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Synthesis of Novel Thieno[3,2-*b*]thienobis(silolothiophene) Based Low Bandgap Polymers for Organic Photovoltaics

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Thieno[3,2-*b*]thienobis(silolothiophene), a new electron rich hexacyclic monomer has been synthesized and incorporated into three novel donor-acceptor low-bandgap polymers. By carefully choosing the acceptor co-monomer, the energy levels of the polymers could be modulated and high power conversion efficiencies of 5.52% were reached in OPV devices.

The development of organic photovoltaic cells has received a lot of attention during the last decade and performances of 10% have now been achieved.^{1, 2} The design of new semiconducting materials has played a crucial role in this development and recent donor-acceptor polymers have little structural similarity with the well studied poly(3-hexylthiophene) (P3HT).³ These polymers must be considered as not only photon absorbers in bulk heterojunction (BHJ) solar cells, but also with regard to future commercialization, ambient stability and solution processability, which are key criteria in design. Indacenodithiophene (IDT), a ladder type donor moiety has been successfully introduced into semiconducting polymers, which exhibited excellent hole mobilities in organic field effect transistors (OFET) and good photocurrent efficiencies in organic photovoltaic cells (OPV).⁴⁻⁷ We have demonstrated that the judicious choice of bridging atom can not only have an influence on the crystallinity and solubility, but also allows modulating the frontier energy levels.⁸ The introduction of silicon as a bridging atom between adjacent aromatic units has several beneficial effects besides increasing the effective conjugation length and reducing the conformational disorder. The tetravalent silicon offers the possibility to attach solubilising alkyl side chains, which allows tuning the solubility and processability of the polymer. Given the fact that a silicon-carbon bond is slightly longer than a carbon-carbon bond, the anti-bonding lobes located on the butadiene fragments adjacent to the silicon bridge are separated further from each other, which ultimately should lead to a reduction of the highest occupied molecular orbital (HOMO) energy level.⁹ This reduction of the HOMO manifests as an increase in solar cell open circuit voltage and a potential increase in efficiency.

The substitution of the central benzene ring in the IDT unit with a less aromatic thieno[3,2-*b*]thiophene has been shown to promote the electron donating character of the monomer.¹⁰ Due to

synthetic limitations, the hexacyclic thieno[3,2-*b*]thiophene based donor units reported so far are substituted with para-alkylated benzene rings, which can lead to undesirable nanoscale morphologies, causing low fill factors (FF) in OPV devices and limiting performance to 2.5%.^{10, 11} Herein we report a high yielding and versatile synthetic route towards a new silicon bridged ladder type donor, thieno[3,2-*b*]thienobis(silolothiophene) (Si4T). The incorporation of silicon as a bridging atom should therefore not only have an effect on the frontier energy levels, but also allow introducing linear alkyl side chains onto the hexacyclic donor moiety.

The synthesis of Si4T and the corresponding polymers is shown in Scheme 1. The α -positions of commercially available 3,6-dibromothiopheno[3,2-*b*]thiophene (**1**) were iodated and via a selective Negishi coupling between **2** and (3-bromothiophen-2-yl)zinc bromide, the 3,6-dibromo-2,5-bis(3-bromothiophen-2-yl)thieno[3,2-*b*]thiophene (**3**) could be assembled. In order to improve solubility of **3** and to minimize the possibility of side-reactions during the following synthetic steps, the free α -positions of **3** were lithiated and subsequently quenched with chlorotrimethylsilane to afford compound **4**. The ring-closure was induced by lithiation of all four brominated positions on compound **4** and by slowly quenching the reaction with dichlorodicyclohexylsilane. Single crystals of **5** were grown from an acetonitrile/diethyl ether mixture, and X-ray studies confirmed both the chemical structure and the planarity of the fused Si4T unit, the central C₁₄Si₄S₄ unit being coplanar to within ca. 0.03 Å (Figure 1).

In order to incorporate the new hexacyclic donor unit into low-bandgap polymers via Stille coupling, the trimethylsilane groups

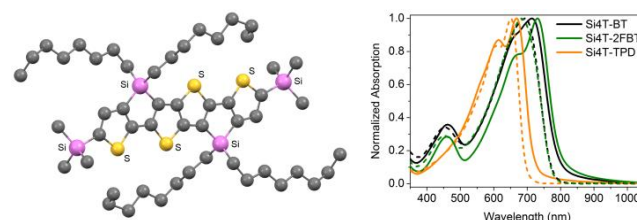
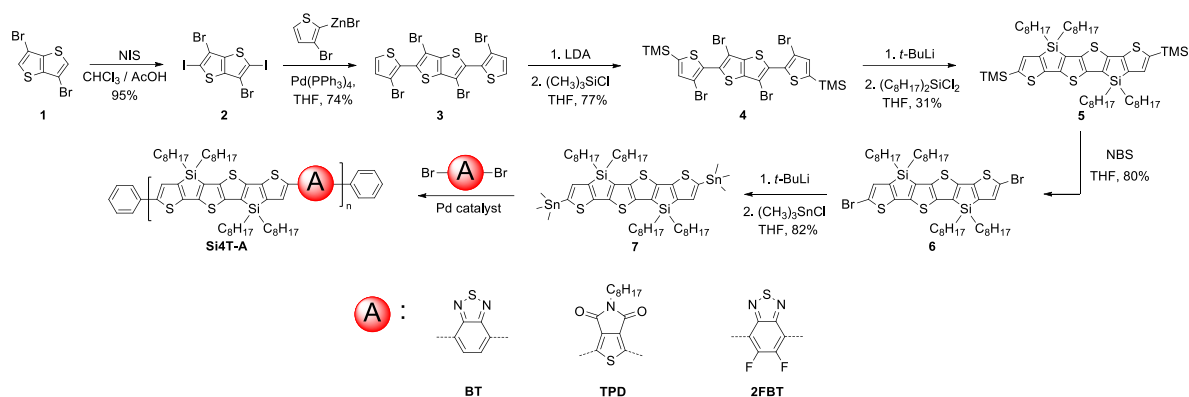


Figure 1. Single crystal structure of compound **5** (left). Normalized optical absorption spectra of Si4T polymers (right) in dilute chlorobenzene (CB) solution (dashed lines) and as thin films (full lines) spin-cast from CB solution.



Scheme 1. Synthetic route towards the novel **Si4T** monomer and polymers.

were cleaved with *N*-bromosuccinimide before compound **6** was stannylated. All three polymers were synthesized by microwave assisted Stille polycondensations by reacting one equivalent of distannylated monomer **7** with one equivalent of the corresponding dibrominated co-monomer (**A**). All polymers were purified by a series of Soxhlet extractions and were recovered as dark fibrous solids with high molecular weights (Table 1). Thermal gravimetric analysis (TGA) (Figure S5 in the ESI) confirmed that all **Si4T** polymers are stable above 420°C. Differential scanning calorimetry (DSC) did not show significant thermal transitions for any of the polymers (Figure S6 in the ESI).

Density functional theoretical (DFT) studies predict the lowest lying HOMO energy level for the **Si4T-TPD** polymer and a homogenous distribution of both frontier energy levels along the polymer backbone (Figure S8 in the ESI). The energy levels for **Si4T-BT** and **Si4T-2FBT** are calculated to be the same, with the HOMO in both cases delocalized over the polymer backbone, but the LUMO mainly localized on the **BT** and **2FBT** units respectively (Figures S7 and S9 in the ESI).

Polymer **Si4T-BT** was obtained by co-polymerizing monomer **7** with benzo[*c*] [1,2,5]thiadiazole (**BT**). The polymer has a very broad thin film absorption in the visible range extending from 400 up to 800 nm with two absorption bands, one with a maximum around 450 nm from the π - π^* transition and a much stronger intramolecular charge transfer (ICT) absorption band with a maximum at 714 nm (Figure 1). The ionisation potential of the polymers were measured as thin films by photoelectron spectroscopy in air (PESA). The measured HOMO energy level of **Si4T-BT** was around -5.0 eV. Replacement of the **BT** unit with thieno[3,4-*c*]pyrrole-4,6-dione (**TPD**) led to an 0.3 eV lower HOMO energy level in the **Si4T-TPD** polymer (Table 2). However, given the fact that **TPD** is a weaker acceptor than **BT**, the absorption spectra of **Si4T-TPD** were significantly blue

Table 1. Molecular Weights and Thermal Stability of the **Si4T** Polymers

Polymer	M_n^a (kg/mol)	M_w^b (kg/mol)	PDF ^c	T_d^d (°C)
Si4T-BT	19	53	2.8	428
Si4T-TPD	21	26	1.2	423
Si4T-2FBT	40	58	1.5	428

^a Number-average molecular weight. ^b Weight-average molecular weight. ^c M_w/M_n . ^d Decomposition temperature (5% weight loss) determined by thermal gravimetric analysis under nitrogen.

shifted, both in solution and thin film and the bandgap was raised by 0.1 eV. In thin film, the absorption band of **Si4T-TPD** presents a more defined vibronic structure, than in solution, with two peak maxima at 615 nm and at 668 nm, respectively. In order to reduce the HOMO energy level of the **Si4T** polymers without compromising the bandgap, monomer **7** was co-polymerized with 5,6-difluorobenzo[*c*] [1,2,5]thiadiazole (**2FBT**). Due to the electron withdrawing character of fluorine, both frontier energy levels should be similarly lowered and therefore the bandgap is expected to remain unaffected.¹² The absorption spectrum of **Si4T-2FBT** in solution is nearly identical to that of **Si4T-BT**. In the solid state, however there are significant differences between the spectra of both polymers. The **Si4T-2FBT** spectrum is further red-shifted than the **Si4T-BT** spectrum, perhaps correlated to the higher number average molecular weight of **Si4T-2FBT**. The **Si4T-BT** absorption band shows some indication of a shoulder at lower wavelengths, whereas the absorption band of **Si4T-2FBT** presents a well defined shoulder feature at higher energies. We speculate that the more defined vibronic structure of the **Si4T-2FBT** absorption band is caused by a reduction of the rotational freedom between donor and acceptor units in the polymer backbone, due to favourable attractive interactions between the sulphur's lone pair electrons on the **Si4T** unit and the electronegative fluorine atoms on the adjacent **BT** moiety. This hypothesis is also supported by the quantum mechanical calculations, which suggest a dihedral angle of 3.87° between the **Si4T** and the **BT** unit and a slightly smaller angle of 2.87° in case of the **Si4T-2FBT** polymer. The barrier of planarization, defined as the difference between the energy of the planar (constraint) and the fully optimized structures, of **Si4T-BT** amounts to 0.23

Table 2. Optical Properties and Frontier Energy Levels of **Si4T** Polymers

Polymer	λ_{\max}^a (nm)	λ_{\max}^b (nm)	exp. HOMO / calc. HOMO / LUMO ^c (eV)	LUMO ^d (eV)	E_g^e
Si4T-BT	694	714	-5.0 / -3.4	-4.5 / -3.1	1.6
Si4T-TPD	651	668	-5.3 / -3.6	-4.7 / -2.9	1.7
Si4T-2FBT	684	731	-5.1 / -3.5	-4.6 / -3.1	1.6

^a Dilute CB solution. ^b Thin film spin-coated from CB solution (5 mg/ml, 1000 rpm). ^c LUMO energy level estimated by adding the absorption onset to the HOMO energy level which was measured by photoelectron spectroscopy in air. ^d energy levels calculated by DFT using B3LYP/6-31G* model. ^e Optical band gap determined from the onset of absorption in the solid state.

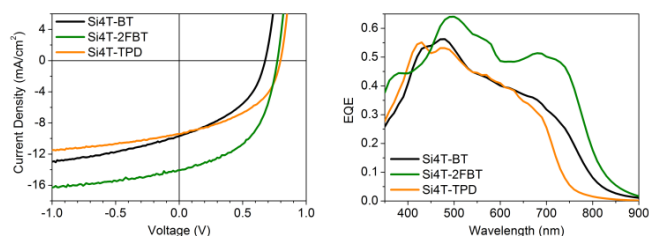


Figure 2. J-V curve (left) and external quantum efficiencies spectra (right) of **Si4T**-polymer:PC₇₁BM OPV devices.

kJ/mol, which is nearly double the energy needed to planarize **Si4T-2FBT** (0.12 kJ/mol).

The HOMO energy levels of **Si4T-BT** and **Si4T-2FBT** are both higher than the corresponding silaindacenodithiophene (**SiIDT**) polymers previously reported.^{13, 14} The increase in HOMO energy level confirms that the incorporation of the more electron rich thieno[3,2-*b*]thiophene into the **IDT** unit significantly increases the electron rich character of the fused ring system. The absorption spectra of **Si4T** polymers are about 60-80 nm red shifted compared to **SiIDT** polymers. When blended with [6,6]-phenyl C71 butyric acid methyl ester (PC₇₁BM), **Si4T-BT** afforded a V_{oc} of 0.67 V and a short-circuit current (J_{sc}) of 9.67 mA/cm² in OPV devices, which corresponds to a rather low photocurrent efficiency (PCE) of 2.79% (Table 3). The **Si4T-TPD** polymer has a much lower HOMO energy level, which translates into a higher V_{oc} of 0.80 V (Figure 3). However, a similar J_{sc} value of 9.42 mA/cm² and the moderate FF of 0.46 resulted in average device performances of 3.46%. The **Si4T-2FBT** polymer exhibited the best performance in OPV devices. The low HOMO energy level of the **Si4T-2FBT** polymer manifests as a large V_{oc} of 0.77 V comparable to the **Si4T-TPD** polymer, but the J_{sc} increased by nearly 70% to 14.07 mA/cm² which led to high device efficiencies of 5.52%. The external quantum efficiency (EQE) spectra are shown in Figure 2 and all three devices exhibit a broad response from 350 up to 750 nm for **Si4T-TPD**, up to 800 nm in the cases of **Si4T-BT** and **Si4T-2FBT**, respectively. However, the lower EQE response at higher wavelengths suggests that in the case of **Si4T-BT** and **Si4T-TPD** most of the current is generated by the PC₇₁BM and not by polymer excitons. **Si4T-2FBT** is the only of the three polymers with an EQE above 40% between 600 and 750 nm, which therefore contributes significantly to the charge generation in the OPV device at higher wavelengths.

The surface morphologies of the polymer:PC₇₁BM blends were studied by atomic force microscopy (Figures S10 to S12 in the ESI). All blends form very smooth high quality films when spin-casted from *o*-dichlorobenzene. The three films are very homogenous with little apparent phase separation and low surface roughness. The **Si4T-2FBT** film is slightly rougher than the other

Table 3. Photovoltaic Properties of the **Si4T** Polymers

Polymer	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
Si4T-BT	9.69	0.67	0.43	2.79
Si4T-TPD	9.42	0.80	0.46	3.46
Si4T-2FBT	14.07	0.77	0.51	5.52

Conventional device architecture ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al with a polymer:PC₇₁BM blend ratio of 1:3.5 processed from *o*-dichlorobenzene.

films and contains small granular features. The formation of these granular domains might be favoured by the higher molecular weight component of the polymer, which tends to preferentially favour phase separation from the PC₇₁BM.

In conclusion, we have synthesized a novel thieno[3,2-*b*]thiophene based ladder type donor monomer, whose fused and planar structure was determined by single crystal X-ray diffraction. The incorporation of silicon bridging atoms allowed the introduction of linear alkyl side chains onto the novel thieno[3,2-*b*]thienobis(silolothienophene) monomer and we synthesized three soluble and easily processable new donor-acceptor polymers. By judiciously choosing the acceptor monomer, we were able to adjust the polymer frontier energy levels, which lead to high V_{oc} values and excellent PCE values of 5.52% in OPV devices.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, characterization data, AFM images, graphical representations of frontier energy levels and crystallographic data. See DOI: 10.1039/b000000x/

- G. Dennler, M. C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf and C. J. Brabec, *Advanced Materials*, 2008, **20**, 579-583.
- J. Peet, A. J. Heeger and G. C. Bazan, *Accounts of Chemical Research*, 2009, **42**, 1700-1708.
- C. L. Chochos and S. A. Choulis, *Progress in Polymer Science*, 2011, **36**, 1326-1414.
- C. Yu, C. Chen, S. Chan, G. Hwang, C. Ting, *Chemistry of Materials*, 2009, **21**, 3262-3269.
- W. M. Zhang, J. Smith, S. E. Watkins, R. Gysel, M. McGehee, A. Salleo, J. Kirkpatrick, S. Ashraf, T. Anthopoulos, M. Heeney and I. McCulloch, *Journal of the American Chemical Society*, 2010, **132**, 11437-11439.
- H. Bronstein, D. S. Leem, R. Hamilton, P. Wobkenberg, S. King, W. M. Zhang, R. S. Ashraf, M. Heeney, T. D. Anthopoulos, J. de Mello and I. McCulloch, *Macromolecules*, 2011, **44**, 6649-6652.
- J. Wang, S. K. Hau, H. Yip, J. A. Davies, K. Chen, Y. Zhang, Y. Sun and A. K.-Y. Jen, *Chemistry of Materials*, 2011, **23**, 765-767.
- I. McCulloch, R. S. Ashraf, L. Biniek, H. Bronstein, C. Combe, J. E. Donaghey, D. I. James, C. B. Nielsen, B. C. Schroeder and W. Zhang, *Accounts of Chemical Research*, 2012, **45**, 714-722.
- J. Ohshita, *Macromolecular Chemistry and Physics*, 2009, **210**, 1360-1370.
- H. Bronstein, R. S. Ashraf, Y. J. Kim, A. J. P. White, T. Anthopoulos, K. Song, D. James, W. M. Zhang and I. McCulloch, *Macromolecular Rapid Communications*, 2011, **32**, 1664-1668.
- Y.-J. Cheng, C.-H. Chen, T.-Y. Lin and C.-S. Hsu, *Chemistry – An Asian Journal*, 2012, **7**, 818-825.
- H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angewandte Chemie International Edition*, 2011, **50**, 2995-2998.
- R. S. Ashraf, Z. Y. Chen, D. S. Leem, H. Bronstein, W. M. Zhang, B. Schroeder, Y. Geerts, J. Smith, S. Watkins, T. D. Anthopoulos, H. Siringhaus, J. C. de Mello, M. Heeney and I. McCulloch, *Chemistry of Materials*, 2011, **23**, 768-770.
- B. C. Schroeder, Z. Huang, R. S. Ashraf, J. Smith, P. D'Angelo, S. E. Watkins, T. D. Anthopoulos, J. R. Durrant and I. McCulloch, *Advanced Functional Materials*, 2012, **22**, 1663-1670.