



Highly soluble diketopyrrolopyrrole-based donor-acceptor type small molecule for electrochromic applications

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ABSTRACT

Despite the great potential presented by small molecular compounds, small molecule electrochromic materials receive less attention than polymer-based electrochromic materials. In this work, the synthesis of a novel π -conjugated small molecular electrochromic material, LGC-D055, is described. This material contains dithiophene-phenylene with a bulky trihexylsilyloxy side chain at its core, diketopyrrolopyrrole with a siloxane-terminated hybrid alkyl chain as the linker, and ethylrhodanine as the end group. LGC-D055 presents excellent solubility in organic solvents due to the presence of these bulky side chains. The spin-coated films of LGC-D055 exhibit blue/transparent electrochromism with a fast switching speed of 0.4 s and high coloration efficiency over 300 cm²/C.

1. Introduction

Electrochromism is a phenomenon in which a change in transmittance and/or reflectance occurs through an electrochemical oxidation/reduction reaction [1]. Due to various advantages such as low working voltage, high color contrast, and bistability, electrochromic materials have found applications in windows [2–4], mirrors [5,6], and information displays [7,8]. Compared with inorganic materials, organic electrochromic materials present unique properties such as fast switching speed [9,10] and superior coloration efficiency [11,12]. Many researchers have attempted to develop novel electrochromic materials by controlling the energy band gap using structure modification in order to generate different or multiple colors [13,14].

Diketopyrrolopyrrole (DPP) is one of several high performance organic chromophores used in color filters and inks, paints, varnishes, and plastics. DPP has attracted considerable attention due to its excellent stability, high mobility, broad absorption range, and simple synthesis/modification for use in organic electronic applications such as organic thin film transistors, organic light-emitting diodes, organic photovoltaics, and electrochromic devices. Xu and co-workers demonstrated high performance DPP-based electrochromic polymers with exceptional optical contrasts and fast response time in the visible and near infrared regions [15–19]. Recently Chen et al. reported significant electrochromic properties with high coloration efficiency up to 1300 cm²/C

using DPP-thiophene-based semiconducting polymers [20]. We also presented a study on a DPP-based random copolymer (LGC-D148), which showed promising green/transparent electrochromism with a fast switching speed and a coloration efficiency of more than 900 cm²/C [21,22].

A literature survey reveals that the majority of organic electrochromic studies have been conducted using conjugated polymer semiconductors. In the past couple of decades, there have been many improvements in the performance of organic electrochromic devices using conjugated polymer semiconductors. By contrast, there has been far less development of small-molecular-weight materials for use as the electrochromic layer, especially based on DPP [23]. Part of the motivation behind using small molecular materials is related to their well-defined chemical structures, batch-to-batch reproducibility, and amenability to purification techniques commonly used for organic synthesis, which make small molecules a promising candidate for commercialization. As an electrochromic material, small molecules have a relatively high transparency in the bleached state compared to that of conjugated polymers, which is desirable in window-based applications.

In this study, an intermediate-sized small molecular electrochromic material, named LGC-D055, has been synthesized and its thermal, optical, electrochemical, and electrochromic properties were investigated. LGC-D055 featured dithiophene-phenylene with bulky trihexylsilyloxy side chains as core, diketopyrrolopyrrole with siloxane-terminated

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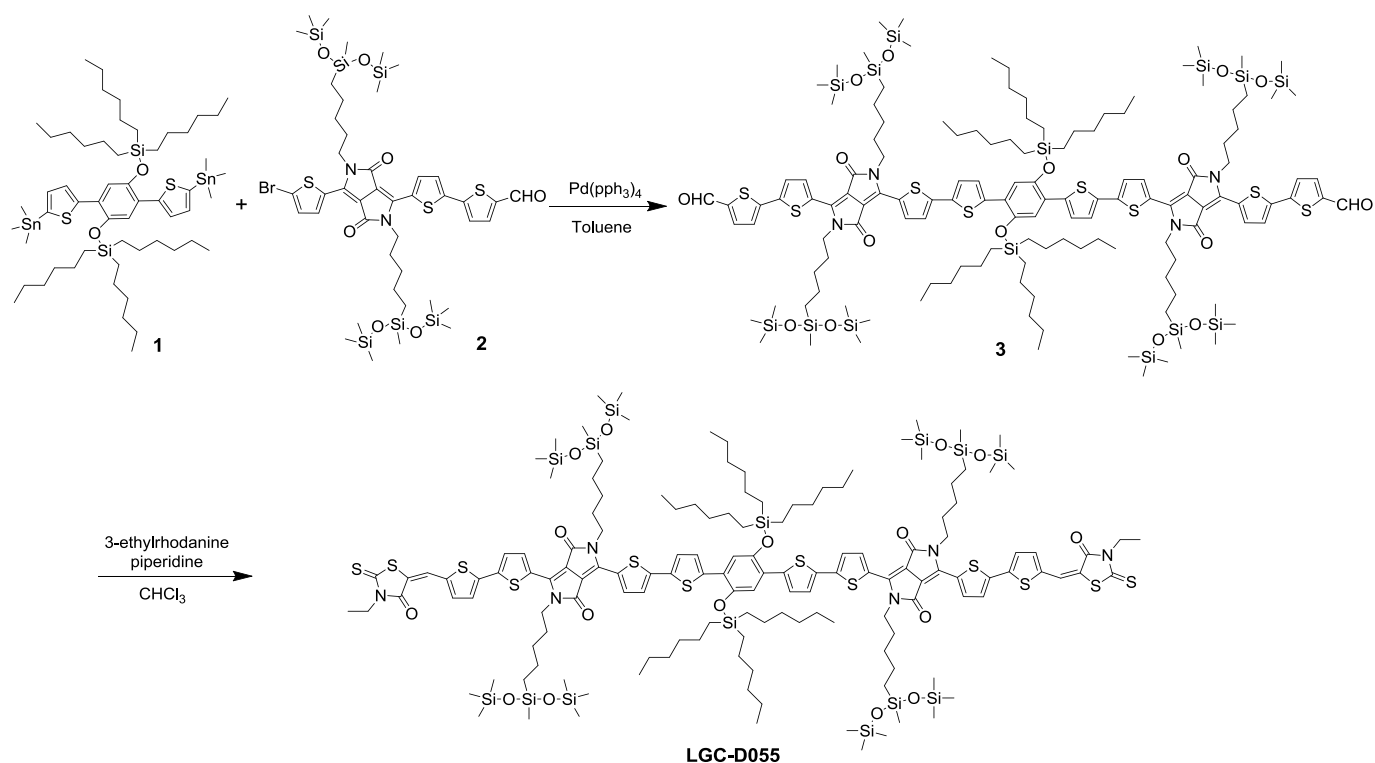
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Scheme 1. Synthetic route of LGC-D055.

hybrid alkyl chains as the linker, and ethylrhodanine as the end group. LGC-D055 has excellent solubility in organic solvents due to the presence of these bulky side chains. LGC-D055 exhibited highly reversible electrochemical reactions and high coloration efficiency with fast switching speed.

2. Experimental section

2.1. Materials

All chemicals used in this study were purchased from commercial suppliers, and used without further purification. Compounds 1 and 2 were synthesized according to reported literature methods [24,25].

2.2. Synthesis

Dialdehyde compound 3, with a bulky trihexylsilyloxy and siloxane-terminated hybrid alkyl chain, was synthesized via the classic Stille cross-coupling reaction as shown in Scheme 1. Compound 1 (0.35 g, 0.3 mmol), compound 2 (0.72 g, 0.67 mmol), Pd(PPh₃)₄ (17.3 mg, 0.015 mmol), and toluene (20 ml) were added and the mixture was heated to 110 °C for 48 h. After reaction, the residue was precipitated in 100 ml methanol, and then filtered. The filtered compound was dissolved in chloroform and washed using water. After the volatiles were removed, the crude product was purified by flash chromatography using hexane/dichloromethane as the eluent. The dark brown solid product was then recrystallized using dichloromethane/methanol and filtered. The solid was copiously washed with methanol and dried under a vacuum for 24 h. The collected product was a dark purple powder. **Yield:** 54% (0.454 g). ¹H NMR (CDCl₃, 500 MHz, [ppm]): δ 9.903 (s, 2H), 9.040 (d, 2H, J = 4.0Hz), 8.888 (d, 2H, J = 4.5Hz), 7.720 (d, 2H, J = 4Hz), 7.490 (d, 2H, J = 4Hz), 7.399 (d, 4H, J = 4Hz), 7.351 (t, 4H, J = 7.5Hz), 7.175 (s, 2H), 4.37 (m, 8H), 1.789 (br, 8H), 1.479–1.254 (m, 64H), 0.869 (t, 30H, J = 13Hz), 0.507 (t, 8H, J = 16Hz), 0.071 (br, 72H), –0.007 (br, 12H); MALDI-TOF: *m/z* 2815.1, calcd 2815.12.

LGC-D055: After the synthesis of compound 3, LGC-D055 was then prepared using the Knoevenagel condensation reaction. Under the protection provided by a nitrogen environment, three drops of piperidine was added to compound 3 (0.23 g, 0.08 mmol) and 3-ethylrhodanine (0.13 g, 0.8 mmol) in a solution of 15 ml of dry CHCl₃. The resulting solution was refluxed and stirred for 72 h under nitrogen. The mixture was then extracted using CH₂Cl₂, washed with water, and dried over MgSO₄. After solvent removal, the mixture was recrystallized with dichloromethane/methanol and then purified by chromatography on a silica gel column using hexane/dichloromethane followed by chloroform eluents. The resulting dark purple solid was recrystallized using chloroform/ethyl acetate and filtered. The solid was washed with copious methanol and dried under a vacuum for 24 h. LGC-D055 was a dark purple solid. **Yield:** 73% (0.182 g). ¹H NMR (CDCl₃, 500 MHz, [ppm]): δ 9.012 (s, 2H), 8.905 (d, 2H, J = 2.5Hz), 7.810 (br, 2H), 7.379 (br, 12H), 7.145 (br, 2H), 4.212 (br, 4H), 4.115 (br, 8H), 1.775 (br, 8H), 1.483–1.263 (m, 70H), 0.862 (br, 30H), 0.508 (br, 8H), 0.069 (br, 72H), –0.002 (br, 12H). ¹³C NMR (CDCl₃, 500 MHz, [ppm]): δ 189.61, 165.25, 159.30, 158.95, 144.39, 142.08, 141.72, 138.86, 138.45, 137.88, 136.14, 135.62, 135.50, 134.21, 133.94, 133.20, 128.37, 125.76, 124.48, 124.42, 124.03, 123.43, 122.61, 122.51, 122.31, 119.75, 116.09, 107.25, 106.15, 40.43, 38.12, 31.44, 29.63, 28.75, 28.70, 28.06, 21.14, 21.10, 20.70, 15.81, 12.53, 12.29, 10.40, –1.889, –2.137, –2.180; MALDI-TOF: *m/z* 3101.1, calcd 3101.09.

2.3. Characterization and measurements

The molecular structures of the intermediated compounds and final compound were confirmed by ¹H NMR, ¹³C NMR spectroscopy (Agilent DD1, 500 MHz), and MALDI-TOF mass spectrometer. The thermal, optical, and electrochemical properties of the final compound were measured using a TA Instrument Q20 differential scanning calorimeter (DSC), Mecasys Optizen Pop UV-Vis spectrophotometer, and an Autolab PGSTAT302N potentiostat/galvanostat, respectively. Colorimetry measurements were performed using a color spectrophotometer (ColorMate, Scinco).

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