



# Silaindacenodithiophene based organic semiconductor for high performance organic field-effect transistors



Bogyu Lim <sup>a,1</sup>, Huabin Sun <sup>b,1</sup>, Yong-Young Noh <sup>b,\*</sup>

<sup>a</sup> Future Technology Research Center, Corporate R&D, LG Chem Research Park, 188, Moonji-ro, Yuseong-gu, Daejeon 34122, Republic of Korea

<sup>b</sup> Department of Energy and Materials Engineering, Dongguk University, 30 Pildong-ro, 1-gil, Jung-gu, Seoul 04620, Republic of Korea

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## ABSTRACT

To study the structure-property relationship of silaindacenodithiophene (SiIDT) based semiconducting small molecules, new donor-acceptor type organic small molecules, LGC-D050, LGC-D075 and LGC-D117 are synthesized. These molecules are composed of SiIDT as the electron-donating core and diketopyrrolopyrrole (DPP, LGC-D050 and LGC-D117) or mono-fluoro-benzothiadiazole (FBT, LGC-D075) as the electron-accepting linkers and alkylrhodanine as the electron-accepting end groups. Both LGC-D050 and LGC-D117 have the same backbone structure but different side chains, such as 2-ethylhexyl attached to SiIDT and *n*-octyl to rhodanine for LGC-D117, and *n*-octyl to SiIDT and ethyl to rhodanine in LGC-D050, to check the effect of alkyl chain length. Top-gate/bottom-contact organic field-effect transistors (OFETs) with LGC-D050 show the best p-type field-effect mobility with a maximum of  $1.14 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  (average  $0.83 \pm 0.22 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) after 140 °C annealing comparing to LGC-D075 (maximum of  $0.90 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) and LGC-D117 (maximum of  $0.69 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ). Meanwhile, LGC-075 also show n-type mobility up to  $0.93 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  after 140 °C annealing, result to a balanced ambipolar charge transport. The best device performance of LGC-D050 is achieved by the combination of SiIDT with the *n*-octyl-alkyl chain and DPP as the linker and ethyl rhodanine as the electron accepting end group, due to its high-ordering and low contact resistance compared to the branched alkyl chain to SiIDT and the octylrhodanine end group (LGC-D117), and FBT linker and the octylrhodanine end group (LGC-D075).

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## 1. Introduction

Solution-processed donor-acceptor (D-A) type organic semiconductors (OSCs) have attracted significant attention for their potential applications in low-cost electronics because of their solution processability and potential toward fabrication of lightweight and flexible large area electronic devices [1–5]. The key advantages of D-A type OSCs relate to the ability to tailor optical and electrical properties, such as optical absorption profiles, electronic energy levels, solubility parameters and self-assembly tendency [6–10]. Moreover, D-A type  $\pi$ -backbones lead to small bandgaps with the lowest unoccupied molecular orbital (LUMO) energies to facilitate charge injection and transport of both holes and electrons under ambient conditions [11]. Last decade, tremendous progress has been made on solution-processable D-A

conjugated polymers as active layers of organic field-effect transistors (OFETs) with a field effect mobility ( $\mu_{\text{FET}}$ ) of over  $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  [6,12–17]. Compared to polymer semiconductors, small molecule OSCs have noticeable advantages regarding well defined chemical and electronic structure, less batch-to-batch variation, reproducibility, easy purification and easy functionalization potential. However, development of small molecule OSCs for the active layer of solution-processable OFETs lags significantly behind, compared with D-A polymer semiconductors.

Performance of OFET can be affected by molecular crystallinity and ordering, which can be controlled by  $\pi$ -conjugated backbones through adding desirable segments or functional groups including alkyl chains [16,18–23]. In addition, well-defined molecular architecture can be created by an appropriate combination of D and A units [24]. Therefore, rational construction of molecular frameworks is an effective strategy to design small molecule OSCs tailored for high performance OFET active materials. Furthermore, proper selection of the side chains is critical not only in improving the solubility of OSCs for solution processing, but also in  $\mu_{\text{FET}}$  of the OFETs [25]. Recently, our groups reported silaindacenodithiophene

\* Corresponding author.

E-mail address: [yynoh@dongguk.edu](mailto:yynoh@dongguk.edu) (Y.-Y. Noh).

<sup>1</sup> Both authors contributed equally to this work.

(SiIDT) based D-A small molecule OSCs with diketopyrrolopyrrole (DPP) linkers containing different side chains, which greatly affected device performance [26].

To investigate the effect of different acceptor linkers and side chains on the electrical properties and thus further exploit the potential of molecular design in tuning the electronic properties of small molecule OSCs, in this context, the SiIDT cored D-A type small molecules, LGC-D050, LGC-D075 and LGC-D117, are designed and synthesized for the semiconducting layers of OFETs. Both LGC-D050 and LGC-D117 consisted of SiIDT as the electron-donating core and DPP as the electron-accepting linker, and rhodanine with an alkyl chain of different length as the electron-accepting end group; whereas LGC-D075 featured SiIDT as the electron-donating core and 5-fluoro-2,1,3-benzothiadiazole (FBT) as the electron-accepting linker, and octylrhodanine as the electron-accepting end group, as shown in Fig. 1. The different acceptor linkers and different side chains are incorporated for constructing the target small molecules to understand the structure-property relationships of the SiIDT-based OSCs. As expected, both LGC-D050 and LGC-D117 show almost similar optical and electrochemical properties, but LGC-D075 exhibits a different tendency compared with both. All molecules were applied as an active layer of top-gate/bottom-contact (TG/BC) LGC-D050 OFETs with CYTOP™ dielectrics. Best device performance is achieved by LGC-D050, indicating that small molecules with a linear alkyl chain SiIDT core, DPP linker and short ethyl rhodanine electron-accepting end group show higher hole mobility than the molecule with branched alkyl chain SiIDT core and long octylrhodanine as the electron-accepting end group (LGC-D117), and linear alkyl chain SiIDT core, long octylrhodanine end group, and FBT linker (LGC-D075). Details of the structure-property relationships will be discussed in this paper.

## 2. Experimental section

### 2.1. Synthesis and characterization

**Materials:** All starting materials and reagents were purchased from commercial supplies unless otherwise specified, and used without further purification. Compounds 1, 2 and 4 were prepared according to procedures in the literature [26–28].

**Compound 3:** Compound 1 (0.50 g, 0.47 mmol), compound 2

(0.78 g, 1.1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (23.1 mg, 0.02 mmol), toluene (15 ml) and DMF (2 ml) were added and the mixture heated to 110 °C for 48 h. Upon cooling, the residue was precipitated in 200 ml methanol, and then filtered. The filtered compound was dissolved in chloroform and washed with water. After the volatiles were removed, the crude was purified by flash chromatography using dichloromethane and then chloroform eluents. The dark brown solid product was recrystallized with dichloromethane/methanol and filtered. The solid was washed with copious methanol, and dried under vacuum for 24 h. The product collected was a dark brown powder.

**Yield:** 73.98% (0.7 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, [ppm]): δ 9.891 (s, 2H), 9.048 (d, 2H, *J* = 4 Hz), 8.883 (d, 2H, *J* = 4 Hz), 7.713 (d, 2H, *J* = 4 Hz), 7.560 (s, 2H), 7.478 (d, 2H, *J* = 5 Hz), 7.377 (d, 2H, *J* = 4 Hz), 7.353 (s, 2H), 7.341 (d, 2H, *J* = 4 Hz), 4.072 (m, 8H), 1.965 (br, 4H), 1.410–1.235 (m, 88H), 0.943–0.850 (m, 36H); MALDI-TOF: *m/z* 2012, calcd 2010.92.

**LGC-D050:** Under the protection of a nitrogen, three drops of piperidine were added to compound 3 (0.523 g, 0.26 mmol) and 3-ethylrhodanine (0.48 g, 3 mmol) in a solution of 30 ml of dry CHCl<sub>3</sub>. The resulting solution was refluxed and stirred for 24 h under nitrogen. The mixture was then extracted with dichloromethane, washed with water and dried over MgSO<sub>4</sub>. After solvent removal, it was purified by chromatography on a silica gel column using chloroform, then chloroform with ethyl acetate as eluents. The resulting dark purple solid was recrystallized with chloroform/acetone and filtered. The solid was washed with copious methanol, and dried under vacuum for 24 h. LGC-D050 was a dark purple solid.

**Yield:** 80.6% (0.5 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, [ppm]): δ 9.075 (d, 2H, *J* = 4.5 Hz), 8.921 (d, 2H, *J* = 4 Hz), 7.793 (s, 2H), 7.504 (s, 2H), 7.394 (d, 2H, *J* = 4 Hz), 7.332–7.280 (m, 8H), 4.178 (quarter let, 4H), 4.067 (br, 8H), 1.969 (br, 4H), 1.433–1.249 (m, 94H), 0.941–0.857 (m, 36H); MALDI-TOF: *m/z* 2297, calcd 2296.89.

**Compound 5:** In a dried flask, n-BuLi (2.5 M, 5 mL, 12.5 mmol) was added dropwise to the mixture of the compound 4 (3.04 g, 9.59 mmol) in 120 mL of THF at –78 °C under nitrogen atmosphere. The reactant mixture was heated up to 0 °C for 2 h. After that, trimethyltin chloride (1 M, 13 mL, 13 mmol) was then added at –78 °C, and then the mixture was heated to room temperature. The mixture was subsequently poured into water and extracted by

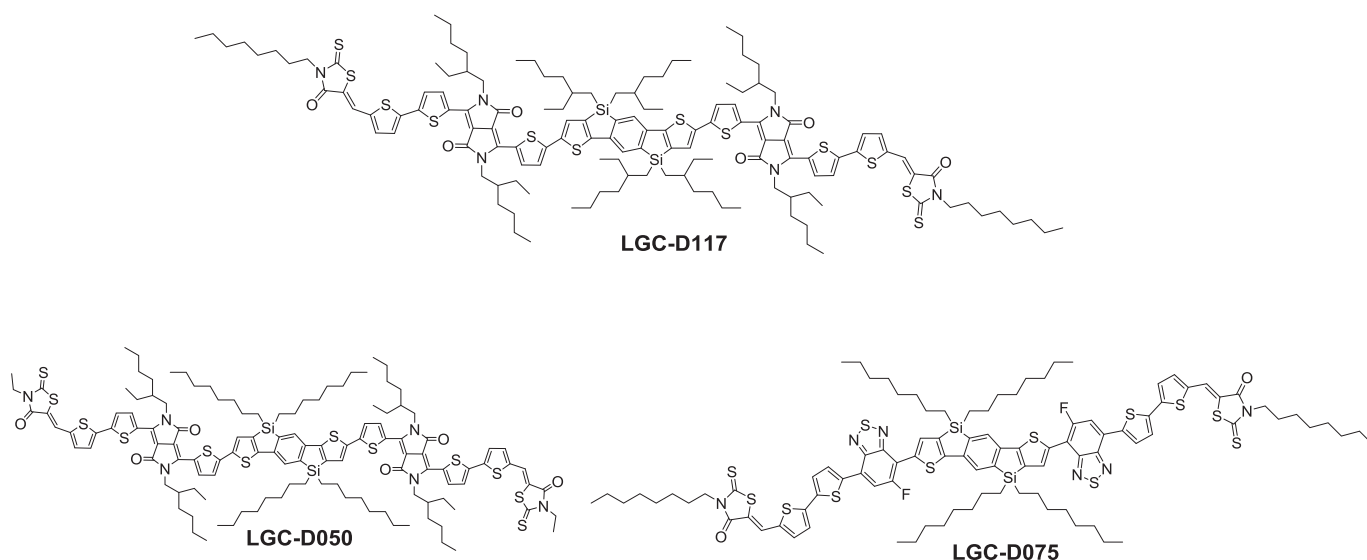


Fig. 1. Molecular structures of LGC-D117, LGC-D050 and LGC-D075.

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