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The synthesis, characterization and energy transfer efficiency of a dithienylpyrrole and BODIPY Based Donor-Acceptor System

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A dithienylpyrrole-BODIPY based donor-acceptor system with 1,4-phenylene spacer as a model system for energy transfer was designed and synthesized. Absorption and emission spectra have revealed an efficient resonance energy transfer from dithienylpyrrole as donor to BODIPY as acceptor.

Key Words: Fluorescence Resonance Energy Transfer, Donor-Acceptor System, Dithienylpyrrole, BODIPY.

Introduction

Artificial systems that absorb/emit light have recently attracted much attention.¹ Therefore, new strategies and new molecular systems that exploit fluorescence resonance energy transfer (FRET) between an absorbing molecular fragment (a donor), which is linked to an emitting fragment (an acceptor) and a proper spacer to observe the fluorescence of the latter by irradiating with a single excitation wavelength have been developed.^{1,2} For bio- and nanotechnological applications, the donor and acceptor units are connected via either conjugated linkers, hence the predominant energy transfer mechanism is through-bond (Dexter mechanism)³ or non-conjugated linkers, which give rise to the domination of through-space (Förster mechanism)⁴ mechanisms.

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The energy transfer (ET) efficiency is influenced in turn by the structure of the donor, acceptor, and the linker fragments along with the orientation of the donor-linker-acceptor connectivity.

In connection with a program aimed at the design and engineering of novel photo- and electroactive hybrid materials,⁵ we became interested in the assembly of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY),⁶ a fluorophore, which have recently attracted a lot of interest from different communities due to its outstanding properties (e.g. high stability, sharp fluorescence emission in the visible region etc.), into an electroactive and polymerizable dithienylpyrrole derivative (SNS).⁷ We envisaged that such a unique combination can be amplified to create an efficient and environmentally robust energy transfer cassette. In addition, polarizable character of SNS unit may found interesting applications for electron and/or energy transfer reactions. Interestingly, to the best of our knowledge, any system consisting of a dithienylpyrrole unit as donor and a BODIPY appendage as acceptor has not been reported so far.⁸ Herein, we wish to unveil a preliminary work on a single type of dithienylpyrrole and BODIPY based donor-acceptor system (**4**), which resulted in a good prediction of the absorption/emission spectra and corresponding energy transfer.

Experimental

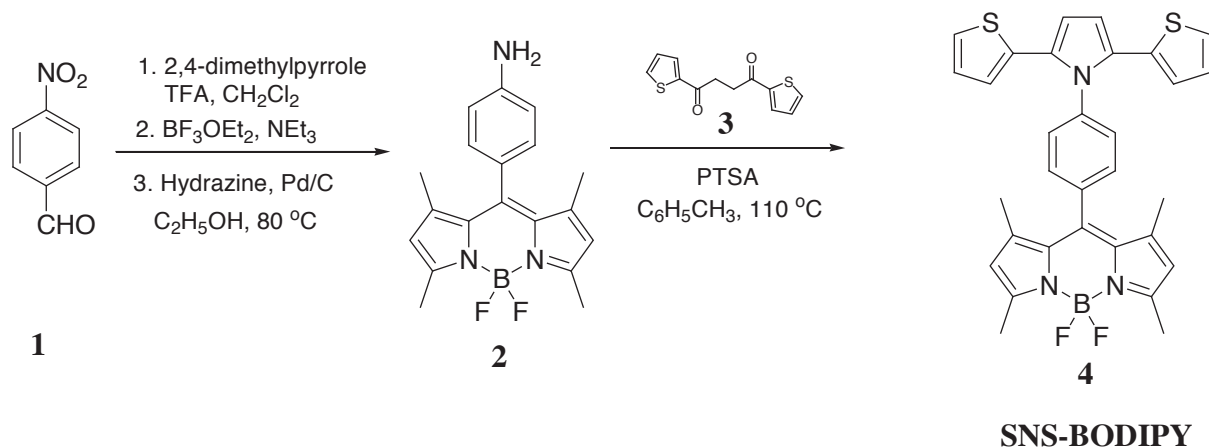
General Methods: All the chemicals were used without further purification unless otherwise indicated. As electrolyte solution, 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) dissolved in freshly distilled (over CaH₂ under N₂ atmosphere) dichloromethane, was used. A platinum disk (0.02 cm²) and a platinum wire were used as working and counter electrodes, respectively, as well as Ag/AgCl in 3 M NaCl(aq) solution as reference. NMR spectra were recorded in CDCl₃. 1,4-Di(thiophen-2-yl)butane-1,4-dione (**3**)⁹ and amino boron-dipyrrin dye (**2**)¹⁰ were synthesized according to literature methods. The FTIR spectra were recorded with a Bruker Vertex 70 spectrophotometer assembled by an attenuated total reflectance.

1-(meso-phenyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene)-2,5-di-2-thienyl-1H-pyrrole (4, SNS-BODIPY): A solution of 125 mg (0.5 mmol) 1,4-di(thiophen-2-yl)butane-1,4-dione, 170 mg (0.5 mmol) amino boron-dipyrrin dye and 5 mg p-toluenesulfonic acid (PTSA) in 50 mL dry toluene were heated under reflux in a Dean-Stark apparatus until all the starting materials were consumed (TLC). The flask was cooled and the solvent was removed under reduced pressure. The residue was filtered through a short pad of silica gel by eluting with CH₂Cl₂ to give analytically pure SNS-BODIPY (235 mg, 0.425 mmol) as a red solid in 85% yield. M.p. 226-227 °C; ¹H NMR (400 MHz, CDCl₃): δ/ppm: 7.32 (d, J= 8.26 Hz, 2H), 7.24 (d, J= 8.10 Hz, 2H), 7.04 (d, J= 5.59 Hz, 2H), 6.72 (dd, J= 3.68 Hz, 2H), 6.51 (d, J= 3.49 Hz, 2H), 6.46 (s, 2H), 5.92 (s, 2H), 2.48 (s, 6H), 1.38 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ/ppm: 155.87, 142.84, 139.44, 135.44, 134.37, 131.25, 130.67, 129.85, 128.99, 126.77, 125.75, 124.69, 121.40, 110.79, 15.33, 14.59. IR (KBr, cm⁻¹): 695, 712, 767, 839, 974, 1081, 1153, 1185, 1262, 1304, 1369, 1407, 1440, 1465, 1508, 1542, 2848, 2922, 3109. Anal. Calcd. For C₃₁H₂₆BF₂N₃S₂: C, 67.27; H, 4.73; N, 7.59; S, 11.59. Found: C, 67.25; H, 4.70; N, 7.50; S, 11.52.

Results and discussion

The synthesis of SNS-BODIPY **4** was carried out via Paal-Knorr reaction of 1,4-di(thiophene-2-yl)butane-1,4-dione (**3**)⁹ with amino boron-dipyrrin dye **2**,¹⁰ which was obtained from *p*-nitrobenzaldehyde (**1**) in 3

steps: condensation of **1** with 2,4-dimethylpyrrole in the presence of catalytic amount of trifluoroacetic acid (TFA) followed by treatment with BF_3OEt_2 and NEt_3 to give nitro BODIPY, which was then converted to corresponding amine **2** with hydrazine monohydrate and Pd/C in ethanol (Scheme 1). The characterization of SNS-BODIPY was based on ^1H , ^{13}C NMR, FT IR, and combustion analysis (see Supporting Information).



Scheme 1. Synthesis of SNS-BODIPY (**4**).

Theoretical calculations (see Supporting Information) have revealed that dithienylpyrrole part (SNS) and BODIPY appendage are coplanar with a nearly perpendicular 1,4-phenylene ring as a spacer (Figure 1).

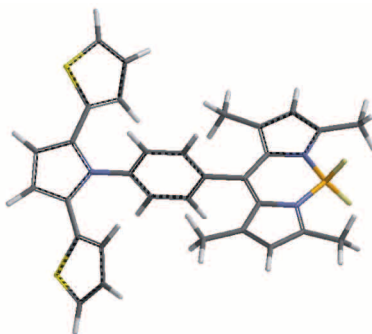


Figure 1. Geometry optimized structure of SNS-BODIPY.

In addition, dithienylpyrrole part (SNS) is mainly contributed to HOMO of the system whereas BODIPY part is contributed to LUMO (Figure 2).

Furthermore, DFT calculations provided information about the mutual direction of the transition dipole moment, which is directed towards the BODIPY part of the system.

We also elaborated the redox behavior of SNS-BODIPY via cyclic voltammetry since reduction and oxidation potentials of BODIPYs are not large, so the compounds are quite easily reduced and also quite easily oxidized.¹¹

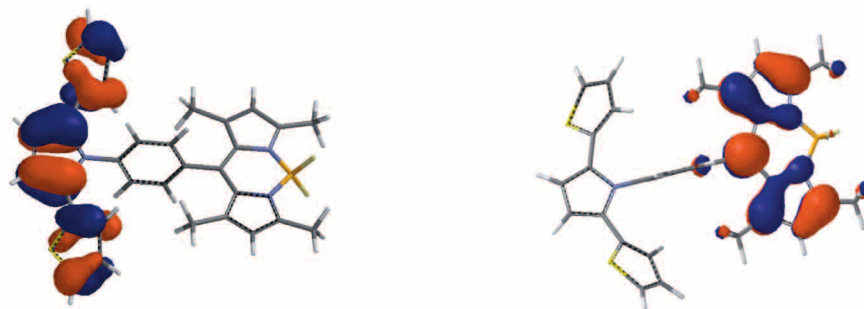


Figure 2. HOMO (left) and LUMO (right) of SNS-BODIPY.

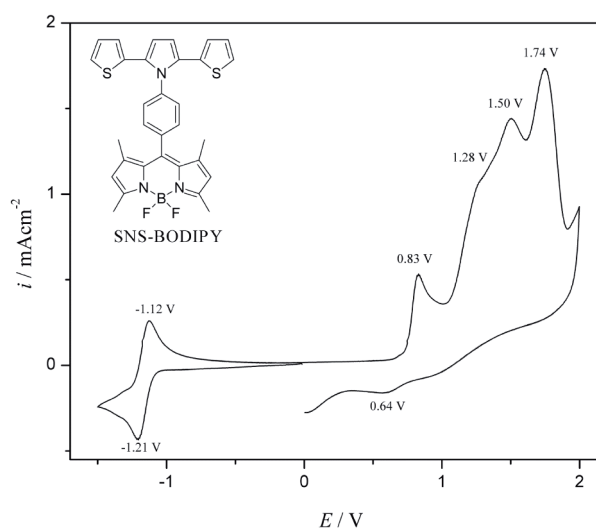


Figure 3. Cyclic voltammogram of SNS-BODIPY in 0.1 M TBAH/CH₂Cl₂ on a platinum electrode vs. Ag/AgCl at a scan rate of 100 mV/s. (TBAH: Tetrabutylammonium hexafluorophosphate).

During the first anodic scan, 4 irreversible oxidation peaks were observed (Figure 3). The first irreversible oxidation peak at 0.83 V was attributed to the radical cation formation from the fluorophore (BODIPY^{•+}), which is consistent with the reported BODIPY derivatives.^{11,12} The oxidation peak at 1.28 V in the voltammogram of SNS-BODIPY was associated with the oxidation of SNS unit to give the radical cation whereas the irreversible oxidation peaks at 1.50 V and 1.74 V were attributed to the oxidation of benzene unit and/or the overoxidation of the compound.¹² We also compared these results with the 2,5-di(-2-thienyl)-pyrrole (SNS) analogue reported by Ferraris and colleagues.¹³ SNS exhibited an oxidation peak at 0.94 V, which was attributed to the oxidation of the dithienylpyrrole.¹⁴ Since BODIPY unit has an electron-withdrawing character, this caused a positive shift on the potential in the case of SNS-BODIPY as expected. On the other hand, during cathodic scan a reversible reduction peak with a half wave potential ($E_{m,1/2}^{red}$) of -1.16 V was observed for stable BODIPY^{•-} formation.^{11a,11b}

The absorption properties of BODIPY were well established in the literature and are characterized by a strong $S_0 \rightarrow S_1$ ($\pi - \pi^*$) transition at around 500 nm.⁶ On the other hand, absorption characteristic of

dithienylpyrrole unit for high energy ($\pi - \pi^*$) transition is at around 300-350 nm.⁵ The absorption spectra of SNS and SNS-BODIPY were depicted in Figure 4. It is noteworthy that the absorption spectrum of SNS-BODIPY was simply the linear sum of SNS, spacer, and BODIPY units. This indicated that there is no electronic interaction between SNS and BODIPY appendage in the ground state.

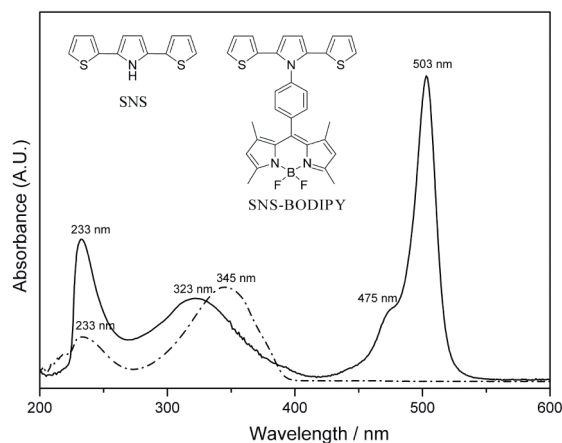


Figure 4. UV-vis absorption spectra of SNS (---) and SNS-BODIPY (—) in CH_2Cl_2 .

Finally, we investigated the energy transfer ability of this unique system on the basis of the fluorescence emission spectra by comparing with the emission spectrum of SNS, which does not include the acceptor part (BODIPY). Although it may not be possible to ascertain how much energy transfer proceeds via through-bond and/or through-space mechanisms when the donor and acceptor units are in close proximity as in the case of SNS-BODIPY system, the overall rate of energy transfer can be measured. The excitation of SNS at the absorption maxima ($\lambda_{max} = 340$ nm) resulted in a broad emission band at around 414 nm (with a shoulder at 395 and a small band at 678 nm), which resulted in a Stokes' shift of 74 nm (Figure 5, left panel).

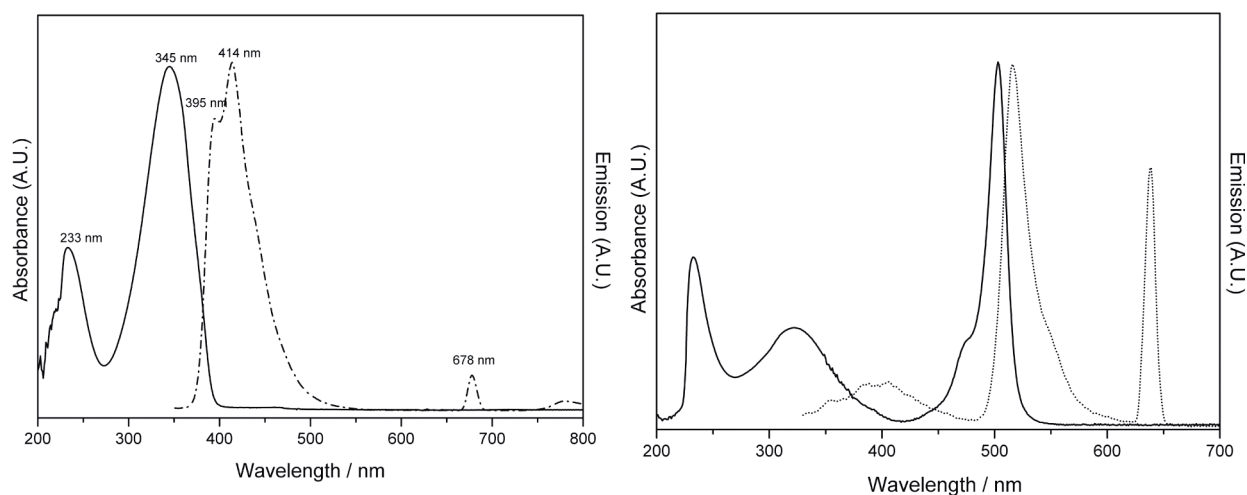


Figure 5. Absorption and fluorescence emission spectra of SNS ($\lambda_{exc} = 340$ nm) (left panel) and SNS-BODIPY ($\lambda_{exc} = 320$ nm) (right panel) in CH_2Cl_2 .

On the other hand, when SNS-BODIPY is excited at the donor's absorption maxima ($\lambda_{\max} = 320$ nm), the emission of donor part was almost quenched and only the emission of the acceptor unit (BODIPY, $\lambda_{\max} = 520$ nm) was predominantly observed. This unambiguously indicated that an efficient and near complete energy transfer process took place from the donor (dithienylpyrrole) to the acceptor (BODIPY) in this system with an artificially enhanced Stokes' shift of 200 nm.

Conclusions

In summary, a preliminary work on a single type of dithienylpyrrole and BODIPY based donor-acceptor system as a model system for energy transfer was described. DFT calculations revealed that dithienylpyrrole part is mainly contributed to HOMO whereas BODIPY part is contributed to LUMO. Furthermore, absorption and emission spectra have proved an efficient resonance energy transfer from dithienylpyrrole unit as donor to BODIPY appendage as acceptor. Considering the ease of synthetic accessibility and perfectly controlled architecture of SNS and BODIPY unit, which allow a fine tuning of intrinsic properties, it is now possible to extend this strategy to the design and engineering of novel photo and electroactive materials, which will find applications in different fields, e.g. sensors, fluorescent switches, light harvesters, and sensitizers for solar cells. Work along these lines is currently underway in our laboratories.

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Supplementary Data

Supplementary data (copies of ^1H NMR, ^{13}C NMR and FTIR spectra, details of DFT calculations) associated with this article is available on the archives of this journal or from the author.

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