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Synthesis and spectroscopic studies of highly fluorescent, solvatochromic diastereomers with differentially stacked bithiophene-substituted quinoxaline rings

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ABSTRACT

Diastereomeric C-shaped molecules containing closely stacked bithiophene-substituted quinoxaline rings were synthesized and characterized by NMR, UV–vis absorption, and fluorescence spectroscopy. The unique geometry of each diastereomer resulted in different degrees of π-overlap between the bithiophene-substituted quinoxaline ring chromophores, modulating their spectroscopic properties. The donor-acceptor nature of this chromophore gave rise to its positive solvatochromism. ^{1}H NMR and UV–vis absorption spectroscopy confirmed the existence of π-π interactions in the ground state between the quinoxaline rings in both molecules but between the bithiophene rings only in the *syn* isomer. They exhibited significant emission maxima bathochromic shifts, a strong, positive solvatochromism, increased band broadening, and larger Stokes shifts when compared to a compound with an unstacked chromophore. Additionally, the *syn* isomer consistently showed $\lambda_{max,em}$ value red-shifts and larger band broadening and Stokes shifts compared to the *anti* isomer due to the greater π-overlap in the *syn* isomer.

1. Introduction

It is well established that organic molecules, especially those with π-conjugation, display significant structure-property relationships.[1–4] A better understanding of these relationships is achieved by studying molecules with unique topologies whose molecular properties can be manipulated by synthetic methods. Aromatic molecules are particularly versatile in this regard because they can be synthetically tuned to produce different properties via direct through-bond conjugation[5–10] or through-space interactions between closely stacked aromatic rings.[11–20] Probing the effects of interchromophore interactions between stacked aromatic rings has been the subject of numerous research studies, owing to their importance in a variety of areas of chemistry, most recently as a key design element in molecular electronics applications.[21–28]

We recently reported the synthesis and characterization of diastereomeric C-shaped molecules containing closely, but differently, stacked thiophene-substituted quinoxaline rings (Fig. 1; *anti*- and *syn*-**BT**)[12] that exhibited interesting spectroscopic properties arising, in part, from their unique molecular architecture. Additionally, the donor-acceptor nature of the thiophene-quinoxaline chromophore resulted in their solvatochromism, significantly expanding their emission color range. The different degrees of π-overlap between the chromophores of the diastereomers, where the quinoxaline rings are overlapped in both *anti*- and *syn*-**BT**, but the thiophene rings are overlapped only in *syn*-**BT**, led to their different electronic structures and, in turn, different spectroscopic properties.[19,24,29,30] These results highlight the importance of having well-defined structures in organic electronics applications, as opposed to having a mixture of different molecular orientations in these complex systems, which can have a significant impact on overall device performance.[24,27,31–34] Moreover, using solvent polarity as a means of controlling chromophore emission properties is an important design element because it is easier to change the solvation environment than the structure of a molecule or polymer.[6,35] In this work, we present the results for the next generation of these diastereomeric C-shaped molecules, which contain differentially stacked bithiophene-substituted quinoxaline rings (Fig. 1; *anti*- and *syn*-**BBT**).

Extending each chromophore by an additional thiophene ring was carried out to increase π-conjugation both through-bond and through-space to observe the subsequent impact on their photophysical properties, particularly on their emission spectra.[16] Model compounds **CQT** and **CQBT** were synthesized and studied as

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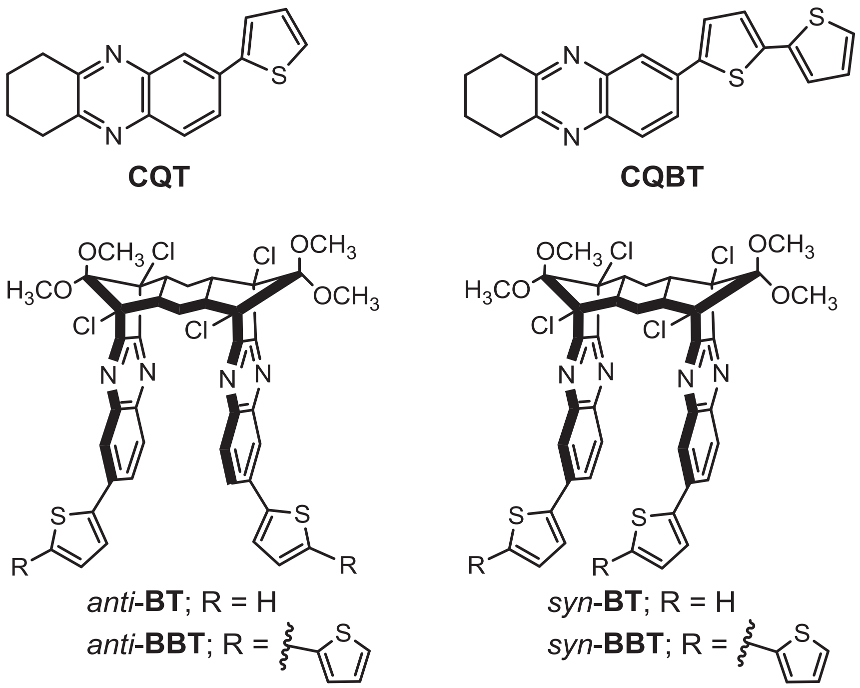


Fig. 1. C-shaped molecules *anti*- and *syn*-**BT** and *anti*- and *syn*-**BBT**; model compounds **CQT** and **CQBT**.

references for understanding the photophysical properties of the lone chromophores in the absence of π-overlap. Herein we present the synthesis and ^{1}H NMR spectroscopy characterization of **CQT**, **CQBT**, *anti*-**BBT**, and *syn*-**BBT** and the results of our analyses of their UV–vis absorption and fluorescence properties as a function of structure and solvent polarity.

2. Results and discussion

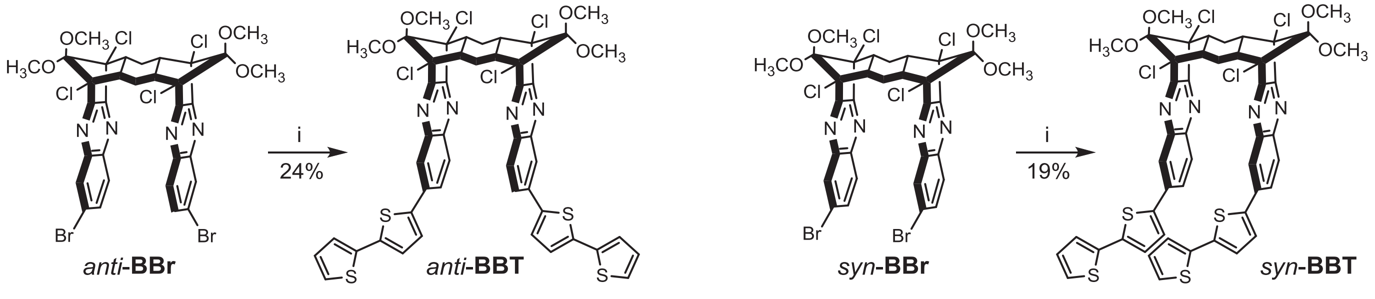
2.1. Synthesis and NMR spectroscopy

Diastereomers *anti*- and *syn*-**BBT** were synthesized from their previously reported bromine-substituted precursors (Scheme 1).[12] A microwave-assisted, Pd-catalyzed Suzuki coupling reaction was used to prepare *anti*- and *syn*-**BBT** from *anti*- and *syn*-**BBr**, respectively, and 2,2′-bithiophene-5-boronic acid. *Anti*- and *syn*-**BBT** were purified by chromatography on silica gel, and their isolated yields were 24% and 19%, respectively.

Model compounds **CQT** and **CQBT** were obtained following similar Pd-catalyzed Suzuki coupling procedures with their bromine-substituted precursor, **CQB** (Scheme 2). **CQB** was synthesized by a Zn-catalyzed condensation reaction under microwave-assisted conditions that was previously reported for the synthesis of *anti*- and *syn*-**BBr**.[12]

1,2-Cyclohexanedione was reacted with 1,2-diamino-4-bromobenzene in the presence of a catalytic amount of $Zn(OAc)_2$ to give **CQB** in a 77% yield after chromatography on silica gel. **CQB** was subjected to a microwave-assisted, Pd-catalyzed Suzuki coupling reaction with 2-thienylboronic acid to give **CQT** in 86% yield and with 2,2′-bithiophene-5-boronic acid to give **CQBT** in 69% yield after purification by chromatographic methods. All compounds reported herein were characterized by ^{1}H and ^{13}C NMR spectroscopy and HRMS analysis, with the data fully corroborating the proposed structures.

The NMR spectroscopy data obtained for *anti*- and *syn*-**BBT** were consistent with our previously reported results for *anti*- and *syn*-**BT**,[12] except for the anticipated differences arising from the new thiophene rings. The *syn* isomers have a σ plane of symmetry that cuts in between the aromatic rings through the methylene carbons of the cyclohexane bridging unit, whereas the *anti* isomers have a C_2 axis of symmetry. As observed for *syn*-**BT**, ^{13}C NMR spectroscopy experiments on *syn*-**BBT** illustrate just how similar, yet still chemically different, the two methylene carbons of the central cyclohexane ring are. At 50 MHz, these two carbons appeared as one unresolved peak at 19.9 ppm, but at 100 MHz, there were clearly two peaks at 19.92 and 19.87 ppm (Figure S-5, Supplementary data). The cyclohexane methylene carbons are furthest from the point of difference in these molecules, where the



Scheme 1. Synthesis of *anti*- and *syn*-**BBT**. i) 2,2′-bithiophene-5-boronic acid, $Pd(PPh_3)_4$, Na_2CO_3, EtOH, toluene, MW 120 °C, 30 min.