On the contrary, only a weak diffraction in the small-angle region was observed for PNSz4T, indicative of an amorphous nature. The significantly reduced crystallinity of PNSz4T is attributable to the larger steric repulsion in the NSz2T-DT moiety than in the oxygen and sulfur analogues, which may cause larger twist in the polymer backbone, as well as the larger atomic size of selenium, which could diminish the  $\pi$ - $\pi$ interaction of the polymer backbones. This structural difference in the series of PNXz4T can be wellcorrelated with the electrochemical and optical properties.

Morphologies of the polymer thin films were investigated by using the atomic force microscopy (AFM). Figure 10 displays the topographic AFM images and the cross-sectional profiles of the polymer thin films on the ODTS-treated Si/SiO<sub>2</sub> substrate. Seemingly the PNOz4T film consists of larger domains compared with the PNTz4T and PNSz4T films, which would facilitate the charge carrier transport. This could explain the slightly higher mobility of PNOz4T than PNTz4T.

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Figure 9. (a–c) 2D GIXD patterns of the thin films on the ODTS-treated Si/SiO<sub>2</sub> substrate for PNOz4T (a), PNTz4T (b), and PNSz4T (c). (d, e) The cross-sectional profiles along the  $q_z$  and  $q_{xy}$  axes, respectively.



Figure 10. AFM height images (top) and cross section profiles (bottom) of the thin films on the actual device treated with ODTS for PNOz4T (a), PNTz4T (b), and PNSz4T (c).

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## Charge carrier transport property of the polymers

OFET devices were fabricated to investigate the charge carrier transport property of the polymers. The device used here has a bottom-gate-top-contact (BGTC) architecture using Si/SiO<sub>2</sub> as the substrate. The substrate surface was treated with surfactants such as 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (FDTS) or octadecyltriethoxysilane (ODTS), forming a self-assembled monolayer (SAM). Spin-coated polymer films were thermally annealed at 200 °C for 30 min, which refers to pre-annealing. After the deposition of the Au electrodes, the devices were again annealed at 200 °C, which refers to post-annealing. Figure 11 shows transfer (a,c,e,g,i,k) and output (b,d,f,h,j,l) curves of the polymer devices measured in air. The OFET characteristics are summarized in Table 4. All the polymers showed p-channel characteristics in the FDTS-treated devices. The hole mobility ( $\mu_h$ ) of PNOz4T was as high as 1.0 cm<sup>2</sup>/Vs with the average of 0.55 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which were about twice as high as those of PNTz4T (maximum 0.56 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, average 0.23 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). In contrast,  $\mu_h$  of PNSz4T was one order of magnitude lower than those of the others (maximum 0.040 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, average 0.026 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). Current on and off ratios ( $I_{on}/I_{off}$ ) were fairly high (10<sup>6</sup>-10<sup>7</sup>). The difference of  $\mu_h$  is quite in good agreement with the 2D GIXD results, where PNOz4T and PNTz4T form crystalline structures and PNSz4T forms an amorphous-like structure.

It is also important to note the effect of molecular weight on the device performance, in particular for PNOz4T and PNTz4T with higher mobilities among the series. We have tested the PNOz4T devices using two other batches with higher and lower molecular weights (higher one:  $M_n = 57.2$  kDa,  $M_w = 416.8$  kDa, and PDI = 7.3, lower one:  $M_n = 34.8$  kDa,  $M_w = 152.1$  kDa, and PDI = 4.4) (Figure S19, Table S1). While the higher molecular weight batch exhibited  $\mu_h$  of ~0.84 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (average 0.55 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), the lower molecular weight batch exhibited ~0.56 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (average 0.34 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) (Figure S30, Table S3). Therefore, it could be mentioned that the molecular weight of the initial batch of PNOz4T ( $M_n = 49.7$  kDa,  $M_w = 240.8$  kDa, see Table 1) is sufficiently high (in the optimal  $M_n$  and  $M_w$  ranges) to maximize the transistor performance. In addition,  $M_w$  or PDI may not affect the device performance as long as  $M_n$  is in the optimal range (> ca. 50 kDa). In the case of PNTz4T, the molecular

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weight shown in Table 1 is also sufficiently high (Figure S19 and S30, Table S1 and S3). As the polymer became insoluble when the molecular weight was increased (synthesized by more harsh conditions), the PNSz4T sample shown here should be the highest level with sufficient solubility. With these additional results, although the molecular weights of the polymers are quite different, the performance of the polymers summarized in Figure 11 and Table 4 can be reasonably evaluated and compared.

In the ODTS-treated devices, it is interesting to note that whereas PNTz4T and PNSz4T showed pchannel characteristics with of 0.22 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 0.059 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, PNOz4T showed ambipolar characteristics with well-balanced  $\mu_h$  and electron mobilities ( $\mu_e$ ) of up to 0.45 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 0.28 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. The observed ambipolar behavior of PNOz4T is ascribed to its deeper LUMO energy level. The difference in the charge carrier polarity between FDTS and ODTStreated devices is probably due to the difference in the dipole between a perfluoroalkylsilane (FDTS) and an alkylsilane (ODTS).<sup>49</sup> A similar phenomenon was also seen in the thienothiophenedione-based polymers.<sup>39</sup>

In the transfer curves (Figures 11a, c, e, g, i, k) was also plotted the mobility as a function of the gate voltage ( $V_g$ ). Whereas the mobilities were mostly independent of  $V_g$  above the threshold in the FDTS-treated devices, they were dependent on  $V_g$  and were somewhat higher in the lower  $V_g$  region in the ODTS-treated devices. It is also noted that, in particular, FDTS-treated devices that use PNOz4T without post-annealing gave a kinked  $V_g$ -( $-I_d$ )<sup>1/2</sup> plot in the transfer characteristics (Figure 12) with a larger threshold voltage in negative direction, resulting in the significantly  $V_g$ -dependent mobility and larger values. We speculate that, in the devices without post-annealing, the contact between the Au electrode and the polymer film might be poor, which causes too high charge accumulation and the charges would pour out at a higher  $V_g$ . The kink, however, disappeared by post-annealing, which is probably due to the improved contacts.

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Figure 11. Current–voltage characteristics of OFET devices fabricated with PNOz4T (a–d), PNTz4T (e–h), and PNSz4T (i–l). (a, e, i) Transfer curves of OFET devices with the FDTS SAM. (b, f, j) Output curves of OFET devices with the FDTS SAM. (c, g, k) Transfer curves of OFET devices with the ODTS SAM. (d, h, l) Output curves of OFET devices with the ODTS SAM. The light-colored curves depicted with the transfer curves are the dependence of the mobility on the  $V_g$ ; the hole mobility for p-operation and the electron mobility for n-operation in the case of PNOz4T with the ODTS SAM modified device.



Figure 12.  $I_d$  vs.  $V_g$  curves (solid and dotted lines) and  $\mu$  vs.  $V_g$  curves (light-colored lines) of OFET devices based on PNOz4T. Blue curves stand for the device with the pre-annealed (200 °C) film. Red curves stand for the device with the pre-annealed films annealing at 200 °C after the deposition of the source and drain Au electrodes.

Table 4. OFET characteristics of the polymers.

FDTS		ODTS					
p-channel		p-channel		n-channel			
$\mu_{ m h}$	$I_{\rm on}/I_{\rm off}$	$\mu_{ m h}$	$I_{\rm on}/I_{\rm off}$	$\mu_{ m e}$	$I_{\rm on}/I_{\rm off}$		
$(cm^2/Vs)$		$(cm^2/Vs)$		$(cm^2/Vs)$			
0.55 [0.22 ~ 1.0]	~10 <sup>7</sup>	0.27 [0.21 ~ 0.45]	$\sim 10^{3}$	0.17 [0.10 ~ 0.28]	~10 <sup>2</sup>		
0.23 [0.18 ~ 0.56]	~10 <sup>7</sup>	$0.15 \; [0.12 \sim 0.22]$	~10 <sup>7</sup>	_	_		
0.026 [0.016 ~ 0.040]	~10 <sup>6</sup>	0.040 [0.008 ~ 0.059]	~10 <sup>5</sup>	-	_		
	FD1S p-channel $\mu_h$ (cm <sup>2</sup> /Vs) 0.55 [0.22 ~ 1.0] 0.23 [0.18 ~ 0.56] 0.026 [0.016 ~ 0.040]	FD1S p-channel $\mu_h$ $I_{on}/I_{off}$ (cm <sup>2</sup> /Vs) 0.55 [0.22 ~ 1.0] ~10 <sup>7</sup> 0.23 [0.18 ~ 0.56] ~10 <sup>7</sup> 0.026 [0.016 ~ ~10 <sup>6</sup> 0.040]	FD1S       p-channel       p-channel $\mu_h$ $I_{on}/I_{off}$ $\mu_h$ (cm²/Vs)       (cm²/Vs)         0.55 [0.22 ~ 1.0]       ~10 <sup>7</sup> 0.27 [0.21 ~ 0.45]         0.23 [0.18 ~ 0.56]       ~10 <sup>7</sup> 0.15 [0.12 ~ 0.22]         0.026 [0.016 ~       ~10 <sup>6</sup> 0.040 [0.008 ~         0.040]       0.059]	FDTS       OL         p-channel       p-channel $\mu_h$ $I_{on}/I_{off}$ $\mu_h$ $I_{on}/I_{off}$ (cm <sup>2</sup> /Vs)       (cm <sup>2</sup> /Vs)       (cm <sup>2</sup> /Vs)         0.55 [0.22 ~ 1.0]       ~10 <sup>7</sup> 0.27 [0.21 ~ 0.45]       ~10 <sup>3</sup> 0.23 [0.18 ~ 0.56]       ~10 <sup>7</sup> 0.15 [0.12 ~ 0.22]       ~10 <sup>7</sup> 0.026 [0.016 ~       ~10 <sup>6</sup> 0.040 [0.008 ~       ~10 <sup>5</sup> 0.040]       0.059]       0.059]       ~10 <sup>5</sup>	FDTSODTSp-channelp-channeln-channel $\mu_h$ $I_{on}/I_{off}$ $\mu_h$ $I_{on}/I_{off}$ $\mu_e$ (cm²/Vs)(cm²/Vs)(cm²/Vs)(cm²/Vs)0.55 [0.22 ~ 1.0]~10^70.27 [0.21 ~ 0.45]~10^30.17 [0.10 ~ 0.28]0.23 [0.18 ~ 0.56]~10^70.15 [0.12 ~ 0.22]~10^7-0.026 [0.016 ~~10^60.040 [0.008 ~~10^5-0.040]0.059]0.059]0.059]0.059]		

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## Conclusion

We have synthesized oxygen and selenium analogues of naphthobischalcogenadiazole, namely, naphthobisoxadiazole (NOz) and naphthobisselenadiazole (NSz), and the corresponding polymers. We found that NOz and NSz had high electron deficiency compared with the sulfur analogue, naphthobisthiadiazole (NTz), which is different from the trend observed in acenedichalcogenophenes. This is probably because the electron negativity of the chalcogen atom is the dominant factor for the frontier orbital energy levels. It is also found that although all the model compounds, NXz2T, were similarly coplanar in the single crystals, steric repulsion between NXz and the adjacent thiophene rings seems to be larger as the chalcogen atom become heavier. The difference of the steric repulsion can rationalize the difference in the electronic structure of NXz2T-DT and PNXz4T, and the ordering structure of PNXz4T: whereas PNOz4T exhibited bathochromic shift in the absorption and similarly high crystallinity in the film, PNSz4T exhibited hypsochromic shift and amorphous-like structure as compared to PNTz4T. Thanks to the higher electron deficiency, the NOz and NSz-based polymers, PNOz4T and PNSz4T, respectively had deeper LUMO energy levels than the NTz-based polymer, PNTz4T. Notably, the LUMO energy level of PNOz4T was found to be -3.65 eV by electrochemistry and -4.00 eV by spectroscopies, which is around the borderline for allowing ambient n-channel behavior in OFETs. In fact, whereas PNSz4T showed only p-channel behavior, as is the case in PNTz4T. PNOz4T exhibited a p-channel and an ambipolar behavior depending on the surfactant used in OFETs. It is also mentioned that the mobilities of PNOz4T were significantly higher than those of PNSz4T. which was consistent with the higher crystallinity of PNOz4T. The hole mobility of PNOz4T in the pchannel devices reached 1 cm<sup>2</sup>/Vs, which was even higher than that of PNTz4T. In the ambipolar devices, PNOz4T demonstrated well-balanced and relatively high hole and electron mobilities of ~0.5  $cm^2/Vs$  and  $\sim 0.3 cm^2/Vs$ , respectively. We have shown the clear correlation between the chalcogen atom in the NXz unit and the properties of the corresponding polymers. Furthermore, these results clearly demonstrate that NOz is an interesting acceptor unit for  $\pi$ -conjugated materials.

## **Experimental section**

Synthesis. 2,6-Diamino-1,5-dinitronaphthalene (1),<sup>37</sup> 1,2,5,6-tetraaminonaphthalene (3),<sup>37</sup> 4-(2decyltetradecyl)-2-trimethylstannylthiophene (6),  $^{28}$  5,5'-bis(trimethylstannyl)-2,2'-bithiophene (9)  $^{50}$  were synthesized according to the reported procedure, respectively. Even in the hydrochloride form, 3 gradually changes the color from gray to bluish gray in air, which may affect the synthesis of NSz. It is recommended to store in an inert atmosphere. All chemicals and solvents are of reagent grade unless otherwise indicated. THF and toluene were purified by a Glass Contour Solvent System (Nikko Hansen & Co., Ltd.) prior to use. Polymerization was carried out with a microwave reactor (Biotage Initiator). Nuclear magnetic resonance (NMR) spectra were obtained in deuterated chloroform and DCB (for polymers) with TMS as internal reference by using a JNM-ECS400 (JEOL RESONANCE). EI-MS spectra were obtained with a GCMS-QP-2010SE spectrometer (SHIMADZU) using an electron impact ionization procedure (70 eV). The molecular ion peaks of the chlorine-, bromine-, sulfur-, selenium-, or tin-containing compounds showed a typical isotropic pattern, and all the mass peaks are reported based on <sup>35</sup>Cl, <sup>32</sup>S, <sup>79</sup>Br, <sup>80</sup>Se, or <sup>120</sup>Sn, respectively. Molecular weights were determined by gel permeation chromatography (GPC) by calibrating with polystyrene standards using a TOSOH HLC-8121GPC/HT at 140 °C with DCB as the solvent.

*Naphtho*[1,2-c:5,6-c']bis[1,2,5]oxadiazole (NOz). 1,5-Diamino-2,6-dinitronaphthalene (1) (5.00 g, 20.1 mmol), 85 % potassium hydroxide (5.3 g, 80.3 mmol), tetrabutylammonium bromide (0.65 g, 2.02 mmol), dichloromethane (100 mL), and water (13.5 mL) were added to a 300 mL three-neck flask. 10% sodium hypochlorite solution (96.0 g, 129.0 mmol) was added slowly. After the mixture was stirred at room temperature for 0.5 h, the mixture was refluxed for 2 h. While concentrating the solvent, 50 % ethanol aqueous solution was added slowly. After cooling to 0 °C, the precipitate was filtered, and then washed by water and 50% ethanol aqueous solution. The crude product (a mixture of **2a-c**) as yellow solid was dried in vacuo and used without further purification (3.59 g, 73%). The mixture of **2a-c** (3.22 g, 13.2 mmol) was added to 80 mL of ethanol in a flask. After the mixture was cooled to 0 °C, hydroxylamine hydrochloride (3.67 g, 52.8 mmol) and water (16 mL) was added, and then 85 %

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potassium hydroxide (7.41 g, 112.3 mmol) and water (16 mL) was added successively. The mixture was stirred at room temperature for 1 h, and subsequently was refluxed for 3 h. Water was added slowly to the reaction mixture, which was then cooled to 0 °C. The precipitate was collected by filtration. After washing with water, the crude product was purified by recrystallization from chloroform/ethanol/water to give NOz as orange solid (2.04 g, 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.52 (d, *J* = 9.2 Hz, 2H), 8.09 (d, *J* = 9.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.9, 147.5, 128.6, 122.9, 117.4. EI-MS (70 eV) *m*/*z* 212 (M<sup>+</sup>). Anal. Calcd for C<sub>10</sub>H<sub>4</sub>N<sub>4</sub>O<sub>2</sub>: C, 56.61; H, 1.90; N, 26.41. Found: C, 56.60; H, 2.09; N, 26.21.

*Naphtho*[1,2-*c*:5,6-*c*']*bis*[1,2,5]*selenadiazole* (*NSz*). 1,2,5,6-Tetraaminonaphthalene tetrahydrochloride (0.50 g, 1.50 mmol) and pyridine (7.8 g) were added to a 300 mL three-neck flask. After cooling to 0 °C, seleninyl chloride (1.10 g, 6.63 mmol) was added dropwise. The solution was heated to 70 °C, and stirred for 2 h. Water was added dropwise into the reaction mixture, which was then cooled to 0 °C. The resulting precipitate was filtered, washed by water and isopropanol, and dried under vacuum. The crude product was purified by recrystallization from DCB to give NSz as dark yellow solid (345 mg, 68%). <sup>1</sup>H NMR (400 MHz, DCB-*d*<sub>4</sub>, 150 °C):  $\delta$  8.63 (d, *J* = 9.3 Hz, 2H), 7.76 (d, 2H, *J* = 9.3 Hz). EI-MS (70 eV) *m*/*z* 340 (M<sup>+</sup>). Anal. Calcd for C<sub>10</sub>H<sub>4</sub>N<sub>4</sub>Se<sub>2</sub>: C, 35.53; H, 1.19; N, 16.57. Found: C, 35.37; H, 1.18; N, 16.45.

*5,10-Dibromonaphtho*[*1,2-c:5,6-c']bis*[*1,2,5]oxadiazole* (*4*). NOz (2.25 g, 10.6 mmol) was dissolved in concentrated sulfuric acid (112.5 g) in a 200 mL three-neck flask. NBS (5.66 g, 31.8 mmol) was added in several portions over the period of 1 h, and then the reaction mixture was stirred for 24 h at room temperature. The reaction mixture was poured into cold water, and the resulting precipitate was filtered. The collected product was washed with water, NaHCO<sub>3</sub> aq., ethanol and THF, which was then purified by recrystallization from chloroform/isopropanol to give **4** as yellow solid (2.92 g, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.68 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  149.5, 146.7, 130.6, 122.6, 1110.9. EI-MS (70 eV) *m*/*z* 370 (M<sup>+</sup>). Anal. Calcd for C<sub>10</sub>H<sub>2</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: C, 32.47; H, 0.54; N, 15.14. Found: C, 32.63; H, 0.59; N, 15.09.

*5,10-Dibromonaphtho*[*1,2-c:5,6-c']bis*[*1,2,5]selenadiazole* (*5*). NSz (3.00 g, 8.87 mmol) was dissolved in concentrated sulfuric acid (150 g) in a 200 mL three-neck flask. NBS (4.74 g, 26.6 mmol) was added in several portions over the period of 1 h, and then the reaction mixture was stirred for 6 h at room temperature. The reaction mixture was poured into cold water, and the resulting precipitate was filtered. The collected product was washed with water, NaHCO<sub>3</sub> aq., ethanol and THF. The residue was then stirred in hot DCB, filtered and dried in vacuo, giving **5** as dark yellow solid (3.66 g, 83%). <sup>1</sup>H NMR (400 MHz, DCB-*d*<sub>4</sub>, 150 °C):  $\delta$  8.81 (s, 2H). EI-MS (70 eV) *m/z* 496 (M<sup>+</sup>). Anal. Calcd for C<sub>10</sub>H<sub>2</sub>Br<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>: C, 24.22; H, 0.41; N, 11.30. Found: C, 24.21; H, 0.47; N, 11.27.

*5,10-Bis*(*4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis[1,2,5]oxadiazole (NOz2T-DT).* 4 (1.02 g, 2.76 mmol), 4-(2-decyl)tetradecyl-2-(trimethylstannyl)thiophene (6) (4.02 g, 6.89 mmol), and 136 mL of toluene were added to a 200 mL three-neck flask and purged with argon for 40 min. Tetrakis(triphenylphosphine)palladium(0) (127 mg, 0.110 mmol) was added, and then the reaction mixture was refluxed for 16 h. After cooling to room temperature, KF aq. was added and the mixture was extracted with toluene. The organic layer was washed with water, and then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel with hexane-dichloromethane (3:1), followed by recrystallization from ethyl acetate to give NOz2T-DT as orange solid (2.68 g, 93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.57 (s, 2H), 8.08 (s, 2H), 7.12 (s, 2H), 2.65 (d, *J* = 6.9 Hz, 4H), 1.77-1.65 (m, 2H), 1.37-1.18 (m, 80H), 0.86 (t, *J* = 6.7 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.0, 147.7, 144.1, 136.6, 132.1, 124.3, 124.0, 121.8, 121.5, 38.9, 35.1, 33.3, 31.9, 30.0, 29.7, 29.4, 26.6, 22.7, 14.1. ESI-MS *m/z* 1050 [M+H]<sup>+</sup>. Anal. Calcd for C<sub>66</sub>H<sub>104</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 75.52; H, 9.99; N, 5.34. Found: C, 75.33; H, 10.02; N, 5.20.

5,10-Bis(4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis[1,2,5]selenadiazole (NSz2T-DT). 5 (537 mg, 1.083 mmol), 6 (1.39 g, 2.38 mmol), and 55 mL of toluene were added to a 100 mL three-neck flask and purged with argon for 40 min. Tetrakis(triphenylphosphine)palladium(0) (50.0 mg, 0.043 mmol) was added, and then the reaction mixture was refluxed for 16 h. After cooling to room temperature, KF aq. was added and the mixture was extracted with toluene. The organic layer was

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washed with water, and then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel with hexanedichloromethane (2:1), followed by recrystallization from ethyl acetate to give NSz2T-DT as purple solid (1.02 g, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.00 (s, 2H), 8.00 (d, *J* = 1.2 Hz, 2H), 7.09 (s, 2H), 2.65 (d, *J* = 6.8 Hz, 4H), 1.77-1.67 (m, 2H), 1.40-1.17 (m, 80H), 0.86 (t, *J* = 6.9 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.5, 157.9, 142.8, 138.8, 130.1, 128.0, 126.3, 123.7, 123.4, 39.0, 35.2, 33.4, 31.9, 30.1, 29.7, 29.7, 29.4, 26.7, 22.7, 14.1. ESI-MS *m/z* 1178 [M+H]<sup>+</sup>. Anal. Calcd for C<sub>66</sub>H<sub>104</sub>N<sub>4</sub>S<sub>2</sub>Se<sub>2</sub>: C, 67.43; H, 8.92; N, 4.77. Found: C, 67.34; H, 8.95; N, 4.65.

*5,10-Bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis[1,2,5]oxadiazole (7).* NOz2T-DT (2.68 g, 2.56 mmol) and 210 mL of THF were added to a 300-mL three-neck flask and cooled to 0 °C. NBS (1.08 g, 6.09 mmol) was added, and the reaction mixture was stirred for 18 h at room temperature. NaHCO<sub>3</sub> aq. was added, and the mixture was extracted with toluene. The organic layer was washed with brine, and then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel with hexane-dichloromethane (2:1), followed by twice recrystallization from ethyl acetate to give 7 as red solid (2.72 g, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.44 (s, 2H), 7.92 (s, 2H), 2.60 (d, *J* = 7.1Hz, 4H), 1.83-1.72 (m, 2H), 1.44-1.16 (m, 80H), 0.86 (t, *J* = 6.8 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  147.8, 147.3, 143.6, 136.2, 131.6, 123.2, 121.5, 121.5, 114.2, 38.6, 34.3, 33.4, 31.9, 30.0, 29.7, 29.4, 26.6, 22.7, 14.1. ESI-MS *m/z* 1208 [M+H]<sup>+</sup>. Anal. Calcd for C<sub>66</sub>H<sub>102</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 65.65; H, 8.51; N, 4.64. Found: C, 65.54; H, 8.54; N, 4.52.

# 5,10-Bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)naphtho[1,2-c:5,6-c']bis[1,2,5]selenadiazole

(8). NSz2T-DT (223 mg, 0.190 mmol) and 14 mL of THF were added to a 50 mL three-neck flask and cooled to 0 °C. NBS (71.0 mg, 0.399 mmol) was added, and the reaction mixture was stirred for 3 h at room temperature. NaHCO<sub>3</sub> aq. was added, and the mixture was extracted with toluene. The organic layer was washed with brine, and then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel with hexane-

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dichloromethane (2:1), followed by twice recrystallization from ethyl acetate to give **8** as purple solid (203 mg, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.81 (s, 2H), 7.75 (s, 2H), 2.59 (d, J = 7.2 Hz, 4H), 1.84-1.73 (m, 2H), 1.43-1.16 (m, 40H), 0.85 (t, J = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  158.0, 157.3, 141.9, 138.2, 128.7, 126.9, 126.0, 122.2, 113.9, 38.7, 34.4, 33.4, 31.9, 30.1, 29.7, 29.7, 29.4, 26.6, 22.7, 14.1. ESI-MS *m*/*z* 1335 [M<sup>+</sup>+H]. Anal. Calcd for C<sub>66</sub>H<sub>102</sub>Br<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Se<sub>2</sub>: C, 59.45; H, 7.71; N, 4.20. Found: C, 59.40; H, 7.74; N, 4.07.

*PNOz4T.* 7 (120.7 mg, 0.10 mmol), **9** (49.2 mg, 0.10 mmol), tetrakis(triphenylphosphine)palladium(0) (2.30 mg, 2 µmol) and toluene (4 mL) were added in a 5 mL reaction vessel. The vessel was purged with argon and subsequently sealed. The vessel was put into a microwave reactor and heated at 140 °C for 24 min. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol (100 mL) and concentrated hydrochloric acid (10 mL), and then vigorously stirred for 6 h at room temperature. The precipitate was filtered and subjected to sequential Soxhlet extraction with methanol, hexane, chloroform to remove low molecular weight fraction. The residue was extracted with CB, which was reprecipitated in methanol. The precipitate was filtered and dried in vacuo, yielding PNOz4T (114 mg, 94%) as metallic purple solid. GPC (DCB, 140 °C):  $M_n = 49.7$  kDa,  $M_w = 240.8$  kDa, PDI = 4.8. <sup>1</sup>H NMR (400 MHz, DCB- $d_4$ , 150 °C):  $\delta$  8.51 (s, 2H), 8.22 (s, 2H), 7.25 (m, 2H), 7.24 (m, 2H), 2.97 (m, 4H), 2.01 (m, 2H), 1.18-1.58 (m, 80H), 0.84 (m, 12H). Anal. Calcd for C<sub>74</sub>H<sub>106</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub>: C, 73.34; H, 8.82; N, 4.62. Found: C, 73.10; H, 8.78; N, 4.38.

*PNSz4T.* 8 (66.7 mg, 0.05 mmol), 9 (24.6 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium(0) (1.15 mg, 1 μmol), and toluene (2 mL) were added to a 2 mL reaction vessel. The vessel was purged with argon and subsequently sealed. The vessel was put into a microwave reactor and heated at 180 °C for 48 min. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol (100 mL) and concentrated hydrochloric acid (10 mL), and then vigorously stirred for 6 h at room temperature. The precipitate was filtered and subjected to sequential Soxhlet extraction with methanol, hexane, chloroform to remove low molecular weight fraction. The residue was extracted with CB, which was reprecipitated in methanol. The precipitate was filtered and dried in vacuo, yielding

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PNSz4T (45 mg, 67%) as metallic dark purple solid. GPC (DCB, 140 °C):  $M_n = 28.7$ kDa,  $M_w = 60.6$  kDa, PDI = 2.1. <sup>1</sup>H NMR (400 MHz, DCB- $d_4$ , 150 °C):  $\delta$  9.10 (s, 2H), 8.27 (s, 2H), 7.25 (m, 2H), 7.22 (m, 2H), 3.00 (m, 4H), 2.05 (m, 2H), 1.17-1.63 (m, 80H), 0.83 (m, 12H). Anal. Calcd for  $C_{74}H_{106}N_4S_4Se_2$ : C, 66.44; H, 7.99; N, 4.19. Found: C, 66.12; H, 8.27; N, 3.77.

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# **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website:

CIF file for NOz2T

CIF file for NTz2T

CIF file for NSz2T

Methods, synthesis of NOz2T and NSz2T, NMR spectra, GPC charts of the polymers. Cyclic voltammograms and UV-vis absorption spectra, and HOMO and LUMO geometries of NXz. Computation and PL spectra of NXz2T. Photoelectron spectra, DSC and TGA curves, 2D GIXD patterns, OFET properties of the polymers.

# TOC figure

