

Poly(3-hexylthio) thiophene Field-effect Transistor Device Performance: Impact of the Content of Hexylthio Side Chain on Backbone

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Electronic Supplementary Information

Abstract Regioregular poly(3-hexylthio)thiophene (**P3HTT**) has emerged tremendous potential in organic electronic applications due to the strong noncovalent interactions from the sulfur atom linked to thiophene. However, **P3HTT** generally exhibits low charge mobility mostly due to poor solution processability attributed to dense arrangement of hexylthio side chain in polymer, which led to strong noncovalent interactions among sulfur atoms. To balance the nonvalent interaction and aggregation for **P3HTT**, herein, we systematically study the effect of hexylthio side chain content in polymer backbone on the structure and properties. A series of regioregular **P3HTT**-based homopolymers (**P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25**) were prepared via Kumada catalyst transfer polycondensation method from a set of mono-, bi-, ter- and quarter-thiophenes containing different contents of hexylthio side chain. The DFT calculation shows the planarity of polymers backbone could be improved through reducing the density of hexylthio side chain in polymer mainchain. And significant changes in their crystallinity, aggregation and optical properties were observed with the content of hexylthio side chain reducing. The **P3HTT-33** displayed the highest field-effect transistor hole mobility of $2.83 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ resulting from a balance between the crystallinity and planarity. This study demonstrates modulating the content of hexylthio side chain in **P3HTT** is an effective strategy to optimize the opto-electronic properties of polymer obtaining excellent semiconductor device performance.

Keywords Conjugated polymer; Polythiophene; Noncovalent interaction; Molecular aggregation; Organic field-effect transistor

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INTRODUCTION

Semiconducting polymers have attracted tremendous attentions mostly due to their excellent solution processability and unique optoelectronic properties, which can construct tunable, low-cost, lightweight, flexible device, such as organic field-effect transistors (OFETs),^[1–5] organic photovoltaics (OSCs),^[6–9] organic light-emitting diodes (OLEDs)^[10–13] compared with inorganic materials. In the past decade, much efforts have been focused on achieving high mobility conjugated polymers (CPs).^[14–18] By the rational molecule design, especially the emergence of donor-acceptor conjugated polymer, the mobility of CPs-based OFETs has been up to $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[19–22] However, the conjugated polymer with high mobility unavoidable requires synthesizing complex conjugate

unit. Poly(3-alkylthiophene) (P3ATs), especially poly(3-hexylthiophene) (P3HT) of the most widely studied polythiophene, has been regarded as one of the most promising organic semiconductor materials for commercial application.^[23–30] Based on tremendous studies, it is concluded the parameters of conjugated polymers including the number-average molecular weight (M_n), molar-mass dispersity (D_M), and regioregularity (R.R.) have a great influence on their optoelectronic properties.^[31–35] Especially the development of Grignard metathesis (GRIM) polymerization has made it possible to obtain well-defined P3ATs with predicted M_n , low D_M , and high R.R. up to 99%,^[36,37] which make mobility of OFETs around $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^[38] and a power conversion efficiency of P3HT-based OSCs achieve about 4%–5%.^[39] However, their device performance is inevitably limited by the contradiction between high crystallinity and excellent soluble processability. To further improvement the device performance of P3HT-based OFET, it has been proved that introducing heteroatom into polymer backbone is one of the most effective strategies to change the photoelectric and crystalline properties of polymers. Heeney

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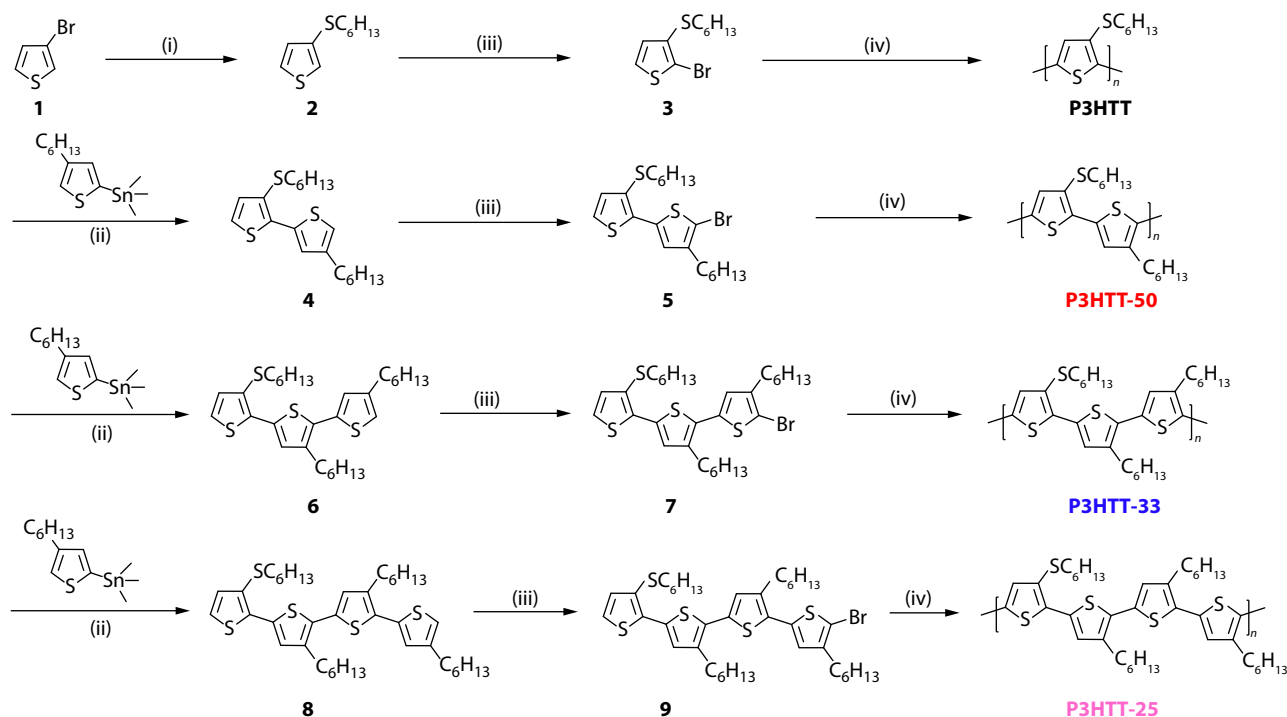
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et al. reported three relatively regioregular (93% regioregularity) fluorinated poly(3-alkyl) thiophenes, which were synthesized by Kumada catalyst transfer polycondensation of 2,5-dibromo-3-fluoro-4-alkylthiophene.^[40] All three polymers exhibited improved charge carrier mobilities compared with P3TH resulting from improved coplanarity through leading the fluorine atom into backbone. Mario Leclerc *et al.* studied the effect of the degree of fluorination along polymer backbone on photoelectric properties of regioregular P3HT, which indicated that property breakpoint was around 33% fluorination point.^[41] Beyond fluorine atom, connecting alkylthio side chain with polymer backbone also can validly regulate the polymer chain conformation, aggregation, and crystallinity.^[42–45] Computation and experiment have proposed that sulfur atom with 3p π -orbital and empty 3d-orbital can overlap with π -conjugated backbone (S $\cdots\pi$) and neighboring sulfur atoms (S $\cdots$ S) on the same chain or neighboring chain.^[46,47] Therefore, it is expectable that alkylthio side chain would exhibit high potential on enhancing the electrical properties of PAHT derivatives through promoting π -electron delocalization and changing aggregation behavior, which is driven by potential S $\cdots$ S chalcogen–chalcogen and S $\cdots\pi$ intra/intermolecular interactions. Based on these, abundant research has reported that poly[(3-alkylthio) thiophene] (P3ATT) can be synthesized through diverse polymerization methods, especial GRIM polymerization, which can obtain high Mn polymer.^[48–50] However, the obtained polymers generally show poor solubility mostly due to the strong S $\cdots$ S and S $\cdots\pi$ intra/intermolecular interactions. Tomoya Higashihara *et al.* synthesized a series of P3ATTs consisting of P3DTT, P3HTT and branched moiety P3EHTT,^[51] and results indicated although the P3HTT displayed more better crystallinity and orientation in film compared with P3HT,

especially the shorter lamellar and π - π packing distance for P3HTT from sulfur atom on side chain, the hole charge mobility of P3HTT was observed lower than it of P3HT due to poor solubility of polymer attributed to strong nonvalent interactions from densely arrangement of hexylthio side chain in polymer backbone. Therefore, how to balance the crystallinity and solubility of **P3HTT** is the big challenge to obtain high hole charge mobility for **P3HTT**. For this reason, we prepared a series of reioregular P3HTT-based homopolymers *via* synthesizing four thiophene monomers with different contents of hexylthio side chain through iterative 3-hexyl thiophene couplings. We systematically investigated the effect of orderly hexyl thio side chain content on crystallinity, aggregation, the optical and electronic properties for polymers. The highest mobility can reach up to $2.83 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ of **P3HTT-30** attributed to modulating the banlance between the crystallinity and planarity of polymer through optimizing the content of hexylthio side chain on polymer backbone. This study demonstrates that modulating the content of hexylthio side chain on **P3HTT** backbone has a beneficial impact on the polymer conformation, aggregation, crystallinity and charge transport device performance.

RESULTS AND DISCUSSION

The synthetic routes to four thiophene monomers with different hexylthio chain contents and corresponding regioregular conjugated polymers are shown in Scheme 1. The starting 3-hexylthio-5-bromo-thiophene (3HT5BrT) **3** was synthesized according to the reported literature.^[52] Following a series of iterative Stille coupling reactions by using trimethyl(4-hexylthiophen-2-yl) stannane^[53] were undertaken to obtain



Scheme 1 Synthetic routes to **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25**. (i) $n\text{BuLi}$, S, -78°C , THF; $t\text{BuOK}$, $\text{C}_6\text{H}_{13}\text{Br}$, MeOH, 80°C ; (ii) $\text{Pd}_2(\text{dba})_3$, $\text{P}(\text{o-Tol})_3$, toluene, reflux; (iii) NBS, THF, 0°C ; (iv) 1.1 equiv. of $\text{TMPMgCl}\cdot\text{LiCl}$, THF, $0\text{--}35^\circ\text{C}$, then 1.5 mol% $\text{Ni}(\text{dppp})\text{Cl}_2$, 50°C , 5 h.

compounds **4**, **6** and **8**. Interestingly, the viscosity and activity of these compounds showed higher as increasing the number of thiophene unit. The final desired monomers **5**, **7** and **9** were then synthesized through the bromination of **4**, **6** and **9** by using *N*-bromosuccinimide (NBS) (1 equiv.) in tetrahydrofuran at $-10\text{ }^{\circ}\text{C}$. It is worth noting that no dibromo byproducts can be found on these bromination reactions, resulting from the higher activity of terminated hydron atom on hexyl-thiophene unit than it at hexylthio-thiophene unit, which means hexylthio chain exhibits more electron withdrawing effect compared with hexyl chain at thiophene unit. **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25** were prepared by GRIM polymerization of monomer **3**, **5**, **7** and **9**, respectively. Similar polymerization condition was performed on these four monomers by modification of previously reported procedure about **P3HTT**.^[54] Firstly, forming Grignard intermediate on hexylthio-thiophene unit through Grignard reagent 2,2,6,6-tetramethylpiperidinyl-magnesium chloride, lithium chloride (TMPMgCl·LiCl) at $0\text{ }^{\circ}\text{C}$ in THF, followed by adding [1,3-bis(diphenylphosphino)-propane] dichloronickel(II) ($\text{Ni}(\text{dppp})\text{Cl}_2$) to mixture system and heating at $35\text{ }^{\circ}\text{C}$ for 5 h. The crude polymers were purified by Soxhlet extraction using methanol, *n*-hexane, dichloromethane and chloroform. The fraction in chloroform was precipitated in methanol, affording four polymers. The polymerization results of four polymers are summarized in Table 1. The number-average molar mass (M_n) was measured by size exclusion chromatography (SEC) as shown in Fig. S15 (in the electronic supplementary information, ESI). The value of regioregularity for these polymers was calculated by the integration of α -methylene protons of hexylthio group and hexyl group. It can be found that the molecular weight of obtained polymers

extracted from chloroform became higher as the content of hexylthio chain thiophene unit reduces, which shows the solubility for these polymers in chloroform become better as the hexyl side chains in polymer increases. Four polymers were found to be soluble in chloroform and chlorobenzene. The ^1H -NMR spectra of four monomers and corresponding polymers shown in Figs. 1(a) and 1(b) were measured in deuterated chloroform at $25\text{ }^{\circ}\text{C}$ in the 600 MHz ^1H -NMR spectra, considering the molecular weight and the solubility in chloroform of these polymers. In the spectra of **P3HTT**, as shown in Fig. 1(b), the chemical shift of the central aromatic proton appears at 7.30–7.39 ppm (HT) and 7.10 ppm (TT). The signal at 2.93 ppm corresponds to the methylene linked to the sulfur atom of hexylthio side chain. For **P3HTT-50**, the chemical shifts of the central aromatic proton on hexylthio thiophene unit and on hexylthio unit appear at 7.23 and 7.10 ppm, respectively. The signal at 2.93 ppm corresponds to the methylene linked to the sulfur atom of hexylthio side chain and the peak of the methylene linked to the hexyl side chain is located at 2.79 ppm. In addition, For **P3HTT-33** and **P3HTT-25**, the signal for aromatic protons in monomers appears at 7.23–6.9 ppm and the peak appeared at 2.93 and 2.79 ppm corresponds to methylene of hexylthio and hexyl thiophene unit. Furthermore, it is noted that the integral ratio of the two peak for **P3HTT-33** and **P3HTT-25** is almost 1:2 and 1:3, respectively, which corresponds the proton ration on monomers.

The crystallinity and thermal properties of these polymers were examined by using DSC measurements. Fig. 2 shows the 2nd heating and 1st cooling thermograms of the **P3HTT**, **P3HTT-50**, **P3HTT-33**, and **P3HTT-25**, and Table 2 summarizes their characteristics. Cooling and heating cycles of **P3HTT**

Table 1 Molecular weight, molar-mass dispersity, degree of polymerization, regioregularity HOMO, LUMO and energy bandgap of **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25**.

	M_n^a (kg/mol)	$\bar{D}_M^a$	DP ^a	R.R. ^b (%)	HOMO ^c (eV)	LUMO ^c (eV)	E_g^c
P3HTT	6.2	1.36	31	66.67	−5.03	−2.79	2.24
P3HTT-50	8.1	1.38	22	90.09	−4.37	−2.39	1.98
P3HTT-33	9.3	1.48	18	90.09	−4.66	−2.51	2.15
P3HTT-25	18.5	1.78	26	93.45	−4.65	−2.47	2.18

^a Number-average molar mass (M_n), molar-mass dispersity ($\bar{D}_M$) and degree of polymerization (DP) were measured by size exclusion chromatography (SEC);

^b Regioregularity (R.R.) was determined from integration of the resonances in ^1H -NMR spectra; ^c HOMO, LUMO and E_g were calculated from DFT.

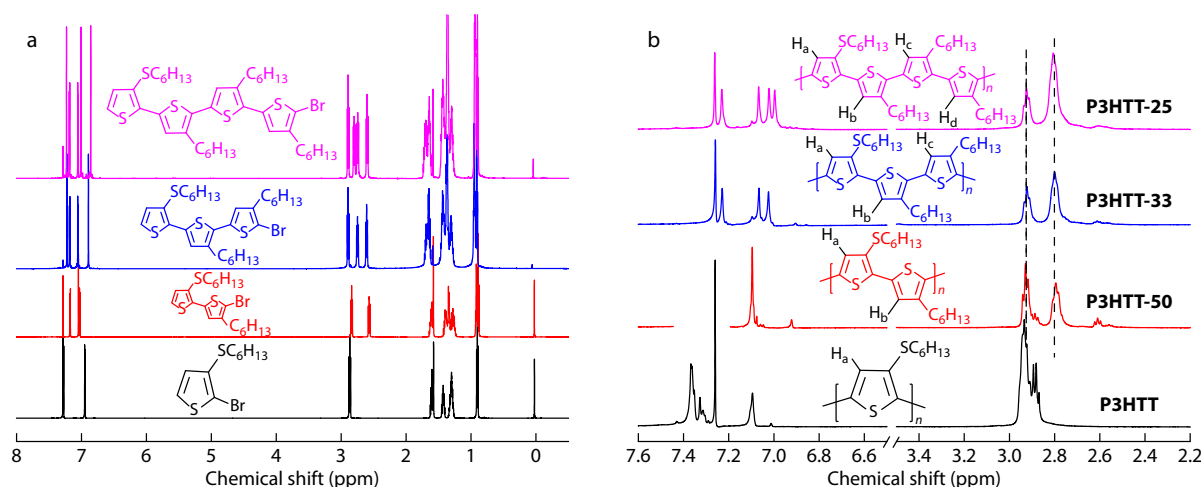


Fig. 1 ^1H -NMR spectra of (a) four monomers; (b) **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25**.

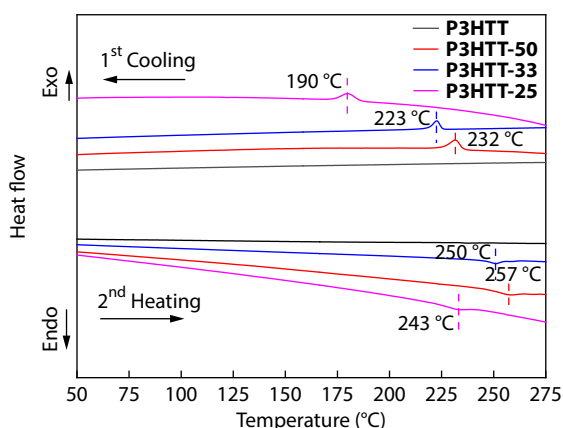


Fig. 2 DSC thermograms of **P3HTT**, **P3HTT-50**, **P3HTT-33**, and **P3HTT-25** for first cooling cycle and second heating cycle.

had no peak for crystallization and melting, which agreed well with the previously reported the thermal properties for **P3HTT**.^[51] These results indicated **P3HTT** had no crystalline phase transition. Considering the strong crystallization peak shown in the XRD pattern of **P3HTT**, the reason could be the strong S...S and S... π intra and interaction of polymer backbone resulting in the melting temperature greater than the thermal decomposition temperature. The melting temperature (T_m) of **P3HTT-50**, **P3HTT-33**, and **P3HTT-25** decreased from 257 °C to 250 °C and to 243 °C in heating cycle of these polymers, meanwhile a similar trend could be observed in the crystallization temperature (T_c) from the cooling cycle. The T_c values of **P3HTT-50**, **P3HTT-33** and **P3HTT-25** decreased from 232 °C to 223 °C and to 190 °C, respectively. These values of the T_m and T_c indicated the changing the content of hexylthio side chain in **P3HTT** backbone could effectively lower inter interaction of polymer chain, which another three polymers were observed evident crystallization behaviors in DSC compared with **P3HTT**. Moreover, the strongly decreasing in T_m and T_c of **P3HTT-50**, **P3HTT-33**, and **P3HTT-25** implied the lower content for the hexylthio thiophene segment in monomer could led to weaken inter interaction from S...S and S... π intra and interaction and more distorted backbone of polymers. In addition, these three polymers displayed relatively sharp crystallization peaks, indicating a high regioregularity for **P3HTT-50**, **P3HTT-33**, and **P3HTT-25**.^[53] All four polymers also display high thermal stability, which was confirmed by TGA, with 5 wt% loss temperature ($T_{d,5\%}$), which is shown in Fig. S17 (in ESI).

We employed density functional theory (DFT) calculations to investigate the relationship between monomer containing different hexylthio thiophene unit contents and the correspondingly polymer backbone conformation. To reduce the

computational complexity and to simplify the potential energy surface, we replaced all hexyl groups with methyl group with the common assumption that change of alkyl chain would have a little influence on their electronic properties. Our calculations were performed on model oligomers of the four polymers we synthesized experimentally, which the results were used to analyze the conformation of single polymer chain. Considering the different numbers of thiophene unit in monomer, four oligomer models containing twelve thiophene units in accordance with monomer structure was optimized by using the B3LYP/6-311+G (d, p)-D3BJ.^[41] The conformation structures of four polymers are shown in Fig. 3, which were all-*anti* conformers according to the previous study. We referred to the dihedral angle between the two thiophene units as SCCS, which included the two sulfur atoms and connecting carbons between adjacent thiophene units. In **P3HTT**, the SCCS dihedral angles ranged from 12.1° to 23°, which indicated **P3HTT** polymer backbone chain exhibited a relatively distorted conformation mostly due to the S...S interaction between the sulfur atom for hexylthio side chain and the sulfur atom of the adjacent thiophene unit.

Moreover, the SCCS dihedral angles of **P3HTT-50** ranged from 0° to 22°, with the central SCCS dihedral angle being virtually planar, which the best backbone planarity of all four polymers was mainly due to reducing S...S interaction caused by hexylthio thiophene unit *via* inserting one hexylthiophene unit into monomer. In **P3HTT-33**, the SCCS dihedral angles ranged from 1.2° to 23°, with the central SCCS dihedral angle being virtually planar (1° out-of-plane twist), and in **P3HTT-25** the SCCS dihedral angles range from 7.5° to 24.4°, which means the change of the planarity of conjugated backbones for four polymers could be resulted from the balance between the steric effect and electronic effect of the sulfur atom. The twisted chain plane of **P3HTT** derives from the Steric effects effect of sulfur atoms on hexylthio side chain. And for **P3HTT-50** and **P3HTT-33**, the S-S and S- π interaction and the ratio of hexylthio side chain in polymer chain could keep the relative plane conformation. However, for **P3HTT-25**, the content of hexylthio side chain is lowest and the the S-S and S- π interaction is the weakest in four polymers, which the chain conformation exhibits more twisted than **P3HTT-33** and **P3HTT-50**. These results indicated the strategy of inserting different number of hexylthiophene unit into 3-hexylthio thiophene monomer could effectively improve the polymer backbone planarity. In addition, the energy levels of the HOMO and LUMO for four oligomers were also evaluated as shown in Fig. S18 (in ESI) and the characteristics are summarized in Table 1. Our results are consistent with many other reports of increasing HOMO energies with increased proportions of hexylthiophene unit in backbone. The smallest

Table 2 Thermal properties of **P3HTT**, **P3HTT-50**, **P3HTT-33**, and **P3HTT-25**.

	T_m^a (°C)	T_c^a (°C)	$\Delta H(T_c)^a$ (J/g)	$\Delta H(T_m)^a$ (J/g)	T_d^b (°C)
P3HTT	—	—	—	—	350
P3HTT-50	257	232	12.23	11.65	377
P3HTT-33	250	223	9.17	8.6	334
P3HTT-25	243	190	11.93	11.27	379

^a Melting temperature (T_m), crystallization temperature (T_c), enthalpy of crystallization ($\Delta H(T_c)$), and enthalpy of Melting were measured by differential scanning calorimetry (DSC); ^b Degradation temperature (T_d) was determined at 5% weight loss *via* thermogravimetric analysis (TGA).

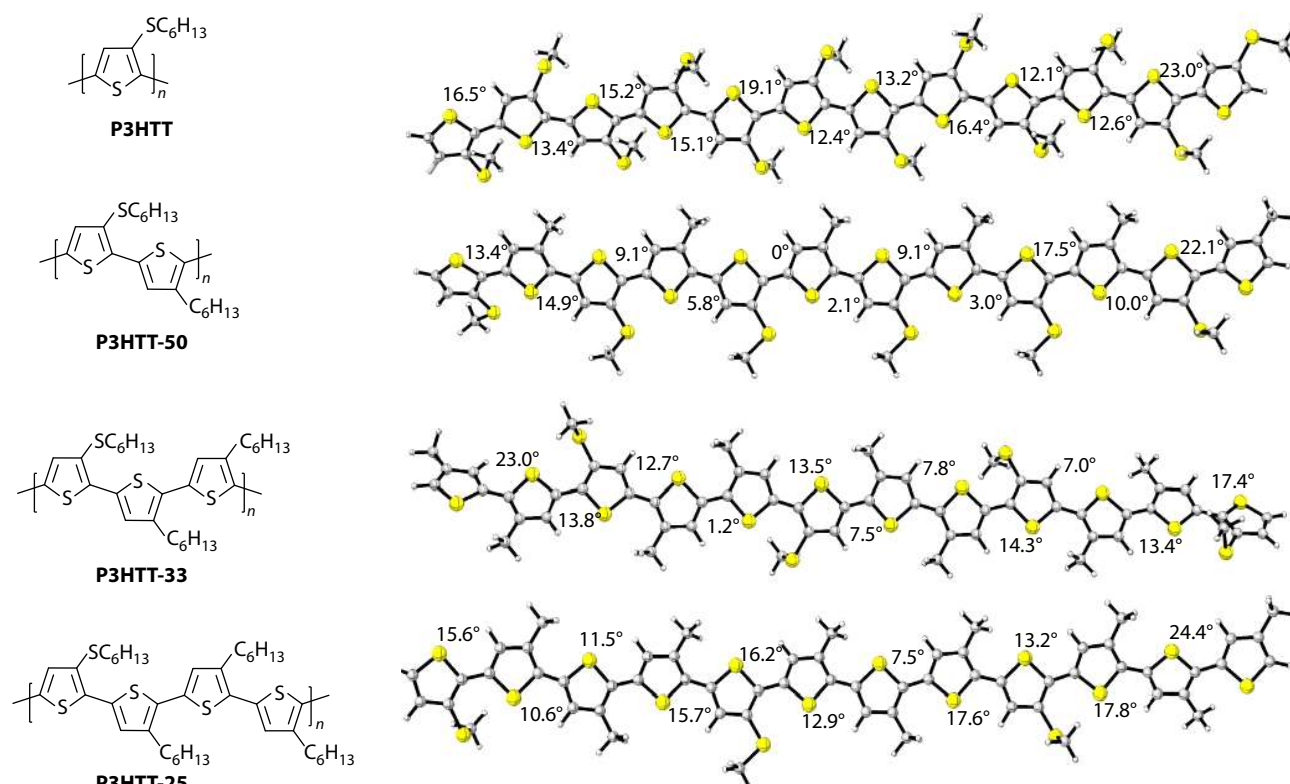


Fig. 3 The all-anti conformation of **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25** oligimer computed using B3LYP/6-311+G (d, p)-D3BJ.

HOMO-LUMO gap of **P3HTT-50** resulted from the most extensive delocalization of the frontier molecule orbital.

The aggregation of these four polymers in solution and film were analyzed by UV-Vis absorption. The spectra of four polymers in chloroform solution and in solid state are shown in Fig. 4 and Fig. S2 (in ESI) and numerical values are detailed in Table 3. The absorption peak of **P3HTT**, **P3HTT-50**, **P3HTT-25** and **P3HTT-33** solution appeared at 510, 489, 480 and 472 nm, respectively, which indicated the absorption peak was red-shifted as decreasing the content of hexylthio thiophene unit in polymer, mostly due to the electron-donating ability from hexylthio side chain. Meanwhile, it was noticed that a vibronic shoulder peak was observed at 616 and 612 nm for **P3HTT-50** and **P3HTT-33**, which implied a high polymer backbone planarity for **P3HTT-50** and **P3HTT-33** led to molecular exhibiting aggregation behavior in solution. In addition, the spectra of **P3HTT-50** and **P3HTT-33** exhibited evidently temperature-dependent in solution, which the absorption peak from conjugated backbone were blue-shifted and the absorption peak from aggregation (616 nm for **P3HTT-50**, 612 nm for **P3HTT-33**) disappeared with increasing the temperature from 20 °C to 60 °C. In contrast, the absorption spectrum from aggregation of **P3HTT-25** was weak, and the absorption spectra from conjugated backbone of **P3HTT-25** and **P3HTT** were slightly blue-shifted, indicating their negligible aggregation in solution. As for the thin film shown in Fig. 4, all four polymers showed similar red-shifted absorption spectra and more sharply shoulder at higher wavelength, which indicated the aggregation in the solid state showed enhancement compared with solution attributed to more strongly intra- and inter- molecular S...S and S... π interactions.

The two principal absorption peaks appeared at 548/599, 566/615, 562/611 and 555/600 nm for **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25**, respectively, which were assigned to the A_{0-0} and A_{0-1} vibronic transitions. The ratio of the intensity of these two absorption peaks (A_{0-0}/A_{0-1}), which could be used to analyze the molecule ordering and conjugation length along the polythiophene backbone, was measured for these four polymers. The A_{0-0}/A_{0-1} value of the **P3HTT** was 0.76, a result from balance between the strong molecule interaction due to hexylthio chain and distorted polymer backbone conformation.^[54] The A_{0-0}/A_{0-1} value of the **P3HTT-50** (0.99) and **P3HTT-33** (0.92) was higher than **P3HTT** (0.76), suggesting an increase in the effective conjugation due to higher planarity, although reducing the nonbond interaction from sulfur atom. Apart from these, it can be observed that the A_{0-0}/A_{0-1} value of the **P3HTT-25** was lower than **P3HTT** (0.76). This result indicated that S...S, S... π molecule interaction from the hexylthio thiophene unit in **P3HTT-25** became weaker considering the reduce of that content and the improvement in chain conformation could not compensate for weak S-S and S- π interaction of **P3HTT-25**.

The optical bandgap of four polymers was calculated using the solid-stated UV-Vis spectra and the values are summarized in Table 3. The bandgap of **P3HTT** was 1.90 eV, which was same with the previously reported **P3HTT**. **P3HTT-50** (1.89 eV) and **P3HTT-33** (1.89 eV) exhibited the narrow bandgap. In addition, the bandgap of **P3HTT-25** increased to 1.93 eV as the reduce of the hexylthio thiophene unit. The HOMO of all four polymers changed very little, which was measured using cyclic voltammetry. Moreover, the LUMOs were calculated from the HOMO and optical bandgaps. It

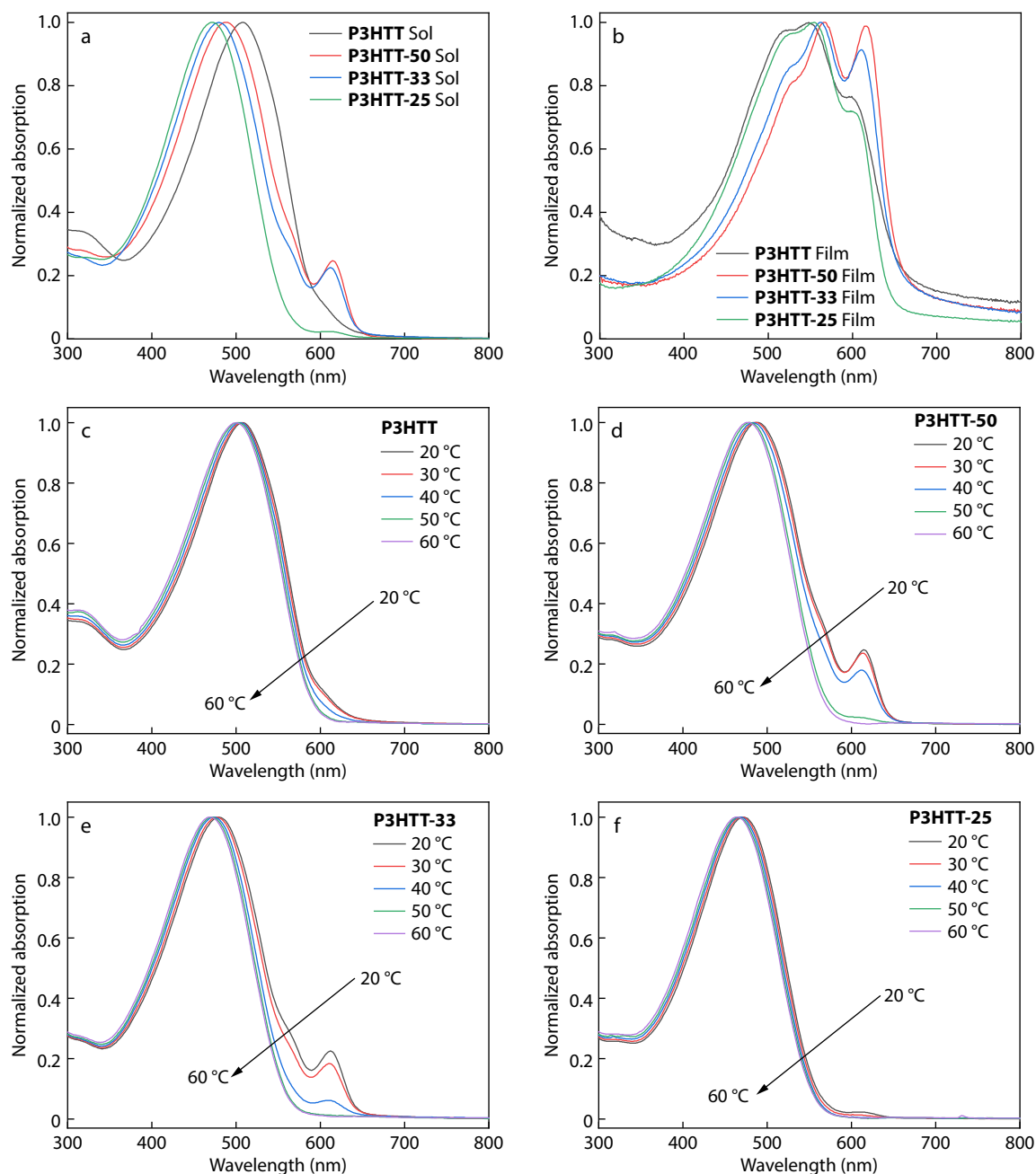


Fig. 4 Normalized UV-Vis absorption spectra of **P3HTT**, **P3HTT-50**, **P3HTT-33**, and **P3HTT-25** in (a) chloroform and (b) thin films. Temperature-dependent absorption spectra of (c) for **P3HTT**, (d) for **P3HTT-50**, (e) for **P3HTT-33** and (f) for **P3HTT-25** in chloroform.

Table 3 The optical properties and HOMO/LUMO energies of **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25**.

	$\lambda_{\max}$ (sol) ^a (nm)	$\lambda_{\max}$ (film) ^b (nm)	$E_{g,opt}$ ^c (eV)	A_{0-0}/A_{0-1}	HOMO ^d (eV)	LUMO ^e (eV)
P3HTT	510	548, 599	1.89	0.76	−5.14	−3.25
P3HTT-50	489, 616	566, 615	1.89	0.99	−5.22	−3.33
P3HTT-33	480, 612	562, 611	1.90	0.92	−5.22	−3.32
P3HTT-25	472	555, 600	1.93	0.72	−5.18	−3.25

UV-spectra were obtained from ^a chloroform and ^b films, ^c estimated from the absorption spectra; ^d Estimated from the electrochemical measurements; ^e $E_{LUMO} = E_{HOMO} + E_{opt}$.

could be observed the HOMO value upshift from −3.24 eV in **P3HTT** to −3.15 eV in **P3HTT-25**. As the decrease of the hexylthio thiophene unit content, which was agreed with the

previously report.

To study the relationship between the hexylthio side chain content in polythiophene with the charge transport proper-

ties. BGTC OFETs for these four polymers were fabricated. All these polymers are deposited *via* spin-coating of chloroform. The output and transfer plots of the p-type OFETs of four polymers are shown in Fig. 5. The detailed values are summarized in Table 4, including average and maximum charge carrier mobilities, on/off current ratios, and threshold voltages for four polymers at two conditions (as-spin and 150 °C heat annealing). All four polymers exhibited p-type transport characteristics. The hole mobilities of these polymers were found to be increased an order of magnitude from as-spin to TA. The **P3HTT** displayed the worst hole mobility attributed to the strong S⋯S intra and interaction of polymer backbone. Furthermore, the hole mobilities for these polymers were observed increasing as the reduce of the hexylthio side chain content. These results indicate that the charge carrier mobility for thin-film of **P3HTT** can be effectively improved through reducing S⋯S interaction *via* changing the hexylthio side chain content in polymer backbone. In addition, the highest mobility was obtained with **P3HTT-33** at 150 °C ($0.0283 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) possibly due to a well balance between the increasing polymer backbone planarity and surpassing crystallinity when the content of hexylthio side chain is re-

duced, which is agreed with the previous report for fluorinated polythiophenes. Grazing incidence X-ray diffraction (GIXD) of the thin films was studied to reveal the variation of the crystallinity of the four type films. In the 1D out-of-plane GIXD patterns (Fig. S19 in ESI), the diffraction peaks of all four polymer films appear at 5.23° , corresponding to a d -spacing of $17.2 \text{ \AA}$, which are indexed to (100) plane. It was noted that the intensity for the TA films exhibits decreasing with the content of hexylthio side chain reducing.^[55] These results indicated the crystallinity for these polymers becomes weaker when increasing the content of hexyl side chain in the polymer backbone for **P3HTT**. For **P3HTT-33** of 150° annealing, the diffraction peak ($2\theta=33.1^\circ$) shows obvious enhanced, which is the direction of π - π stacking. The thin-film morphology for these polymers were monitored *via* AFM to explore the variation of the crystallinity and continuity following the change of the hexylthio side chain content. As shown in Fig. 6, all the films for these polymers display evidently aggregation, especially for these film with TA. However, the poor continuity for films of **P3HTT**, which led to the poor hole mobility, indicated strong S⋯S and S⋯ π intra and interaction of polymer backbone could make polymer more prone to aggregation

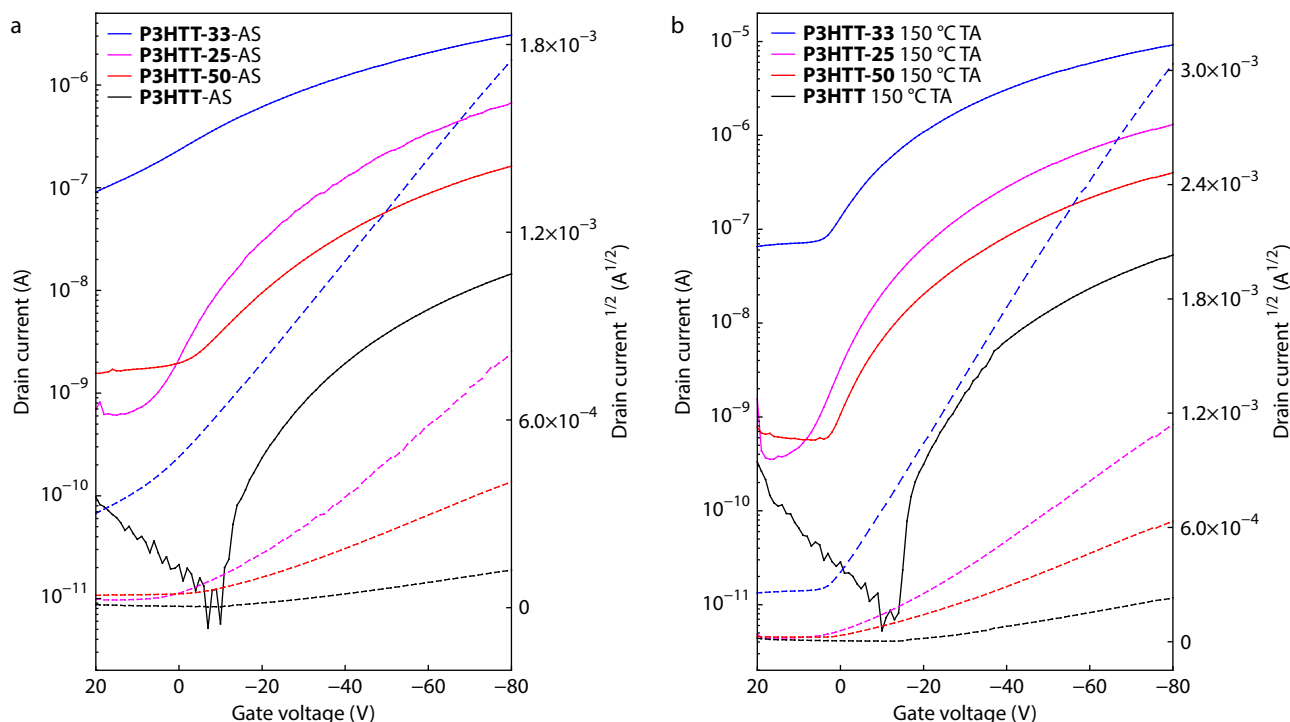


Fig. 5 Transfer plot of **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25** OFET devices in (a) as spin; (b) 150 °C TA.

Table 4 The OFET performance of **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25**.

Sample	T (°C)	$\mu_{\max}$ ($\times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)	M_{avg} ($\times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)	$I_{\text{ON/OFF}}$	V_{TH}
P3HTT	AS	0.0049	0.0048	1.49×10^2	-9.49
P3HTT	150	0.022	0.020	1.6×10^2	-13.84
P3HTT-50	AS	0.049	0.046	1.04×10^2	-1.07
P3HTT-50	150	0.13	0.11	5.18×10^2	-0.82
P3HTT-33	AS	0.59	0.56	3.38×10^1	-28.17
P3HTT-33	150	2.83	2.39	1.41×10^2	-9.3
P3HTT-25	AS	0.19	0.18	9.65×10^2	-1.01
P3HTT-25	150	0.44	0.39	2.09×10^3	-1.86

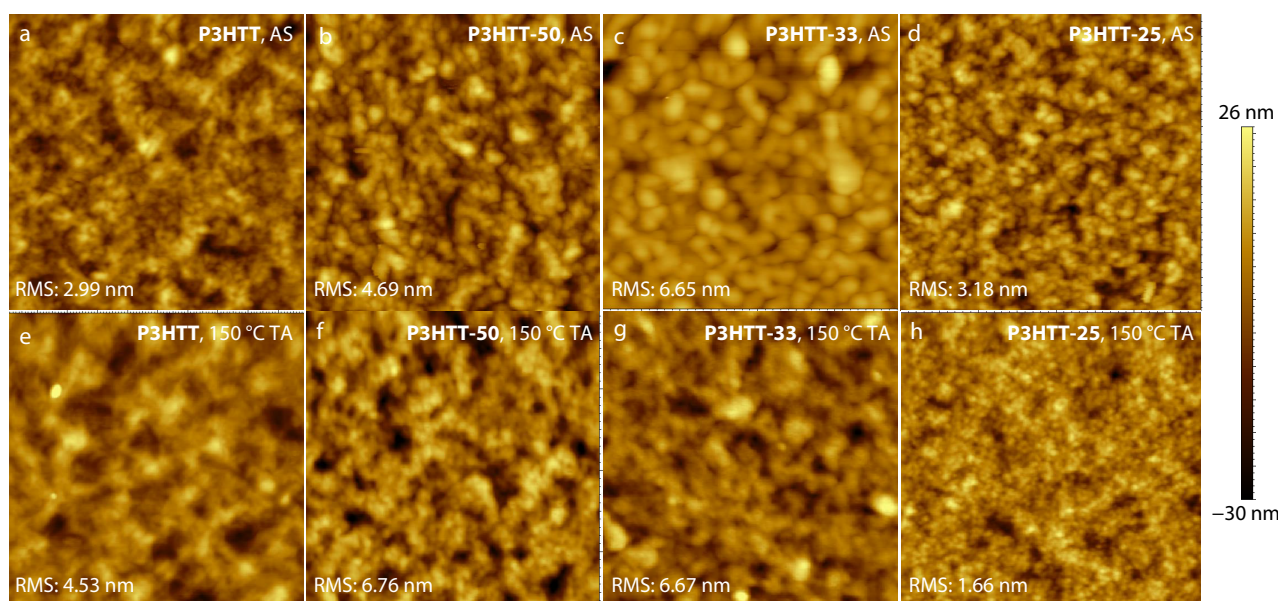


Fig. 6 AFM images of **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25** films (500 nm × 500 nm) in (a–d) as spin and (e–h) 150 °C TA.

but bad for continuity of film. As the content of hexylthio side chain reduces, the continuity of film for **P3HTT-50**, **P3HTT-33**, and **P3HTT-25** exhibits better due to the improvement of planarity of polymer backbone, which is benefit for the charge mobility. The morphology for these polymer films could be agreed with the device performance.

CONCLUSIONS

In summary, four derivatives of polymer (3-hexylthio-thiophene) containing different contents of hexylthio side chain were reported. Regioregular **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25** were prepared by KCTP of corresponding monomers which were synthesized using iterative Stille couplings from 3-hexylthio-5-bromo-thiophene (3HT5BrT). The influence of the hexylthio side chain of different contents on crystallinity, aggregation, optical and electronic properties was systematically studied. The computational analyses by DFT indicated that the planarity of **P3HTT** polymer backbone would be improved through inserting the hexyl chain thiophene unit on the polymer mainchain mostly due to reducing the S...S intra interaction and balancing the steric hindrance of sulfur atom linked to hexyl chain. UV-Vis absorbance spectra confirmed the aggregation on film enhanced as the content of hexylthio side chain reducing to 33%. Optical bandgaps for **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25** were 1.90, 1.89, 1.89 and 1.93 eV, respectively. The HOMO energy levels of −5.14, −5.22, −5.22 and −5.18 eV for **P3HTT**, **P3HTT-50**, **P3HTT-33** and **P3HTT-25** were measured by electrochemical measurements. These results indicated the little influence of hexylthio side chain on electrochemical properties of **P3HTT**. **P3HTT-33** also exhibited the best results in field effect transistors, reaching hole charge mobilities of $2.83 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which implied modulating the planarity and aggregation of **P3HTT** polymer backbone via changing the content of hexylthio side chain on polymer chain is an effective strategy to optimize charge carrier transport in a range of OFETs devices.

Conflict of Interests

Mei-Fang Zhu is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

Electronic Supplementary Information

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