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Synthesis and Cyclization-Induced Charge Transfer of Rectangular Bisterthiophenesiloxanes

Chensen Li,[a] Jian Hu,[b] Kohji Tashiro,[c] Zhongjie Ren*[a] and Shouke Yan*[a,b]

Abstract: Cyclization modified terthiophene displays the change of emission behavior from locally excited (LE) state to the intramolecular charge transfer (ICT) state. The rectangular bisterthiophenesiloxanes (DSiTh) was successfully prepared by π-π stacking aided hydrogen bonding interactions. Cyclization-induced ICT in DSiTh can apparently be observed, which is confirmed by absorption spectra, fluorescence spectra and quantum chemistry analysis. The cyclization produces a strong intramolecular electron redistribution of a highly packed π-conjugated terthiophene. And thus a distinctive variation of dipole moment and a through-space ICT happen.

π-conjugated cyclic molecules are considered to exhibit unique optical and electronic behaviors and have potential applications in organic electronics, such as switches.[1-3] The synthesis of the well-defined cyclic molecules is still a big challenge. On one hand, there exists a high tendency to form five- or six membered rings during cyclization due to the small ring strains. On the other hand, the exclusion of side-reactions and an almost quantitative conversion of the starting materials into the targeted ring molecules is a much tough task.[4] Self-assembly has extensively been used for constructing the regular shaped molecules.[5-7] Over the last decades, shape-persistent conjugated cyclic molecules composed of benzene, thiophene, pyridine, and acetylene moieties have been prepared.[8] In particular, Si-containing π-conjugated macrocycles possessing the interesting properties, including excellent heat, radiation or chemical resistance and film-forming ability as well as low dielectric constants. Therefore, they have been investigated as potential materials for semiconductors, light emitters, and photovoltaic systems.[9-11]

It is widely accepted that the sp^3-hybridized silicon linkages with π-conjugated structure allow for electronic delocalization through the σ-π conjugation.[12-13] Therefore, the preparation of σ-π conjugated macrocycles consisting of alternative arrangements of siloxane and π-conjugated moieties is highly desirable to enable the discovery of novel structural features and thus photophysical properties. It should be pointed out that self-assembly method is usually assisted by the metal ions during self-assembly.[14] Herein, we synthesized the rectangular bisterthiophenesiloxanes (DSiTh) directed by π-π stacking aided hydrogen bonding interactions. The σ-π conjugated DSiTh features through-space intramolecular charge transfer (ICT) between the two terthiophene planes, which can be identified by absorbance, fluorescence spectra and theoretical calculations of ground and excited states. As well known, an efficient ICT usually happen in these alternating donor-acceptor architectures.[15,16] Our work reports an example of cyclization-induced ICT in macrocycles without donor-acceptor.

The synthetic route of DSiTh is shown in the Scheme S1. 5,5''-bis(dimethylsilyl)-2,2':5',2''-terthiophene was synthesized by coupling of 2,2':5',2''-terthiophene and dimethyl chlorosilane under n-BuLi. Then, [2,2':5',2''-terthiophene]-5,5''-diylbis(dimethylsilanol) can be obtain in a yield of 82.5% by hydroxylation of 5,5''-bis(dimethylsilyl)-2,2':5',2''-terthiophene in the presence of Pd/C catalyst. The target DSiTh was obtained by condensation of [2,2':5',2''-terthiophene]-5,5''-diylbis(dimethylsilanol) in anhydrous toluene under acidic condition at 60 ºC. Generally, [2,2':5',2''-terthiophene]-5,5''-diylbis(dimethylsilanol) would grow into linear polymer by polycondesation of two silanol groups under this condition. However, the previous results have confirmed that the organosilanols can form the square-planar H-bonding in crystal and in solution.[17,18] Therefore, for our case, two [2,2':5',2''-terthiophene]-5,5''-diylbis(dimethylsilanol) molecules also can assembly into a rectangular structure by H-bonding and weak π-π interactions between two terthiophenes as shown in Figure 1. In this way, two [2,2':5',2''-terthiophene]-5,5''-diylbis(dimethylsilanol) molecules condensed under H-bonding confined environment and the rectangular molecules DSiTh was obtained with a yield of 52%. DSiTh displays good solubility in common solvents, such as, DCM, THF and toluene and thus it also shows good film-forming ability. ^{1}H NMR, ^{13}C NMR and MALDI-TOF MS confirm the structure of all the compounds (Figures S1-10). Thermal properties of DSiTh were evaluated by thermal gravimetric analysis (TGA) performed under nitrogen with the decomposition temperature of 5% weight loss above 300 °C (Figure S11), which is evidently higher than that of terthiophene. The siloxane connected rectangular structure significantly increases the thermal stability of DSiTh.

In order to confirm the molecular conformation, we obtained the single crystals of DSiTh by the slow solvent vapor diffusion method (chloroform/methanol). Upon standing at ambient temperature, the high-quality single crystals of DSiTh has been obtained, indicating the thermodynamically stable crystalline state as shown in Figure S12. The two siloxane-connected terthiophenes display a rectangular configuration (Figure 1b). In this configuration, each terthiophene unit has an approximate coplanar structure within the mean plane deviation of 0.10 Å. The mean distance between two terthiophene planes is 3.78 Å with an anti-conformation. The double connections of the terthiophene skeletons at the 2,5'' positions by the short siloxane seem suitable to maintain the high planarity of the terthiophene skeleton without any severe strain, even in solution.[19] In addition, DSiTh displays herringbone packing in a triclinic unit cell with the *P1* space group. The rectangular molecules are piled up in a slipped edge-to-face arrangement. The intermolecular distance between two adjacent terthiophene planes is 4.32 Å and the slipped angle of two adjacent terthiophene units is 84.03° (Figure S13).

The optical and electronic properties of DSiTh were investigated by UV-Vis absorption and fluorescence spectroscopy. The UV-vis absorption spectrum of DSiTh in DCM solution is shown in Figure 2a. The common π–π* absorption peak of terthiophene around 360 nm with the molar extinction coefficient ε of 14760 M^{-1} cm^{-1} can be observed. Different with terthiophene (Figure S14), an unusual weak absorption band between 400 and 425 nm probably can be assigned to intramolecular charge transfer (ICT).

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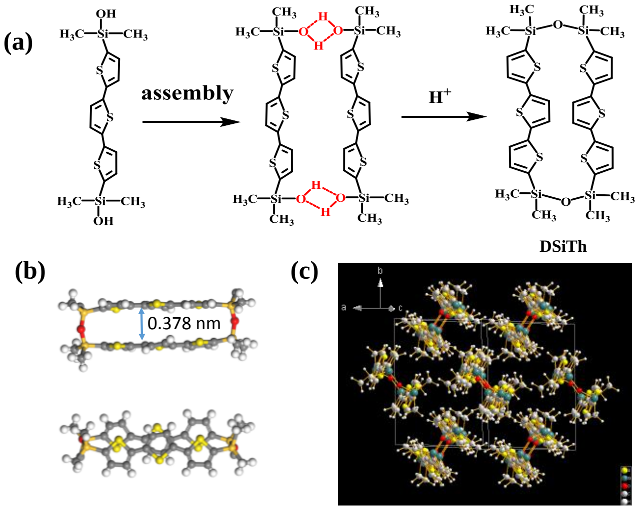

Figure 1. (a) Synthetic routes for DSiTh. (b) The single-crystal structures of DSiTh observed from the top-view and side-view. (c) Herringbone packing of DSiTh in single-crystal.

Similarly, we can also observe the well-resolved fluorescence emission peaks located at 405, 430 and 460 nm, indicating local excited singlet state possessing π–π* transition character. These emission peaks are similar with terthiophene. In addition, a distinguishingly broad and structureless emission around 516 nm, which cannot be found in emission of terthiophene in DCM solution (Figure S14), could be ascribed to an ICT transition.[20] Moreover, the evident ICT emission can also be found in the film states. Comparing with π-π* transition emission, the relative intensity of ICT emission in the film is lower than that in DCM solution, which may be caused by the aggregation-induced quenching in the solid states. In addition, the emission at ca. 516 nm is strongly quenched in the polar acetone, supporting the assignment of it to the ICT emission again. To further confirm the ICT character, the transient photoluminescence (PL) decay characteristics of DSiTh is measured in the solution as shown in Figure 2b. Obviously, the emission at 516 nm shows a slower decay with a longer lifetime of 13.08 ns than that at 405 and 430 nm with lifetimes of 3.05-3.11 ns.

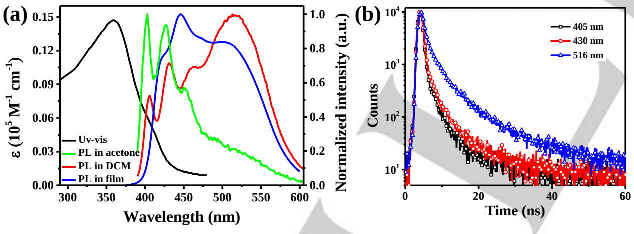

Figure 2. (a) UV-vis absorption measured in DCM and fluorescence spectra of DSiTh measured in film state and in DCM and acetone solution at room temperature. (b) Transient PL decay curves at 405, 430 and 516 nm for DSiTh.

The ICT property has clearly been identified from fluorescence spectra. Therefore, the origin of the emission is further explored. Density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculations using the Gaussian 09.D.01 version[21] were employed to reproduce the S_0 and S_1 geometries, respectively. The S_0 geometry was optimized using the B3LYP functional with 6-31G (d, p) basis set. Then, the geometries on the S_1 state were optimized by TD-DFT at the ωB97XD/6-31G (d, p) level. The electronic cloud distribution of frontier molecular orbitals is almost fully located on terthiophene units for both terthiophene and DSiTh (Figure S15). The HOMOs possess an anti-bonding character and the LUMOs show bonding character for them. DSiTh exhibits a stronger electron-donating ability than terthiophene and the HOMO value increases from -5.28 eV of terthiophene to -5.05 eV of DSiTh. Meanwhile, compared with terthiophene (LUMO: -1.88 eV), a relatively weak electron-accepting ability of DSiTh with a LUMO of -1.69 eV can also be observed. This is consistent with cyclic voltammograms results. The HOMO levels of terthiophene and DSiTh are calculated to be -5.30 and -5.24 eV, respectively (Figure S16). Furthermore, molecular surface electrostatic potential (ESP) analysis shows the much more electron-rich centers offered by sulfur and oxygen atoms for DSiTh comparing to the referenced terthiophene (Figure S17). In some extent, the electrostatic induction effect would increase HOMO of DSiTh. In addition, the through space charge delocalization between two terthiophene planes drags up the LUMO from the condensed partial negative sites. As a result, the molecular polarity of DSiTh can probably be increased. The large gap between HOMO and LUMO orbitals in DSiTh might lead to a CT character with a large dipole moment (Figure S18). The dipole moments for DSiTh are calculated to be 1.43 D (X: 1.19, Y: -0.79, Z: -0.17), which is enhanced dramatically compared with terthiophene (0.66 D (X: 0.00, Y: 0.66, Z: -0.08)). Moreover, the dipole moments in three dimensions change apparently by cyclization from approximate Y direction to X direction. The strong intramolecular through space charge interactions and the large dipole moment along X-axis in DSiTh probably led to a redistribution of electron density during the electron transition process.

However, the electronic cloud distribution of the frontier molecular orbitals is not enough to describe the transition process. Thus, natural transition orbitals (NTOs) were further calculated. [22, 23] The dominant hole-electron contributions of the NTOs are illustrated for the first excited states in terthiophene and DSiTh. As shown in Figure 3a, both the hole and electron of terthiophene mainly localize on the middle thiophene region (45.66 and 45.83%, respectively), exhibiting the character of main local exciton (LE or Frenkel exciton) transition state (Figure S19 and Table S1). Differently, the hole and electron of DSiTh exhibit the distinguishable transition character and distribute on the different thiophene rings in the S_1 state (Figure 3b). The hole mainly occupy in thiophene ring Ⅰ and Ⅳ for 36.78 and 56.27% (Table S1), respectively. While the electron mainly takes up in thiophene ring Ⅱ and Ⅴ for 22.61 and 21.62%, respectively. The results indicate an evident transition from hole to electron between different thiophene rings, which cause the CT emission. The exciton binding energy (E_b), defined as the energy for dissociating excitons to free polarons through an intermediate state of bound polaron, is one of the key parameters that determine the CT properties.[24,25] E_b can be expressed as the Coulomb interaction energy (E_{Coul}) between the positive (D+) and negative centers (A-) of a molecule. The calculated E_{Coul} of terthiophene and DSiTh is 4.96 and 3.41 eV, respectively. The easier separation of electron and hole of DSiTh than that of terthiophene, indicating the distinct CT character in DSiTh.

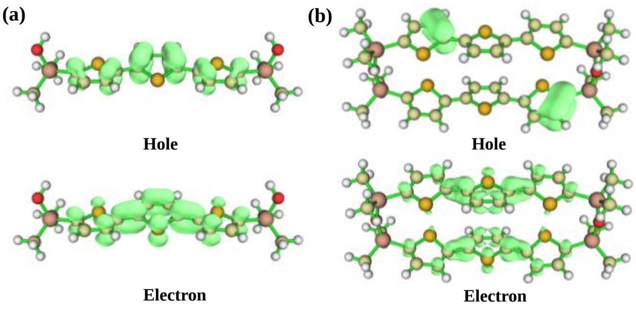

Figure 3. Natural transition orbital (NTO) analyses of the S_1 excited states of (a) terthiophene and (b) DSiTh.

Multiwfn is a multifunctional program for wavefunction analysis, which can calculate and visualize real space function, perform bond order and orbital composition analysis, conduct topology analysis for electron density and so on. [26] We further calculate wave function of electron-hole pairs of S_1 state from the transition density matrix by Multiwfn 3.6. Charge transfer amount via interfragment charge transfer method to calculate sum of square of transition density matrix elements. Stepsize between labels is 2. The number of interpolation steps between grids is 10. The two dimensional site representation of the transition density matrix can clearly indicate the generation of an electron-hole pair or exciton. It also can quantify the constituent of the excited state. Furthermore, the atoms mainly affected by the electron transition and the strongly coherent atom pairs during electron transition can be demonstrated by the brightness of mapping.[27] As shown in Figure 4a, the diagonal part represents the LE component, while the off-diagonal region denotes the CT component. The transition density matrix of terthiophene is mainly localized on the middle thiophene ring in the diagonal direction, suggesting the transition of the S_1 state is the LE character. Oppositely, the initial S_1 excited state of DSiTh exhibits the main CT transition character between donors (atoms No. 7, 12 and 42, 43) and acceptors (atoms No.1, 4, 5 and 35, 36, 39) **(**Figure 4b, c**)**. Specifically, the hole of thiophene ring Ⅰ does not only transfer to the adjacent thiophene ring Ⅱ, but also transfer through bond to opposite electron-rich centers of the thiophene ring Ⅴ. It is reasonable for an effective through-space CT in the short distance between the two terthiophene planes. The change of transition mode from LE of terthiophene to CT of DSiTh indicates that the increased intramolecular delocalized electron interactions and dipole moments could enhance the CT state character. Meanwhile, the hole and electron of S_2 state of DSiTh show mainly localized characters (Figure S20), which is consistent with the highly resolved emission band in PL spectra.

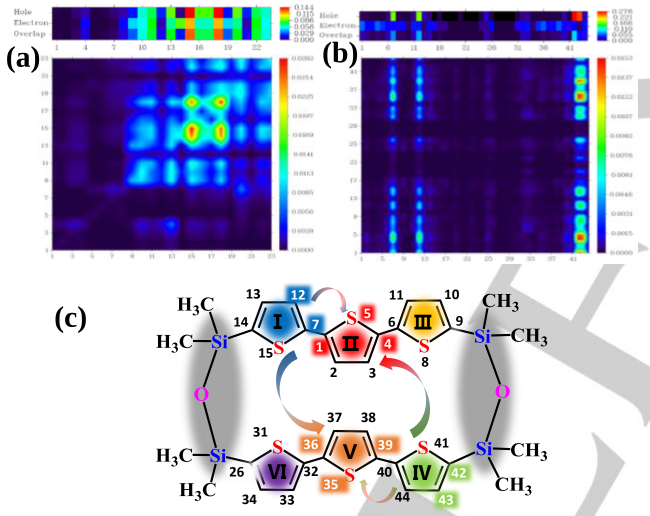

Figure 4. Transition density matrix heat map of terthiophene (a) and DSiTh (b). (c) Diagram of intramolecular charge transfer of DSiTh.

In summary, a kind of rectangular bisterthiophenesiloxanes is efficiently produced by the condensation of terthiophene silanol directed by π-π stacking and hydrogen bonding interactions. Single-crystal X-ray diffraction analysis reveals that DSiTh exhibits a rectangular configuration and herringbone packing mode in the triclinic unit cell with the *P*1 space group. Cyclization-induced ICT can obviously be found in DSiTh. Therefore, cyclization by siloxane linkages is a useful strategy for tuning of the photophysical properties of terthiophene. This strategy enables to produce a strong intramolecular electron redistribution of a highly packed π-conjugated structure, which leads to a distinctive variation of dipole moment and thus results in a through-space ICT property. The present results provide a comprehensive understanding for the nature of photophysics based on a family of the silicon-π heterojunction macrocycles. It will also guide future design of silicon-containing conjugated macrocycles materials for light-emitting.

Experimental Section

Synthesis of DSiTh: [2,2':5',2''-terthiophene]-5,5''-diylbis(dimethylsilanol) (1.19 g, 3 mmol), concentrated sulfuric acid (0.1 mL) and anhydrous toluene (50 mL) were stirred for 24 h at 60 ºC. The solution was extracted by DCM and washed with water. Afterwards, the organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to produce a brown solid of 0.59 g (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.42 (CH_3, s, 12H), 6.84 (ArH, s, 2H), 7.00-7.02 (ArH, d, *J* = 3.6 Hz, 2H), 7.04-7.05 (ArH, d, *J* = 3.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ_C 0.19, 126.4, 126.5, 127.6, 127.7, 129.0, 136.0, 137.7, 138.1, 139.6, 140.0, 142.3, 146.2. MALDI-TOF-MS [M+ Na]: m/z= 779.3. Anal. calcd for $C_{32}H_{36}O_2S_6Si_4$: C 50.75, H 4.79, O 4.23, S 25.40, Si 14.83. Found: C 50.78, H 4.77, S 25.39. Mpt > 350 °C.

CCDC 1907045 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: terthiophene • intramolecular charge transfer • cyclization • rectangular molecules

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Entry for the Table of Contents

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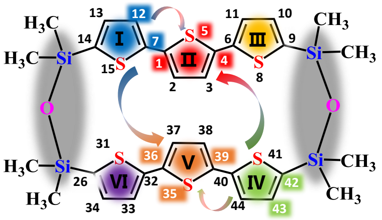
Comparing with terthiophene exhibiting LE characters, cyclization-induced ICT in a rectangular bisterthiophenesiloxane can obviously be observed and confirmed. This behavior indicates that cyclization produces a strong intramolecular electron redistribution of a highly packed π-conjugated structure, which leads to a distinctive variation of dipole moment and thus results in a trough-space ICT properties.



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