Photophysical and Electrochemical Investigations of the Fluorescent Probe, 4,4'-Bis(2-benzoxazolyl)stilbene

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Supporting Information

ABSTRACT: In solution, 4,4'-bis(2-benzoxazolyl)stilbene (BBS) was found to exhibit consistently high absolute fluorescence quantum yields ($\Phi_{\rm fl} \ge 0.88$) and a monoexponential lifetime, both independent of BBS concentration. The BBS steady-state and time-resolved photophysics were investigated by different techniques to understand the various deactivation pathways. Nonradiative deactivation of BBS singlet excited state by intersystem crossing was found to be negligible. Other than fluorescence, the excited state of BBS was found to be deactivated by *trans-cis* photoisomerization. At low concentrations ($\approx 5 \ \mu g/$



mL), UV spectroscopy and laser flash photolysis showed concordant results that the photoinduced *cis* isomer gradually replaced the original absorption spectrum of the pure *trans* isomer. However, at high concentrations ($\approx 0.2 \text{ mg/mL}$), ¹H NMR and DOSY measurements confirmed that irradiating BBS at 350 nm induced a conversion from the *trans*-BBS into its *cis* isomer by photoisomerization. It was further found that the stilbene moiety of both isomers was photocleaved. The resulting photoproduct was an aldehyde that was oxidized under ambient conditions to its corresponding carboxylic acid, i.e., 4-(1,3-benzoxazol-2yl)benzoic acid. The structure of the photoproduct was unequivocally confirmed by X-ray diffraction. Spectroscopic investigation of BBS showed a limited photoisomerization after irradiation at 350 nm of a *trans* solution. The BBS electrochemistry showed irreversible oxidation, resulting in an unstable and highly reactive radical cation. Similarly, the cathodic process was also found to be irreversible, giving rise to a radical anion and showing its n-doping character.

1. INTRODUCTION

An extended π -conjugation gives 4,4'-bis(2-benzoxazolyl)stilbene (BBS) optical properties that can lead to its use as photoactive switches^{1,2} and as a fluorescent brightener in textiles,³ detergents, and other materials.^{3,4} Furthermore, BBS's capacity to form excimers, leading to a change of its color under UV illumination at high concentrations in polymer films, has opened the door for applications in host–guest systems as a molecular probe of deformation and temperature.^{5–7} Its anisotropic flat shape could also be used to produce polarized light in oriented macromolecular matrices.⁸ In addition, BBS exhibits resistance to solvent extraction as well as high melting and degradation temperatures, above 300 °C, that satisfy the regulations of the U.S. Food and Drug Administration (FDA), thus enabling its use as an additive for food and consumer packaging materials.⁹

The spectroscopic properties of BBS are in part courtesy of the central stilbene. This provides a conjugated framework across which the electron rich benzoxazoyl termini delocalization can occur, resulting in a high degree of conjugation. The rigid framework is additionally responsible for its intense emission. Similar to other stilbene derivatives, BBS potentially can photoisomerize between its *trans* and *cis* isomers.^{10–13} This competing excited-state deactivation process could affect BBS' fluorescence properties, and in turn, limit its use in applications that require intense emission.^{14–16} For this reason, it would be

beneficial to determine whether BBS can be photoisomerized and under what conditions. To the best of our knowledge, the BBS photoisomerization dissipating energy processes have not been previously studied.

Although BBS has been used for different applications because of its optical and thermal properties, no extended optoelectrochemical studies of this fluorophore have been pursued. In particular, it would be interesting to probe the BBS photophysics to get a clear idea about the different energy dissipating processes that may be responsible of the lowering of its fluorescence quantum yield, which remains its greatest asset. Such studies are pivotal for determining the fluorescence BBS limitations and for its use as a universal fluorophore. Our purpose is to report the BBS photophysics and electrochemistry to try to better exploit its advantages.

2. EXPERIMENTAL SECTION

Materials. 4,4'-Bis(2-benzoxazolyl)stilbene (97%, melting point >300 $^{\circ}$ C) was purchased from Aldrich Chemicals. The compound was purified by sonicating and heating the material in the given solvent. The undissolved solids were subsequently

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removed by filtering upon cooling the solution and the filtered solution was then used for the measurements.

Spectroscopic Measurements. Absorbance measurements were done on a Varian Cary-500 UV-visible spectrometer, and the solvent absorption spectra were subtracted from the spectra of the analyzed samples, having a concentration of 5 μ g/mL. Fluorescence emission spectra were recorded at ambient temperature in 10 mm cuvettes, excited at the corresponding absorption maximum, using an Edinburgh Instruments FLS-920 combined steady-state and time-resolved fluorometer. The fluorescence lifetimes were measured according to standard time-correlated single photon counting methods, with the FLS-920 apparatus, by fitting the data with a monoexponential decay function. The calculated values have an experimental error of approximately 10%. Absolute fluorescence quantum yields were measured by using an integrating sphere and used to quantify the efficiency of the emission process by taking the ratio of photons absorbed to photons emitted through fluorescence at a particular wavelength in the same period of time.^{17,18}

The HOMO and LUMO frontier molecular orbitals were calculated semiempirically using DFT methods available in Spartan 06 with the $6-31g^*$ basis set. The bond angles, distances, torsions, and other parameters used for the theoretical calculations were experimentally derived from the X-ray data for BBS.¹⁹

Laser Flash Photolysis (LFP). The triplet-triplet absorption spectra were measured in anhydrous 1,1,2,2-tetrachloroethane (TCE) (from Aldrich Chemicals) at a BBS concentration of 5 μ g/mL using a Luzchem mini-LFP system, excited at 355 nm from the third harmonic of a Continuum YAG:Nd Sure-lite laser, using a 175 W xenon lamp. An average of 15 shots per wavelength was used for generating the transient absorption spectrum. The samples were dissolved in anhydrous TCE in static quartz cuvettes and had an absorbance of less than 0.4. All samples were purged with nitrogen for more than 20 min before LFP analyses.

Photoirradiation. The sample for UV measurement was degassed in a 20 mL vial by bubbling nitrogen directly into the solution for about 30 min before sealing the container to avoid contamination from air. The sample was then irradiated with 350 nm lamps in a Luzchem photoreactor. A small volume of the irradiated solution was removed from the reactor and transferred into a quartz 10×10 mm cell at prescribed times, and the absorbance spectrum was measured. For the NMR studies, the sample was introduced into a J-Young 7 mm tube at high concentration ($\approx 0.2 \text{ mg/mL}$). The tube was heated and placed in an ultrasound bath flowed by three successive freezepump-thaw cycles before it was sealed and irradiated at 350 nm in the same photoreactor. The NMR tube was then taken out at different times for measuring NMR spectra. For the crystallographic studies, a degassed 0.2 mg/mL BBS solution in TCE was irradiated for 10 h by using 350 nm lamps in the Luzchem photoreactor.

¹**H NMR Spectroscopy.** A typical sample was prepared by dissolving a 0.2 mg/mL solution of BBS in CDCl₃ or in deuterated TCE (both from Aldrich Chemicals) in a J-Young 7 mm tube by alternating between heating and placing the sample in an ultrasound bath to avoid precipitation and to accelerate solubility. The tube was sealed and it was subjected to three successive freeze–pump–thaw cycles. Spectra were run on a Bruker AV-400 MHz spectrometer for all compounds dissolved in CDCl₃. MestRe-C and TopSpin software was used for NMR

data processing. Chemical shifts were found relative to TMS, and they were derived from spectral simulations using both ChemDraw Ultra 8.0 and DFT calculations. Diffusion experiments were performed at 298 K on a Bruker AVII-400 MHz spectrometer, which was equipped with a diff60 probe. A standard stimulated-echo pulse sequence was used with a gradient duration (δ) of 1 ms, a diffusion time (Δ) of 40 ms, a repetition time of 5 s and 16 gradients values. An average of around 128 scans were accumulated.

Crystallographic Study. A needle yellow crystal (0.20 × 0.03 × 0.03 mm³), suitable for X-ray diffraction analysis, was obtained by partial slow evaporation from a TCE solution after UV irradiation at 350 nm, triggering an increase of the concentration of 0.2 mg/mL to about 0.8 mg/mL. The single crystal study was carried out at 100 K using a Bruker APEX II diffractometer equipped with an Incoatec microsource generator producing Cu K α radiation, a three-circle platform goniometer and an APEX2 CCD detector.

The structure was solved by direct methods using SHELXS 97.²⁰ All atoms from the main molecule were refined with anisotropic thermal displacement parameters. Hydrogen atoms were positioned geometrically and refined with a riding model, with C-H distances of 0.95 Å and U_{iso} (H) values constrained to be 1.2 times U_{eq} of the carrier atom. The structure contained an included solvent molecule that was found highly disordered. Several electron density peaks were located that did not assemble to a recognizable fragment of TCE molecule. So the solvent contribution was taken on using the SQUEEZE option²¹ implemented in the PLATON software.²²

3. RESULTS AND DISCUSSION

The photophysical properties of BBS were measured in TCE at a concentration of 5 μ g/mL, where it exhibits an absorption maximum at 374 nm, an emission maximum at 434 nm and a molar absorption coefficient of 65 000 M⁻¹ cm⁻¹. Chlorinated solvents (TCE, CHCl₃, and CDCl₃) were chosen for evaluating the physical properties of BBS owing to the high solubility of BBS in these solvents.²³ Though chlorinated solvents are assumed not to be ideal solvents for photophysical studies because of their propensity to produce radicals upon direct photoirradiation, these undesired byproducts can be avoided by irradiating at wavelengths >350 nm. Photophysical studies of BBS were therefore done by irradiating at wavelengths outside the absorbance windows of the solvents, being at wavelengths >254 nm. Irradiations were done in Pyrex instead of quartz glassware because of its optical transmission cutoff of <350 nm. Using Pyrex glassware therefore ensures the removal of UV wavelengths from the broad emitting lamps that could potentially induce radical formation upon direct excitation of the chlorinated solvents.

The BBS solution emission has a unique lifetime on the order of 1 ns. The monoexponential emission confirms the absence of bimolecular species. The consistent unimolecular lifetime was observed even when the BBS concentration was increased. Given that previously reported BBS emission yields were done by relative actinometry, which is an imprecise method,²⁴ we measured its absolute fluorescence quantum yields ($\Phi_{\rm fl}$) more accurately with an integrating sphere.²⁵ BBS was found to fluoresce strongly in solution with $\Phi_{\rm fl}$ = 0.88 in TCE. The measured value is higher than that of *trans*-stilbene (0.80 at 25 °C).²⁶

The measured absolute $\Phi_{\rm fl}$ confirms that BBS is highly fluorescent. However, the lower than unity $\Phi_{\rm fl}$ indicates that

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deactivation processes other than fluorescence occur. The nonradiative deactivation processes were subsequently investigated, notably its photoisomerization. The BBS *trans-cis* photoisomerization was investigated by both steady-state and time-resolved techniques according to UV spectroscopy and laser flash photolysis (LFP), respectively. Figure 1 shows that



Figure 1. BBS *trans-cis* photoisomerization in TCE measured by absorbance spectroscopy at room temperature at 0 (black box), 10 (red box), 30 (blue box), 40 (green box), 60 (black circle), 80 (red circle), 100 (blue circle), 120 (green circle), 160 (black triangle), 190 (red triangle), 220 (blue triangle), 250 (green triangle), and 320 min (open box) after irradiation at 350 nm with a 16 W light source.

the absorbance spectrum of trans-BBS exhibits three peaks at 358, 374, and 395 nm. Upon irradiating at 350 nm, at room temperature, these three peaks decrease considerably in intensity over a period of 5 h, without disappearing completely. This is accompanied by a concomitant increase in absorbance at 308 nm, which is assigned to the cis-BBS. Figure 1 also shows the existence of an isosbestic point at 330 nm, at which point the trans and cis isomers have the same extinction coefficient. This isosbestic point indicates that only two species that vary in concentration contribute to the absorbance. It further confirms the interdependence of the two species, being the interconversion of the trans and cis isomers. It should be noted that at longer irradiation times at 350 nm, the isosbestic point vanishes (data not shown) and the intensity of both isomers eventually disappears. This implies that both isomers are converted into a new product with extended irradiation (vide infra).

In a second step, BBS was investigated by LFP to confirm the *trans-cis* photoisomerization. The advantage of the time-resolved method versus steady-state irradiation is that the transients are instantaneously produced within the short laser pulse (ca. 10 ns). The intense laser power further produces sufficient transients within its pulse for them to immediately be detected. This is in contrast to steady irradiation that requires extended irradiation times to detect any light induced species.

The inset of Figure 2 shows the transient absorbance spectra of BBS measured in TCE at 9.5 and 18.5 μ s after the laser pulse. The negative Δ absorbance at 350 nm corresponds in part to the ground-state bleaching of the *trans*-BBS and the signal at 300 nm is ascribed to the *cis* isomer. Meanwhile, the



Figure 2. BBS average transient absorbance response at 308 nm (red line), specific to *cis*-BBS, and 374 nm (black line), characteristic of *trans*-BBS, in TCE measured 0.3 μ s after the laser pulse at 355 nm. Inset: transient absorbance spectra of BBS recorded in TCE at 9.79 (black square) and 27.09 μ s (red square), after the laser pulse at 355 nm.

new absorbance at 450 nm is assigned to the BBS triplet. This was based on its monoexponential decay and its lifetime (8 μ s) that is consistent with triplets.²⁷ Unequivocal proof for the triplet was obtained by quenching the transient with 1,3-cyclohexadiene, which is a well-known triplet deactivator.²⁸

The transient absorbance kinetics were measured at both 308 and 374 nm to confirm the identity of the photoinduced products. These wavelengths were chosen because they correspond to the absorbance maximum measured at steady state. As seen in Figure 2, the absorbance at 308 nm grows according to first-order kinetics with a lifetime of 3.5 μ s. It is further obvious that the transient signal does not decay within the time resolution of the LFP instrument. The transient kinetic at 374 nm is the mirror image of that observed at 308 nm. The negative signal is a result of the ground state being depleted. Similar to what was observed at 308 nm, the signal at 374 nm does not recover during the course of the measurement. This implies that the absorbance at 374 nm is irreversibly converted into a photoproduct whereas the absorbance at 308 nm is the formation of a photoproduct that is stable within the time resolution of the instrument. Though the exact photoisomerization mechanism and the lifetimes of the discrete processes cannot be determined, the overall *trans* \rightarrow *cis* photoconversion is 2.5 μ s, according to the LFP measurements. The similar microsecond kinetics and the mirror image of the two absorbances confirm the interdependence of the signals at 308 and 374 nm. The signal of the trans-BBS at 374 nm is therefore converted into the cis isomer, which is observed at 308 nm. The results are consistent with the steady-state measurements. From the plateau regions of the kinetics, the molar absorption coefficient (ε) of the *cis* isomer can be approximated to be 38 500 M^{-1} cm⁻¹ at 308 nm.

The efficiency of photoisomerization cannot accurately be quantified from either the time-resolved or steady-state analyses. However, taking into account the absolute $\phi_{\rm fl}$ and assuming a minor triplet contribution as per the absorbance at 450 nm, the *trans* \rightarrow *cis* photoisomerization efficiency is approximately 10%.

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Chart 1. BBS trans-cis Photoisomerization and Conversion of Both Isomers in BBA



Figure 3. ¹H NMR spectrum between 6.5 and 10.3 ppm, of *trans*-BBS in $CDCl_3$, after 0 (a), 4 (b), 10 (c), and 20 h (d) of irradiation at 350 nm (light power, P = 16 W).

NMR spectroscopy was used to both investigate the presence of additional photoinduced processes and to confirm the *transcis* photoisomerization. The advantage of NMR spectroscopy is that the *cis* and *trans* isomers of stilbene derivatives can readily be distinguished by their distinctive ${}^{3}J_{\rm HH}$ coupling constants.^{29,30} However, this was not possible because of BBS' high degree of symmetry that gives rise to a singlet for the vinylene protons instead of a doublet. Therefore, the chemical shift of the *cis*-vinylene protons was estimated by theoretical means using commercial software. This is particularly important given the absence of any reported NMR data for *cis*-BBS. To confirm the accuracy of the predicted chemical shifts of *cis*-BBS, the ¹H NMR spectrum of *trans*-BBS was also calculated. The predicted chemical shifts for the vinylene protons were 6.56 and 7.26 ppm, respectively, for the *cis*- and *trans*- BBS isomers. The calculated chemical shift for the *trans*-vinylene proton (located at position f in Chart 1) is in accordance with the experimental value of 7.32 ppm, as per Figure 3a.

Figure 3a shows the NMR spectrum of *trans*-BBS, prior to irradiating at 350 nm. The singlet at 7.32 ppm is assigned proton f (Chart 1). It should be noted that there is no signal at around 6.5 ppm that can be ascribed to the *cis* isomer. Figure



Figure 4. DOSY NMR results for BBS, after 4 (a) and 10 h (b) of UV irradiation. All spectra were recorded in $CDCl_3$ at room temperature at 400 MHz. The x-axis represents the standard ¹H dimension, from 6 to 10.5 ppm, and the y-axis represents the diffusion dimension.

3b displays the BBS NMR spectrum after 4 h of UV irradiation. It is obvious that a new singlet appears at 6.76 ppm, belonging to cis-BBS, in addition to the singlet of trans-BBS. The formation of the *cis* isomer is accompanied by a change of the positions of the closest peaks to the central vinylic bond. Indeed, the intensity of the peaks corresponding to protons at positions d and e, located at 8.33 and 7.74 ppm of trans-BBS, decreased progressively, while new peaks corresponding to the same positions appear at 8.22 and 7.59 ppm for cis-BBS, respectively. It should be noted that the remaining peaks, belonging to the protons at positions a, b, and c remain unchanged. Figure 3c shows the NMR spectrum after 10 h of UV irradiation. The appearance of a well-defined singlet at 10.15 ppm is consistent with a photoproduct having an aldehyde. The new resonance is accompanied by the emergence of new peaks at 8.48 and 8.08 ppm, corresponding to the protons at positions d and e, respectively. Figure 3d shows the NMR spectrum after 20 h of UV irradiation, displaying the disappearance of the *cis* isomer, the increase of the photoproduct singlet at 10.15 ppm and the decrease of the trans-BBS singlet at 7.32 ppm. When the BBS solution is irradiated for longer times, the singlet at 7.32 ppm, specific to trans-BBS, disappears while the peaks specific to the photoproduct become more intense. The emergence of new peaks specific to the protons at positions d and e, in addition to the appearance of a new well-defined singlet at 10.15 ppm, which has been attributed to an aldehyde, confirm the presence of another conversion process.

By integrating the *cis* isomer signal at 6.76 ppm relative to the *trans* peak at 8.33 ppm, it was found that the *cis* integral gradually increases before reaching a plateau of 18% relative to the sum of the *trans* and *cis* isomers after 3 h of UV irradiation in CDCl₃. After which time, the signal decreases until becoming null after around 14 h of UV irradiation. These results show that another process occurs, leading to a simultaneous conversion of both isomers into a photoproduct, thus suppressing the BBS *trans—cis* photoisomerization. Because UV spectroscopy shows a greater conversion from *trans* to *cis*, even when the difference of the molar absorption coefficients of the two isomers was taken into account, a series of absorbance measurements were made with a concentration similar to that used for the NMR study with an initial concentration of ≈ 0.2

mg/mL. After irradiation, an aliquot was removed and it was diluted to 0.005 mg/mL, similar to the concentration used in Figure 1. This was required to not saturate the detector of the UV spectrometer and to get an absorbance below unity for each measurement. This series of measurements led to a trans-cis conversion similar to that found by NMR in Figure 3. It appears that a high *trans-cis* conversion is obtained upon irradiating at low concentrations (Figure 1). In contrast, a low conversion is obtained upon irradiating at high concentrations (Figure 3). This is probably due to an inner-filter effect and/or selfquenching at high concentrations that favor continuous energy transfer between BBS molecules. On the other hand, the aldehyde signal at 10.15 ppm continuously increases relative to the trans peak at 8.33 ppm. Also, the chemical shifts of the a, b, and c protons remain unchanged. These data collectively suggest that the second process does not affect the benzoxazol part of the molecule, but only the stilbene moiety. The higher than normal downfield chemical shift of the aldehyde confirms that it is highly conjugated. This is only possible when it is conjugated with the benzoxazol unit. The photoproduct therefore is most likely from stilbene photooxidation in the presence of trace amounts of residual oxygen. The photocleavage resulting in aldehyde photoproducts is a proven degradation mechanism of stilbenes³¹⁻³³ and it makes the trans-cis photoisomerization irreversible.

To gain more information about the presence of a secondary process, diffusion ordered spectroscopy (DOSY) experiments were conducted. DOSY enables us to differentiate between blend components because, in a solution of a given viscosity, molecules of various sizes diffuse at different rates.^{34–38} The diffusion coefficients ($D_{\rm diff}$) of the individual species can be determined by the DOSY experiments and related to their molecular hydrodynamic volume. These experiments were conducted at identical concentrations and temperatures in CDCl₃.

Figure 4 shows the diffusion coefficient ($D_{\rm diff}$) as a function of the chemical shift between 6 and 10.5 ppm after 4 (a) and 10 h (b) of UV irradiation. Figure 4a shows that the *trans*-BBS original signals at 8.33, 7.74, and 7.32 ppm, as well as the *cis* isomer signals at 8.22, 7.59, and 6.76 ppm, corresponding to protons d, e, and f, have the same diffusion coefficient of 0.8 $\times 10^{-9}$ m²·s⁻¹. Figure 4b shows that, after 10 h of UV irradiation,



Figure 5. Atomic displacement ellipsoid plot of BBA. The second molecule (atoms labeled with suffix A) are generated by the symmetry operation -x - 1, -y - 1, -z. Hydrogen bonds are shown as dotted lines. Ellipsoids are drawn at the 50% probability level and hydrogen atoms are represented by sphere of arbitrary size.



Figure 6. View of the π -stacking interactions between two hydrogen-bonded dimers. Hydrogen bonds and the shortest distances between ring centroids involved in π -stacking interactions are indicated by dotted lines.

the emerging peaks at 8.48 and 8.08 ppm, corresponding to protons d and e, respectively, have higher diffusion coefficients of the order of $(1.2-1.3) \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, as well as the new singlet, located at 10.15 ppm. These results show that these three peaks do not belong to the original BBS, but to a new product. Therefore, the D_{diff} values are so different, before and after a prolonged UV irradiation, that a standard deviation of up to 10% cannot affect the understanding of the conversion. The presence of two singlets at 7.02 and 7.54 ppm are evident in Figure 4. These are assigned to impurities because they are always present. They additionally diffuse rapidly, which confirms that they are smaller than BBS. According to Figure 3A, these impurities are minor and they are present in less than 2 mol %. Although the commercial source of BBS is 97% pure, it was purified by alternating between heating and sonication, followed by filtering. This leads to purer BBS than the original commercial source. Moreover, these impurities do not interfere with the isomerization studies because they do not contain a vinyl group and they do not absorb at the wavelengths used for photoirradiation, owing to their limited degree of conjugation. On the other hand, the solvent $(CDCl_3)$ diffusion coefficient is the same, within uncertainty, for the different solutions, showing similar viscosities before and after irradiation. The Stokes-Einstein equation, applicable for spherical molecules and describing diffusion phenomena, is

$$D_{\rm diff} = \frac{k_{\rm B}T}{6\pi\eta r} \tag{1}$$

where D_{diff} is the diffusion coefficient, r is the hydrodynamic radius of the molecule, k_{B} is the Boltzmann constant, T is the temperature and η is the viscosity. D_{diff} is inversely proportional to the hydrodynamic radius. By assuming that the molecules are spherical, the higher value of D_{diff} after 10 h of UV irradiation proves that the BBS molecule is converted into a molecule of lower hydrodynamic radius. Meanwhile, the new well-defined singlet at 10.5 ppm confirms it has an aldehyde. In contrast, a broad resonance would be observed for a carboxylic acid, whose chemical shift would be concentration-dependent. According to eq 1, the hydrodynamic radius of the photoproduct is estimated to be 1.6 times smaller than BBS.

To gain a deeper understanding of the products formed from UV irradiation and, more specifically, to unequivocally identify both the photoproduct and cis-BBS, crystallographic studies were conducted. For this, a 0.2 mg/mL solution of BBS in TCE, similar in concentration to that used for NMR measurements, was irradiated at 350 nm for 10 h. The resulting solution contained both BBS isomers and the photoproduct. This was confirmed by NMR (Figure 3c). The solvent was then partially evaporated, as described in the Experimental Section. Unlike what was expected, the single crystal that formed upon partial solvent evaporation was neither the cis nor the trans isomer. In fact, the X-ray diffraction of the single crystal confirmed that the photoproduct was a carboxylic acid, 4-(1,3benzoxazol-2-yl)benzoic acid (BBA) (Figure 5). The latter is a result of photocleavage of the stilbene moiety, leading to two half-molecules with an acid terminal function for each. Although an aldehyde photoproduct was observed in NMR studies, this intermediate is readily oxidized to BBA under the aerobic crystallization conditions, according to known means.^{39,40} Irradiation of BBS at 350 nm therefore leads to trans-cis photoisomerization and the two isomers are photooxidized with residual oxygen. The resulting aldehyde photoproduct is further oxidized to BBA. The conversion of both photoisomerization and photocleavage is shown in Chart 1. The photocleavage is concentration-dependent and is slow at concentrations $\leq 5 \ \mu g/mol$ and faster at concentrations ≥ 0.2 mg/mL.

BBA was found to crystallize in the triclinic space group $P\overline{1}$ with one independent molecule in the asymmetric unit. It is almost planar, and the angle between the benzene ring and the benzoxazolyl group is only $1.50(14)^{\circ}$, which is smaller than that found in BBS $(2.30(16)^{\circ})$.¹⁹ The different BBA molecules were stable due to intermolecular interactions. Indeed, Figure 5 shows that two BBA molecules form a dimer, linked by two hydrogen bonds involving the carboxylic acid groups according to the classical graph set motif $R_2^2(8)$.⁴¹

Figure 6 shows that π -stacking interactions between the benzene and the oxazole rings enable a packing with the

shortest centroid to centroid distances of 3.58 and 3.68 Å. The chains of dimers are arranged parallel to the *a*-axis and the molecules from these chains are connected to a neighboring chain via C-H···O interaction (d(C-O) = 3.26 Å) to form layers in the (a, b) plane. It should be noted that the disordered solvent molecules occupy the remaining space between the layers (35% of the unit-cell volume).

The most interesting property of BBS is its fluorescence. Though extended characterization of the *trans* isomer is possible, the *cis* isomer has not previously been characterized. This is primarily owing to the difficulty in isolating the sterically hindered isomer. It would nonetheless be beneficial to characterize the fluorescence of the *cis* isomer for gaining valuable insight into both the photoisomerization process and to determine the limit of usefulness of BBS as a fluorescence probe. For these reasons, we extended our fluorescence studies to include the *cis* and *trans* isomers. However, given the challenges in isolating the pure *cis* isomer, spectral characterizations were done indirectly on mixed samples having both *cis* and *trans* isomers. According to Figure 7, three well-defined



Figure 7. Normalized absorbance and emission spectra in TCE of BBS before UV irradiation: absorbance (red box) and emission (red circle); and after 5 h of irradiation at 350 nm: absorbance (black box) and fluorescence (black circle).

peaks, located at 412, 434, and 464 nm, are seen in the *trans*-BBS fluorescence spectrum. These are assigned to the 0-0, 0-1, and 0-2 radiative transitions, respectively, and they are characteristic of BBS monomers. In comparison, the absorbance spectrum of the irradiated sample exhibits three ill-defined peaks at 358, 374, and 395 nm. Both the absorbance and fluorescenc spectra of the *cis* isomer are hypsochromically shifted further bathochromically shifted relative to *trans* isomer because of its reduced degree of conjugation. No spectral changes were observed for the *trans* absorbance spectrum with increasing the BBS concentration.

Figure 7 also shows the spectroscopic features of a solution of *trans*-BBS irradiated for 5 h at 350 nm. The absorbance spectrum exhibits an intense peak at 308 nm and a shoulder at 375 nm. These are assigned to the absorbance maximum of the *cis* and *trans* isomers, respectively (vide supra). Similarly, the emission spectrum shows a maximum at 422 nm and two

shoulders at 384 and 474 nm, similar to analogous crescent-like conjugated stilbenes.^{42,43} These shoulders are specific to *cis*and trans-BBS, respectively, whereas the emission maximum at 422 nm results from an overlap between the emissions of the two BBS isomers. The emission of the cis isomer is then hypsochromically shifted relative to the trans spectrum and the presence of both isomers even after prolonged irradiation suggests a photostationary cis-trans conversion. This hampers accurate determination of the spectroscopic data specific to cis-BBS. Because the cis isomer was impossible to isolate, the solution obtained after 5 h of UV irradiation was used to measure the fluorescence quantum yield and the lifetime of the cis- and trans-BBS mixture relative to the pure trans isomer. Only qualitative information is possible given that both isomers have different molar absorption coefficients and they do not absorb the same number of photons. Both the mixed isomer and pure trans isomer solutions had similar fluorescence lifetimes, being ca. 1 ns. In contrast, the fluorescence quantum yield decreased from 0.88 for pure trans-BBS to 0.67 for the solution containing a mixture of both isomers. A rough estimate of the energy gap (E_{σ}) , i.e., the absolute energy difference between the ground (HOMO) and excited (LUMO) states, was calculated from the intercept of the normalized absorption and emission spectra (Figure 7). The approximated values are 3.1 eV for trans-BBS and 3.4 eV for the irradiated solution (for 5 h) containing trans and cis isomers.

The energy gaps not only can be obtained from the intercept of the normalized absorbance and fluorescence spectra, as shown in the previous section, but also can be obtained by cyclic voltammetry. According to Figure 8, *trans*-BBS under-



Figure 8. Cyclic voltammogram of *trans*-BBS recorded in TCE at 100 mV/s against SCE with Bu_4NPF_6 as the supporting electrolyte.

goes a one-electron oxidation process, demonstrating its pdoping-type behavior. Similarly, BBS undergoes a one-electron reduction, at low potential, confirming its n-doping character. Both the oxidation and reduction processes observed were irreversible, regardless of the scan rate, indicating highly reactive radical ion intermediates.

From the cyclic voltammetry data, we can calculate $E_{\text{onset}}^{\text{ox}}$ which is the oxidation potential onset versus the SCE electrode, and $E_{\text{onset}}^{\text{red}}$ which is the reduction potential onset. Their values, taken from Figure 8, are given in Table 1. The HOMO energy value can be calculated from the ionization potential (IP), according to the well accepted approximation of IP = $E_{\text{onset}}^{\text{ox}}$ +

Table 1. trans-BBS Electrochemical Properties^a

$E_{\rm ox}^{\ b}/{\rm V}$	$E_{\rm red}^{\ \ c}/{\rm V}$	IP^d/eV	EA ^e /eV	$E_{\rm g}^{\rm elf}/{ m eV}$
1.66	-1.79	5.72	2.87	2.9

^{*a*}The electrochemical data are reported against SCE. ^{*b*}Oxidation potential. ^{*c*}Reduction potential. ^{*d*}Ionization potential. ^{*e*}Electron affinity. ^{*f*}Electrochemical energy-gap.

4.4.^{44–47} Similarly, the LUMO energy level is derived from the electron affinity (EA), according to EA = $E_{\text{onset}}^{\text{red}}$ + 4.4. The IP and EA values of BBS are also reported in Table 1. The difference between the HOMO and LUMO energy levels gives the electrochemical energy-gap, E_{g}^{el} (2.9 eV in Table 1) that is similar to the spectroscopic energy gap, E_{g} (3.1 eV from Figure 7). The high degree of conjugation of the BBS molecule is confirmed, first, by both the electrochemical and spectroscopic data and, second, by the theoretically calculated molecular orbitals that are depicted in Figure 9. The latter show the



Figure 9. BBS LUMO (top) and HOMO (bottom) features calculated by DFT, using the 6-31g* basis set and the X-ray crystal data.¹⁹

delocalization of the HOMO along the rigid backbone of BBS, confirming its high degree of conjugation. Conversely, the LUMO is located exclusively on the central stilbene moiety.

4. CONCLUSIONS

In solution, BBS fluoresces with high quantum yields ($\Phi_{\rm fl} \approx 0.88$), regardless of its concentration. The steady-state and time-resolved photophysics of this stilbene-derivative fluorophore have been investigated for the first time in this study by absorbance, laser flash photolysis, and NMR spectroscopy, to unravel its quenching mechanism, whereas its fluorescent and electrochemical features were studied by fluorescence spectroscopy and cyclic voltammetry, respectively.

Although the primary deactivation mode of the BBS singlet excited state is by fluorescence, it also deactivates by *trans-cis* photoisomerization. Intersystem crossing to the triplet state was found to be negligible and excimer formation was nonexistent, proved by a concentration-independent monoexponential lifetime, of the order of 1 ns.

At low concentrations ($\approx 5 \ \mu g/mL$), irradiating BBS at 350 nm induces a *trans-cis* photoisomerization. However, at higher concentrations ($\geq 0.2 \ mg/mL$), this process is accompanied by formation of an oxidized photoproduct, occurring by photocleavage at the stilbene moiety. The resulting aldehyde is oxidized to its corresponding carboxylic acid under ambient conditions. X-ray crystallography confirmed that the oxidized photoproduct was 4-(1,3-benzoxazol-2-yl)benzoic acid and that it arranged as dimers in the solid state. The secondary process kinetics was found to be concentration-dependent and seems to

be too slow to be detected at low concentrations. The limited photoisomerization at high concentrations was proved by a combined absorbance and emission spectra of both *trans* and *cis* species. Electrochemistry of *trans*-BBS exhibits both irreversible oxidation and reduction.

ASSOCIATED CONTENT

Supporting Information

Magnification of the ¹H NMR spectrum, from 6.5 to 10.3 ppm, of *trans*-BBS in CDCl₃, after 0, 4, 10, and 20 h of irradiation at 350 nm (light power, P = 16 W). ¹H NMR spectrum, from 6.5 to 10.2 ppm, of *trans*-BBS in *d*-TCE, before irradiation at 350 nm (light power, P = 32 W). This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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