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A Triarylamine-Triarylborane Dyad with a Photochromic Dithienylethene Bridge

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ABSTRACT

A molecular triad comprised of a triarylamine donor, a triarylborane acceptor, and a photoisomerizable dithienylethene bridge has been synthesized and explored by cyclic voltammetry, UV-vis and luminescence spectroscopy. The effects of irradiation with UV light and fluoride addition on the electrochemical and optical spectroscopic properties of the donor-bridge-acceptor molecule were investigated. Photoisomerization of the dithienylethene bridge affects the triarylboron reduction potential but not the triarylamine oxidation potential. UV-vis experiments reveal that the association constant for fluoride binding at the triarylborane site is independent of the isomerization state of the

bridge. Irradiation of a THF solution of our donor-bridge-acceptor molecule with UV light followed by F^- addition leads to a different color of the sample than UV irradiation alone or F^- addition alone.

INTRODUCTION

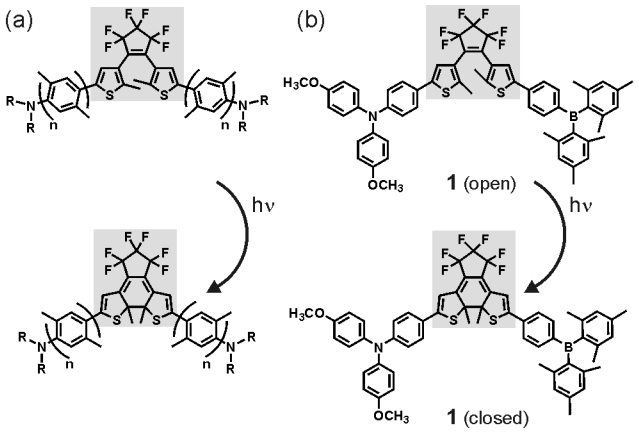
Triarylboranes have received much attention in the context of fluoride sensing in recent years,[1-12] but also their possible application as light-emitting materials or as electron-deficient π-conjugated units of conducting polymers has stimulated much work.[13-22] One branch of research in this multi-faceted area deals with intramolecular charge transfer between electron-rich triarylamine groups and electron-poor triarylborane moieties.[23-29] In systems with π-conjugated bridges amine-to-borane charge transfer commonly manifests as an absorption band in the electronic (UV-vis) spectrum.[1, 24-26, 28-34] There have been recent studies of triarylborane-containing dithienylethenes,[35-36] but we are unaware of prior investigations of triarylamine-triarylborane donor-acceptor systems with photochromic bridges.

In this work, we aimed to explore to what extent the isomerization state of a photochromic bridge affects intramolecular charge transfer between amine and borane groups. The issue of controlling π-conjugation pathways for electron transfer in photochromic systems is of long-standing interest.[37-44] However, it is not trivial to investigate photoinduced electron transfer in photochromic donor-bridge-acceptor molecules because the light energy which is used to trigger electron transfer in many cases also induces photoisomerization.[38, 40, 42, 44] Recent studies on photoswitchable mixed valence systems demonstrated that the extent of charge delocalization between two redox-active centers can be controlled by light when the two redox moieties are connected covalently via a photoisomerizable unit. [45-52] In our own work we had explored the monocationic forms of the dithienylethene-bridged bis(triarylamine) molecules shown on the left of Scheme 1 (n = 0, 1),[53] and we found that by using UV and visible light it is possible to switch between class I, class II, and class III mixed valence behavior,[54] i. e., from complete charge localization to either partial or full charge delocalization. In the present study we synthesized and

investigated the chemically related triarylamine-dithienylethene-triarylborane molecule shown in the right half of Scheme 1 (molecule **1**), and we explored the effects of photoisomerization and fluoride addition on the electrochemical, optical absorption, and luminescence properties of this compound.

The design principle of the investigated molecule is simple. The triarylamine with two *p*-anisyl substituents is a popular electron donor because of its comparatively high chemical stability and relatively low oxidation potential,[55-56] dimesitylborane is a suitable acceptor because the electron-deficient boron atom is sterically protected from its environment and therefore relatively stable, yet at the same time a reasonably good electron acceptor.[1] The photoisomerization reactions of dithienylethenes are highly reversible in many systems hence this particular photochromic unit appeared as an attractive choice,[57-63] also in light of a recent study of fluoride and mercuric(II) cation sensing by a photochromic organoboron compound.[36]

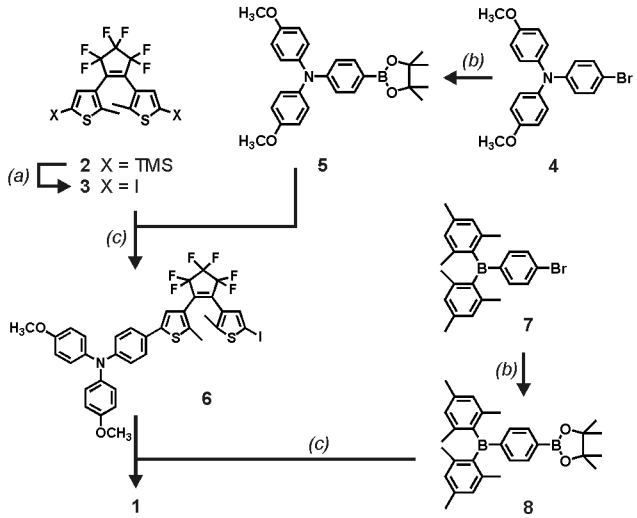
Scheme 1. (a) Open and photocyclized form of two dithienylethene-bridged bis(triarylamines) (n = 0, 1; R = $C_6H_4OCH_3$) the one-electron oxidized forms of which were previously investigated in the context of photoswitchable organic mixed valence.[45, 53] (b) Open and closed form of the donor-bridge-acceptor molecule of central interest in this study.



RESULTS AND DISCUSSION

Synthesis. The photochromic backbone of donor-bridge-acceptor molecule **1** is built into the overall system using dithienylperfluorocyclopentene building block **2** which has been previously described in the literature (Scheme 2).[37, 53] Trimethylsilyl-halogen exchange on molecule **2** yields diiodo-compound **3** which can subsequently be used for Suzuki-type C-C couplings with suitable reagents. The first coupling partner was molecule **5**, which is a boronic acid pinacol ester of the triarylamine unit, prepared in one step from di-*p*-anisyl-*p*-bromophenylamine (**4**).[64] The resulting coupling product is molecule **6**. A boronic acid pinacol ester of the triarylborane unit (**8**), prepared from previously known (4-bromophenyl)dimesitylborane (**7**),[65-66] was subsequently coupled to molecule **6**, yielding the target molecule **1**. Detailed synthetic protocols and product characterization data of all new compounds are given in the Experimental Section. In addition, selected NMR and ESI-TOF-HRMS spectra are shown in the Supporting Information.

Scheme 2. Synthetic steps leading to the donor-bridge-acceptor molecule **1**. (a) ICl, CH_2Cl_2, -5°C; (b) bis(pinacolato)diboron, $Pd(PPh_3)Cl_2$, NaOAc, PEG600, 90°C; (c) $Pd(PPh_3)_4$, THF, Na_2CO_3 (aq), 80°C.



Electrochemistry. Figure 1 shows cyclic voltammograms of the donor-bridge-acceptor molecule **1**. We have found that triarylamine oxidation is best monitored in CH_2Cl_2 or CH_3CN, while triarylborane reduction is much more cleanly detectable in dry THF solution. The upper half of Figure 1 shows oxidative voltage sweeps recorded from a $5 \cdot 10^{-4}$ M solution of molecule **1** in dry and deoxygenated CH_2Cl_2 in presence of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) while the lower half of Figure 1 shows reductive voltage sweeps obtained from a 10^{-3} M solution of molecule **1** in dry and deoxygenated THF in presence of 0.1 M $TBAPF_6$ electrolyte. Trace amounts of decamethylferrocene were added for internal voltage calibration, and this causes the reversible redox waves at -0.51 V vs. Fc^+/Fc in all four voltammograms (dashed vertical line).

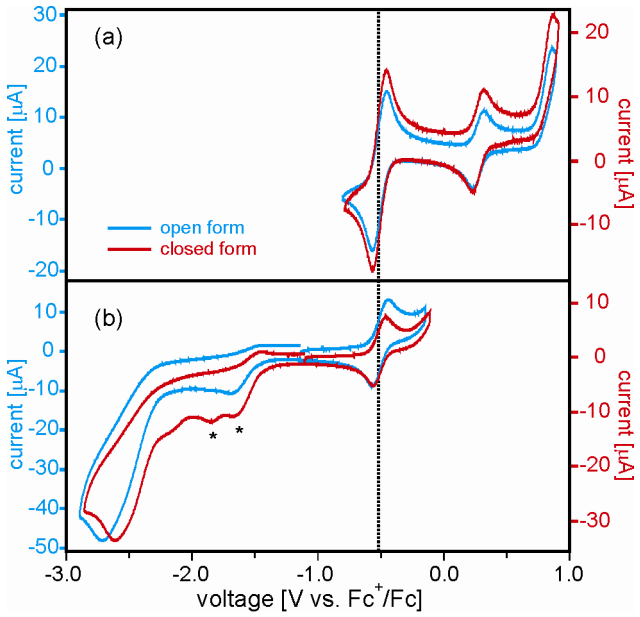


Figure 1. Cyclic voltammograms of the open (blue traces) and closed (red traces) forms of **1**. (a) Oxidative sweeps with 100 mV/s in dry CH_2Cl_2; (b) reductive sweeps with 100 mV/s in dry THF. 0.1 M $TBAPF_6$ was used as an electrolyte in both cases; the waves at -0.51 V vs. Fc^+/Fc are due to the decamethylferrocene internal reference. The waves marked by the asterisks are assumed to be due to electrochemical decomposition products.[67]

The blue traces in Figure 1 are voltammograms obtained from the open form of molecule **1**, whereas the red traces are voltammograms of the photocyclized (closed) form. For photoisomerization the samples were irradiated with a hand-held 8 W UV lamp. According to ^{1}H NMR experiments this leads to a photostationary state comprised of 15% open and 85% closed isomer.[68] The voltammograms in the upper half of Figure 1 are virtually identical to each other. Triarylamine oxidation occurs in a reversible fashion at 0.27 V vs. Fc^+/Fc in both the open and closed isomer of **1**, in agreement with previously reported oxidation potentials for this particular redox-active unit.[69-70] Thiophene oxidations in dithienylcyclopentenes are known to occur at significantly higher potentials and are outside the potential range considered here,[44, 53, 71-72] electrocyclization is not observed.[71-74] The reductive sweeps in the lower half of Figure 1 are significantly different from each other. While the weak currents between -1.5 and -2.0 V vs. Fc^+/Fc are probably caused by impurities, the strong irreversible waves below -2.5 V vs. Fc^+/Fc are attributed to triarylborane reduction, in agreement with literature values for comparable systems.[75-77] It is obvious from Figure 1 that triarylborane reduction occurs at somewhat less negative potentials for the closed form of **1** than for its open isomer: The peak currents are at -2.6 V vs. Fc^+/Fc for the closed form and at -2.7 V vs. Fc^+/Fc for the open isomer. Addition of TBAF (as a fluoride source) has led to very low quality voltammograms which do not permit any meaningful conclusions except that triarylborane reduction cannot be detected any more (data not shown).

Reverse photoisomerization from the closed to the open form is possible when using a 610-nm cut-off filter in front of an incandescent lamp as an irradiation source. However, this process is extremely slow for solutions with mM concentrations (> hours), presumably due to the relatively low photon flux and the low quantum yield for closed-to-open isomerization, which is not an uncommon phenomenon for dithienylethenes.[41,42] What is more, the sample suffers from photodegradation, and therefore it has not been possible to demonstrate that the photoinduced changes in the voltammogram of Figure 1b are indeed reversible.

UV-vis spectroscopy. The blue trace in Figure 2a is the optical absorption spectrum of a $3.2 \cdot 10^{-5}$ M solution of the open form of molecule **1** in THF. This sample is essentially colorless because there are no absorptions in the visible spectral range. Upon irradiation with UV light the sample turns blue because of increasing absorptions at 643 nm, 452 nm, and 398 nm (dotted black traces and upward arrows in Figure 2a); at the same time the absorbance at 352 nm is decreasing. Ultimately, a photostationary state (with 85% closed and 15% open form, see above) is reached (red trace). Figure 2b illustrates the effect of fluoride addition on the optical absorption spectrum of the photocyclized solution; the red trace in Figure 2b is the same spectrum as the red trace in Figure 2a. When adding tetrabutylammonium fluoride (TBAF), the maximum of the longest-wavelength absorption shifts from 643 nm to 620 nm resulting in a color change from blue to blue-green. In addition, there are spectral changes between 500 nm and 250 nm with clean isosbestic points at 514 nm, 465 nm, and 373 nm. After 1 equivalent of F^- has been added, no further spectral changes are observed and the green trace in Figure 2b is obtained.

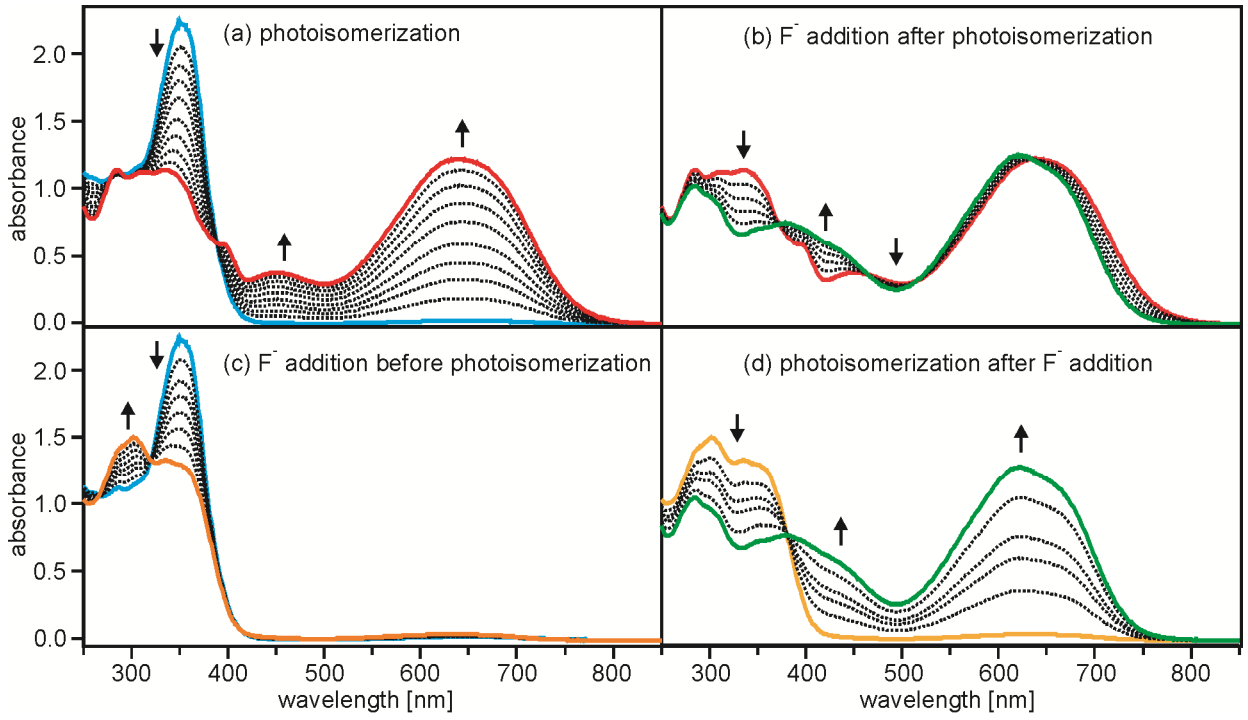


Figure 2. UV-vis spectra of **1** in THF. (a) Photoisomerization of the open form (blue trace) to the closed form (red trace) upon UV irradiation; (b) effect of fluoride addition to the closed form. (c) Titration of

the open form (blue trace) with TBAF; (d) Photoisomerization of the open fluoride adduct (orange trace) to the closed fluoride adduct (green trace). Note that the green traces in (b) and (d) are identical.

When reversing the sequence of light irradiation and F^- addition, one ultimately arrives at exactly the same spectrum, a fact which is illustrated by the lower half of Figure 2: The blue trace in Figure 2c is the same spectrum as the blue trace in Figure 2a, i. e., the spectral signature of the open form of molecule **1** in THF. When adding F^- to this solution the absorbance at 353 nm decreases whereas a band at 302 nm gains intensity. After addition of 1 equivalent of TBAF the spectrum represented by the orange trace in Figure 2c is obtained. The spectrum of this sample is shown again in Figure 2d (orange trace), and when irradiated subsequently with UV light it undergoes the spectral changes shown in Figure 2d. The green trace in Figure 2d is the spectrum of the final photostationary state and corresponds precisely to the green spectrum of Figure 2b, i. e., the solution which has been irradiated prior to fluoride addition. We note that in Figure 2c the band of the closed form at 642 nm is already detectable because part of the sample unavoidably photoisomerizes in the absorption spectrometer.

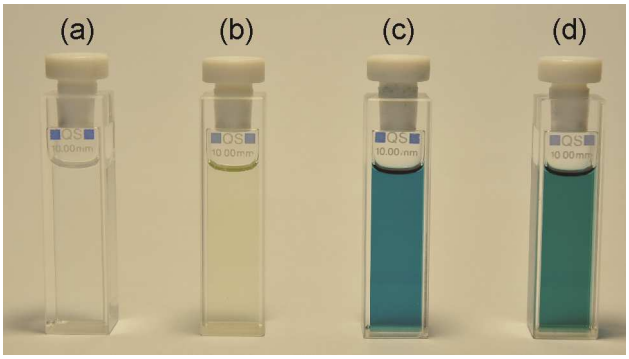


Figure 3. Photograph showing (a) the open form of **1**, (b) the open fluoride adduct of **1**, (c) the closed form of **1**, (d) the closed fluoride adduct of **1**.

The photograph in Figure 3 illustrates the color changes which are associated with UV irradiation and fluoride addition to a THF solution of molecule **1**: Adding F^- to the open isomer has essentially no

influence on the color of the solution, the light yellowish appearance of the solution (Figure 3b) is mostly due to TBAF itself. Photoisomerization alone will produce a blue solution (Figure 3c), photoisomerization combined with fluoride addition leads to a blue-green color (Figure 3d).

From the F^- titrations in Figure 2b and 2c it is possible to determine fluoride binding constants for the closed and open forms of molecule **1**. Figure 4a plots the absorbance of a $3.2 \cdot 10^{-5}$ M THF solution of the *open* isomer at 353 nm as a function of the total (free and bound) F^- concentration. An analogous fluoride titration curve monitoring the absorbance at 335 nm of an equally dilute THF solution of the *closed* form of **1** is shown in Figure 4b. The solid lines in Figure 4 are the results of least-squares fits to the experimental data with equation 1 which is appropriate for determination of binding constants (K_s) of 1:1 adducts.[12, 78]

$$A = A_0 + [(A_{lim} - A_0)/2 \cdot c_0] \cdot [c_0 + c_F + K_s^{-1} - [(c_0 + c_F + K_s)^2 - 4 \cdot c_0 \cdot c_F]^{1/2}] \qquad \text{eq. 1}$$

In equation 1, A_0 is the absorbance of the sample at a selected wavelength in absence of any titrant, A is the absorbance at the same wavelength in presence of titrant, and A_{lim} is the limiting absorbance value obtained once the solution has been saturated with titrant. c_0 is the concentration of molecule **1** ($3.2 \cdot 10^{-5}$ M), c_F is the concentration of added F^- (see x-axes in Figure 4). Fits to the two data sets in Figure 4 yield K_s values of $(1.6 \pm 0.8) \cdot 10^7$ M^{-1} (Figure 4a) and $(2.3 \pm 1.0) \cdot 10^7$ M^{-1} (Figure 4b). Thus, the fluoride binding constants of the open and closed forms of molecule **1** are identical within experimental accuracy. The magnitude of our K_s values (10^7 M^{-1}) is similar to that reported previously for comparable triarylborane systems.[1] We note that fluoride binding constants may be strongly susceptible to trace water impurities in the solvent.

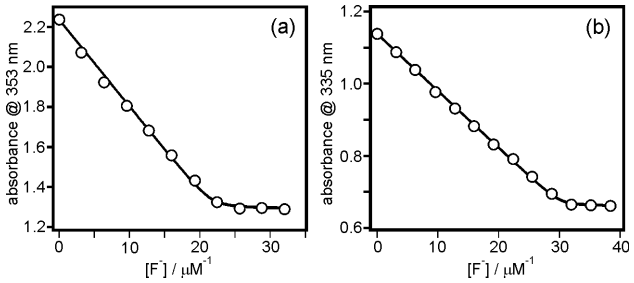


Figure 4. Absorbance changes at (a) 353 nm and (b) 335 nm in the course of TBAF addition to $3.2 \cdot 10^{-5}$ M solutions of the open (a) and closed (b) form of **1** in THF. The solid lines are least-squares fits to the experimental data with equation 1.[12, 78]

^{19}F and ^{11}B NMR spectroscopy. The ^{19}F NMR spectrum of the closed form of molecule **1** in $CHCl_3$ exhibits resonances at -110 ppm and -131 ppm due to the fluorine atoms on the perfluorocyclopentene backbone (see Supporting Information). Upon addition of TBAF an additional resonance shows up at -172 ppm which is typical for F^- bound to a triarylamine group.[1, 29] In the ^{11}B NMR spectrum of the same sample there is a broad resonance at -74 ppm which is typical for triarylborane (see Supporting Information).[1, 29] Upon fluoride addition this resonance shifts to 4 ppm, in agreement with previously reported chemical shifts for fluorinated dimesitylboryl groups.[1, 29] No attempts to determine fluoride binding constants from NMR experiments were made; in light of the high K_s values found above this did not appear to be meaningful.

Discussion of charge transfer properties. We now turn our attention back to the UV-vis data in Figure 2. The fluoride titration experiment in Figure 2c suggests that the absorbance at 353 nm of the open isomer is caused at least in part by an electronic transition involving the boron center. Indeed, in aromatic nitrogen-boron systems there are frequently N → B charge transfer transitions in this spectral range.[1, 25-26, 28] The difference in triarylamine oxidation and triarylborane reduction potentials found above amounts to ~3 V. On this basis one might expect the N → B charge transfer transition at ~24000 cm^{-1} or ~410 nm, but this represents obviously a crude estimate at best. Nevertheless it appears reasonable to conclude that the absorption band at 353 nm (open isomer) has significant N → B charge transfer character.[79]

As outlined in the introduction, we anticipated that photocyclization of the dithienylethene bridge would affect N → B charge transfer. However, it is not straightforward to identify the respective

electronic transition in the closed isomer. One would expect N → B charge transfer to be suppressed when F^- is added, and consequently we are searching for spectral regions in the UV-vis data of Figure 2b in which the absorbance is decreasing upon fluoride addition. This turns out to be the case between 514 nm and 466 nm, as well as between 372 nm and 273 nm; the spectral changes beyond 514 nm are not considered here because the longest-wavelength absorption is quite clearly caused by dithienylperfluorocyclopentene-localized π-π* transitions that may be perturbed by F^- complexation.[40, 44, 57, 61-62, 71-72] From the electrochemical data in Figure 1 we learn that triarylborane reduction is ~0.1 V easier in the closed form of molecule **1** than in its open isomer. One might thus expect a red-shift of the N → B charge transfer transition by ~800 cm^{-1} following photoisomerization, but this cannot be reconciled with the UV-vis data in Figure 2b. The strongly F^- sensitive bands between 372 nm and 273 nm are at higher energy than the N → B transition in the open form, while the weakly F^- sensitive absorbance between 514 nm and 466 nm seems too weak and too red-shifted in order to be assigned to the N → B transition of the closed isomer. Given the more extensive π-conjugation of the photocyclized bridge we would have expected the oscillator strength of the N → B transition to be even higher in the closed form than in the open isomer. Thus, contrary to what we originally hoped, it appears that in-depth computational studies are necessary to gain insight into N → B charge transfer in the two isomers of molecule **1**, but this is beyond the scope of our experimental investigations.

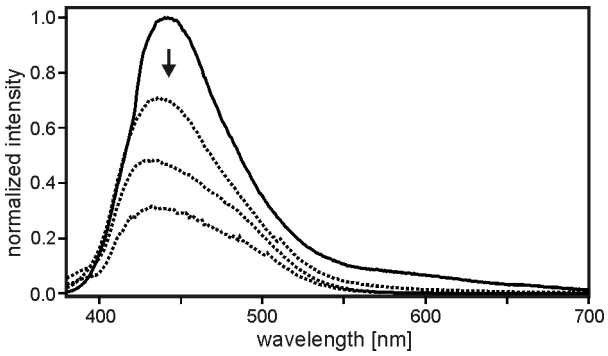


Figure 5. Luminescence of molecule **1** in THF solution measured after different time intervals following irradiation at 355 nm in the fluorimeter. The initial spectrum (solid trace) is from a solution containing

mostly the open isomer. Subsequent spectra (dotted traces) contain an increasing proportion of non-emissive closed isomer. Intensities are normalized arbitrarily to the first spectrum.

Luminescence spectroscopy. The open form of molecule **1** is emissive when irradiated with UV light. Figure 5 shows a series of luminescence spectra which were obtained from a THF solution of the open form of **1**. With increasing irradiation time the emission intensity decreases, which is a manifestation of photocyclization. The closed form of **1** is non-emissive because of energetically low-lying π-π* transitions on the dithienylperfluorocyclopentene bridge (Figure 2a).[41] At long irradiation times a photostationary state is reached (see above), and the remaining percentage (~15%) of open isomer accounts for the residual emission intensity. Compared to the initial luminescence intensity detected from a freshly prepared solution of the open form of **1** the emission intensity decreases only by a factor of ~3, but it should be kept in mind that our samples are highly sensitive to UV light and photoisomerize to a significant extent already in the course of recording the very first luminescence spectrum. This difficulty precludes verification of the F^- binding constants from above by complementary luminescence titration experiments. Samples to which F^- has been added are non-emissive, and it appears plausible to assign the luminescence of the open (and un-fluorinated) form of molecule **1** to a charge transfer transition involving the triarylamine and triarylborane moieties.

SUMMARY AND CONCLUSIONS

The N → B charge transfer transition can easily identified in the open form of molecule **1**, but for its closed isomer this seems impossible with experimental means alone. Thus we conclude that photoisomerizable organic mixed valence systems such as those shown on the left of Scheme 1 [45, 53] represent more attractive models for investigating charge transfer across photoswitchable bridges than our triarylamine-triarylborane donor-acceptor system. In molecule **1** there is a small influence of

photoisomerization on the triarylborane reduction potential but virtually none on the triarylamine oxidation. We anticipate that this influence would be significantly greater in a molecule in which the N and B atoms of the respective redox-active groups would be attached directly to the two different thiophene units of the photoisomerizable bridge. However, in our hands such a molecule turned out to be synthetically much less easily accessible than molecule **1**, despite a prior report of an analogous compound with an organoboron unit attached directly to a thiophene of a dithienylethene bridge.[36]

An interesting finding from our study is that addition of F^- to a solution of molecule **1** induces no significant color change, while photoisomerization alone produces a blue solution. Only the combined input of UV light and F^- ions leads to a blue-green color.

EXPERIMENTAL SECTION

Dithienylperfluorocyclopentene building block **2** was synthesized following previously published protocols.[37, 53] Briefly, 2-methylthiophene was brominated,[80] and the resulting 3,5-dibromo-2-methylthiophene molecule was reacted with *n*-butyllithium and trimethylsilane to produce 3-bromo-2-methyl-5-trimethylsilylthiophene.[81] Subsequent treatment with *n*-butyllithium and perfluorocyclopentene yielded molecule **2** (4.93g/9.6 mmol, 17% yield; starting from 13.9 g/56.1 mmol 3-bromo-2-methyl-5-trimethylsilylthiophene and 4.51 ml/33.6 mmol perfluorocyclopentene).[37] ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.37 (s, 18 H), 2.49 (s, 6 H), 7.11 (s, 2 H). Deprotection of the trimethylsilyl-groups occurred with iodine monochloride following standard protocols,[82-83] and this gave molecule **3** in 72% yield (650 mg/1.05 mmol, starting from 750 mg/1.46 mmol of compound **2**).[53, 82, 84] ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.91 (s, 6 H), 7.20 (s, 2 H).

For the synthesis of molecule **4**, 4-bromoaniline (5.00 g, 29.2 mmol) and 4-iodoanisole (14.4 g, 61.3 mmol) were reacted in toluene (30 mL) in presence of CuI (0.28 g, 1.46 mmol), KOH (12.8 g, 228 mmol), and 1,10-phenanthroline (0.26 g, 1.46 mmol). After heating to 90°C for 3 days, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (200 mL) and washed four times with 150

mL portions of water. The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent evaporated subsequently. Purification of the raw product occurred by column chromatography on silica gel using an eluent mixture comprised of CH_2Cl_2 and pentane (1:1). This procedure afforded molecule **4** in 57% yield (6.35 g, 16.6 mmol).[64] ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.82 (s, 6 H), 6.83 (m, 2 H), 6.85 (m, 4 H), 7.06 (m, 4 H), 7.26 (m, 2 H).

Compound **4** (1.77 g, 4.60 mmol) was dissolved in PEG600 (23 ml) along with bis(pinacolato)diboron (1.75 g, 6.90 mmol), bis(triphenylphosphine)palladium(II) chloride (0.16 g, 0.23 mmol) and sodium acetate (1.77 g, 18.4 mmol). After stirring the reaction mixture at 85°C overnight water was added (50 ml), and the cooled solution was extracted with diethyl ether (50 ml). The resulting organic phase was washed 3 times with 75 ml portions of water, and the aqueous phases were re-extracted subsequently with diethyl ether (3 × 100 ml). The combined ether phases were dried over anhydrous $MgSO_4$, and the solvent was removed on a rotary evaporator. The raw product was purified by column chromatography on silica gel using a 1:1 (v:v) mixture of CH_2Cl_2 and pentane as an eluent. Subsequent washing of the dry product with pentane gave pure compound **5** in 32% yield (0.63 g, 1.46 mmol).[66] . ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.34 (s, 12 H), 3.82 (s, 6 H), 6.85 (d, J = 8.9 Hz, 4 H), 6.89 (d, J = 8.6 Hz, 2 H), 7.09 (d, J = 8.9 Hz, 4 H), 7.62 (d, J = 8.6 Hz, 2 H).

Dithienylethene compound **3** (893 mg, 1.44 mmol) and triarylamine unit **5** (388 mg, 0.90 mmol) were dissolved in a mixture of THF (6 ml) and 1 M aqueous sodium carbonate solution (10 ml). After bubbling with N_2 during 20 minutes tetrakis(triphenylphosphine)palladium(0) (160 mg, 0.14 mmol) was added, and the reaction mixture was heated to 80°C under N_2 overnight. Diethyl ether (25 ml) was added after cooling to room temperature, and the reaction mixture was washed with water (3 × 25 ml). The organic phase was dried over anhydrous $MgSO_4$ prior to evaporating the solvent under reduced pressure. Purification of the raw product occurred using column chromatography on silica gel using a 9:1 (v:v) mixture of pentane and diethyl ether. Molecule **6** was obtained in 32% yield (370 mg, 0.46 mmol) as an amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.90 (s, 3 H), 1.92 (s, 3 H), 3.80 (s, 6 H), 6.84 (d, J = 9.0 Hz, 3 H), 6.90 (d, J = 8.7 Hz, 2 H), 7.06 (d, J = 9.0 Hz, 4 H), 7.09 (s, 1 H), 7.22 (s, 1 H),

7.31 (d, J = 8.7 Hz, 2 H). ^{13}C-NMR: (300 MHz, $CDCl_3$): δ (ppm) = 14.3, 14.5, 29.7, 55.5, 114.8, 119.5, 120.3, 120.6, 126.8, 128.5, 128.7, 133.6, 133.9, 136.2, 140.5, 148.7, 156.1. HRMS (ESI-TOF) m/z: [M^+] Calcd for $C_{35}H_{26}NO_2F_6IS_2$= 797.0354; Found 797.0347.

For the synthesis of triarylborane unit **7** *p*-dibromobenzene (1.75 g, 7.57 mmol) was dissolved in dry diethyl ether (20 ml). After cooling to -78°C 1.6 M solution of *n*-butyllithium in hexane was added dropwise (3.4 ml, 6.6 mmol) and the reaction mixture was stirred for 3 hours at this temperature. Then, trimesitylboron fluoride was added slowly (1.56 g, 5.5 mmol). After stirring the mixture at room temperature overnight it was washed with aqueous NH_4Cl solution (100 ml) and water (100 ml). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed on a rotary evaporator. After recrystallization from pentane molecule **7** was obtained in 67% yield (2.05 g, 5.1 mmol).[65] ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.00 (s, 12 H), 2.31 (s, 6 H), 6.83 (s, 4 H), 7.37 (d, J = 8.2 Hz, 2 H), 7.49 (d, J = 8.2 Hz, 2 H).

Molecule **7** (1.35 g, 3.3 mmol) was dissolved in PEG600 (60 ml) along with bis(pinacolato)diboron (1.26 g, 4.95 mmol), bis(triphenylphosphine)palladium(II) chloride (0.20 g, 0.28 mmol), and sodium acetate (10.8 g, 130 mmol). After heating to 90°C for 4 hours the reaction mixture was cooled to room temperature, diluted with water (300 ml) and extracted with diethyl ether (3 × 200 ml). The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was removed subsequently on a rotary evaporator. Column chromatography on silica gel using a 9:1 (v:v) mixture of pentane and diethyl ether afforded pure product **8** in 90% yield (1.36 g, 3.0 mmol).[66] ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.36 (s, 12 H), 1.98 (s, 12 H), 2.31 (s, 6 H), 6.82 (s, 4 H), 7.50 (d, J = 8.0 Hz, 2 H), 7.77 (d, J = 8.0 Hz, 2 H).

Compound **8** (259 mg, 0.57 mmol) and dithienylethene unit **6** (370 mg, 0.46 mmol) were dissolved together in THF (4 ml) and 1 M aqueous Na_2CO_3 solution (3 ml). Prior to adding tetrakis(triphenylphosphine)palladium(0) (120 mg, 0.10 mmol) the reaction mixture was bubbled with N_2 during 20 minutes. After heating to 80°C under N_2 overnight the mixture was cooled to room temperature and diethyl ether (50 ml) was added. Then the mixture was washed with water (3 × 50 ml), and the combined aqueous phases were re-extracted with diethyl ether (2 × 50 ml). The combined

organic phases were dried over anhydrous $MgSO_4$ before evaporating the solvent under reduced pressure. Column chromatography on silica gel using a 9:1 (v:v) mixture of pentane and diethyl ether afforded the open form of molecule **1** in 57% yield (262 mg, 0.26 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.96 (s, 3 H), 1.97 (s, 3 H), 2.00 (s, 12 H), 2.34 (s, 6 H), 3.82 (s, 6 H), 6.81-6.91 (m, 8 H), 6.93 (d, *J* = 8.7 Hz, 2 H), 7.09 (d, *J* = 8.9 Hz, 2 H), 7.16 (s, 1 H), 7.35 (d, *J* = 8.7 Hz, 2 H), 7.41 (s, 1 H), 7.54 (s, 4 H). ^{11}B NMR (160 MHz, $CDCl_3$): δ (ppm) = 73.9 (s, 1 B). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) = -110.0 (m, 4 F), -131.9 (m, 2 F). HRMS (ESI-TOF-MS) m/z: [M^+] Calcd for $C_{59}H_{52}NO_2BF_6S_2$ = 995.3437; Found 995.3451). Anal. calc. for $C_{59}H_{52}NO_2BF_6S_2 \cdot 0.2\ C_4H_8O$ (%): C: 71.07, H: 5.37, N: 1.38, S: 6.32; found: C: 71.27, H: 5.67, N: 1.21, S: 6.58. Closed isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.03 (s, 12 H), 2.15 (s, 6 H), 2.33 (s, 6 H), 3.83 (s, 6 H), 6.74-6.93 (m, 12 H), 7.11 (d, *J* = 8.7 Hz, 4 H), 7.36 (d, *J* = 8.9 Hz, 2 H), 7.50-7.58 (m, 4 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 14.2, 15.8, 19.8, 20.4, 21.1, 23.5, 24.9, 55.5, 60.4, 115.0, 118.2, 122.8, 127.4, 127.7, 128.1, 128.3, 129.1, 129.3, 136.4, 139.0, 140.8, 141.5, 149.9, 156.9. Melting point: (78±4) °C.

Cyclic voltammetry was performed using a glassy carbon working electrode, a silver counter electrode, and a silver wire served as a quasi-reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$), decamethylferrocene was added in small quantities for internal voltage calibration. Nitrogen was bubbled through the dried solvents before initiating voltage sweeps at 100 mV/s. UV-vis spectra were recorded on a diode array spectrophotometer, luminescence was measured on a commercial fluorimeter equipped with a double monochromator. Quartz cuvettes were used for all optical spectroscopic experiments.

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SUPPORTING INFORMATION

^{1}H and ^{13}C NMR spectra of all new compounds, ^{11}B and ^{19}F NMR spectra of molecule **1**, ESI-TOF-MS spectra of the new compounds **1**and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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SYNOPSIS TOC