Photophysical Study of BBT: A Potential Fluorescent Probe for Polymers

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INTRODUCTION

2,5-bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene (BBT) has interesting spectroscopic properties that are ideally suited for use as an optical brightener[1] or to enhance the emission of liquid crystal displays.[2] It can be used as an electron transporting layer in organic emitting devices[3-7] or as an electron donor for the reinforcement of nanotubes.[8] BBT also shows excellent heat stability useful for improving the color of various plastics.

Despite the extensive use of BBT for various applications related to its inherent spectroscopic and thermal properties, it has never been the subject of extended opto-electrochemical studies. Here, we report the optical and photophysical properties of BBT, in solution and blended with poly(1,4-butylene succinate) (PBS) films, and evaluate its potential as a fluorescent probe.

EXPERIMENTAL

Materials. 2,5-Bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene (BBT) (99%, melting point ~ 200 °C) was purchased from Aldrich and used as received. Poly(1,4-butylene succinate) (PBS) ("Bionolle 1001") was obtained from Showa Highpolymer Company (Japan).

Film Preparation. PBS-BBT films were prepared by melt-blending in a DDRV501/DIGI-SYS Plasti-Corder Brabender by mixing about 20 g of PBS with 0.02 to 2 wt.% of BBT at 200 °C, at 50 rpm, for 10 min. Films with thicknesses of 60-120 µm were obtained by compression-molding the resulting material, previously cooled to room temperature, between two aluminum foils in a Carver Laboratory Press at 200 °C. The samples were left to cool slowly to room temperature before removal from the press.

Spectroscopic Measurements. Fluorescence emission spectra were recorded at ambient temperature using an Edinburgh Instruments FLS-920 combined steady-state and time resolved fluorimeter in 10-mm cuvettes excited at the appropriate absorption maximum. The fluorescence lifetimes were measured according to standard TCSPC methods with the FLS-920 by fitting the curves with a monoexponential decay function. The calculated values contain approximately a 10% experimental error. Fluorescence quantum yields were used to quantify the efficiency of the emission process by taking the ratio of photons absorbed to photons emitted through fluorescence. Absolute fluorescence quantum yields were measured using an integrating sphere.

Laser Flash Photolysis (LFP). The triplet–triplet absorption spectra were measured in anhydrous acetonitrile using a Luzchem mini-LFP system, excited at 355 nm from the third harmonic of a Continuum YAG:Nd Sure-lite laser. An average of 15 shots per wavelength were used for generating the transient absorption spectra. Samples, having an absorbance below 0.4, were dissolved in anhydrous acetonitrile in static quartz cuvettes. All samples were purged with nitrogen for more than 20 min before LFP analyses.

RESULTS AND DISCUSSION

BBT Solution Fluorescence. BBT emission spectra at various concentrations of BBT in THF are shown in Figure 1. The emission spectrum for the lowest BBT concentration is characteristic of a well-defined vibronic structure, attributed to radiative 0-0, 0-1 and 0-2 transitions, respectively. It is observed that the fluorescence spectrum at the lowest BBT concentration shows three well-defined vibronic peaks associated with BBT monomers. The lowest-wavelength vibronic peak disappears when increasing the BBT concentration from 2 µM to 2 mM. This emission spectral change is observed whatever the proticity and polarity of the solvent (tested in a dozen different solvents). Therefore, the change in the intensity of the lowest-wavelength peak is not a consequence of solvent-solute interactions, as is frequently observed in protic solvents. Moreover, since the absorption spectrum remains unchanged even at high BBT concentrations, the disappearance of the high energy vibronic band is not due to intermolecular interactions such as excimer formation.

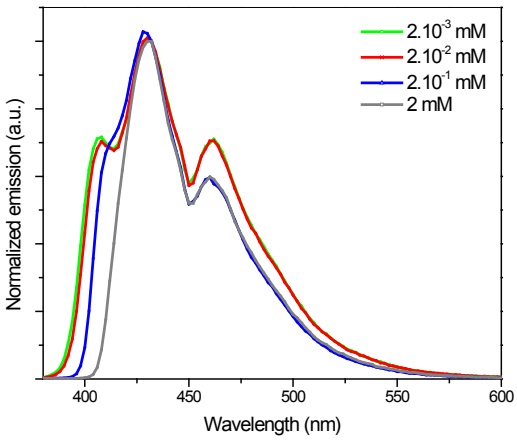

Figure 1. Normalized BBT fluorescence spectra at various BBT concentrations in THF.

PBS-BBT Polymeric Film Fluorescence. Figure 2 shows the fluorescence emission spectra of BBT incorporated into PBS at various concentrations. The PBS-BBT-0.02 wt.% film exhibits the same spectroscopic features as BBT in solution at low concentrations, namely three vibronic peaks at 412, 434 and 464 nm. This may imply that BBT remains in an unaggregated state, molecularly dispersed in the amorphous phase of PBS. A spectral change, similar to that seen in solution, occurs upon increasing the BBT concentration from 0.02 to 0.2 wt.%. Indeed, the 412 nm peak decreases considerably and becomes a shoulder. It further decreases in intensity and completely disappears upon increasing the BBT concentration from 0.2 to 2 wt.%. This modification in the emission spectrum is accompanied by a bathochromic shift of the second and third peaks: the 0-1 transition peak shifts from 434 to 446 nm, while the 0-2 transition peak moves from 464 to 474 nm with increasing the BBT concentration from 0.02 to 2 wt.%.

There is also a broad emission at ca. 500 nm that might at first sight be attributed to excimer formation. However, excimer formation can be ruled out because this emission is present even at low concentrations and also in solution. In solution, the BBT molecules are better dispersed than in PBS films where the molecules may be forced to come into contact with one another due to the relatively high crystallinity of PBS. The lack of any concentration-dependent changes in the BBT absorption spectrum confirms the absence of bimolecular deactivation processes. It can be inferred from these findings, together with the bathochromic shift observed in PBS-BBT fluorescence spectra, that BBT aggregates are formed between molecules in the ground state. Furthermore, the bathochromic shifts of BBT as a function of concentration in PBS confer BBT with potentially useful probe-like properties in polymer matrices.

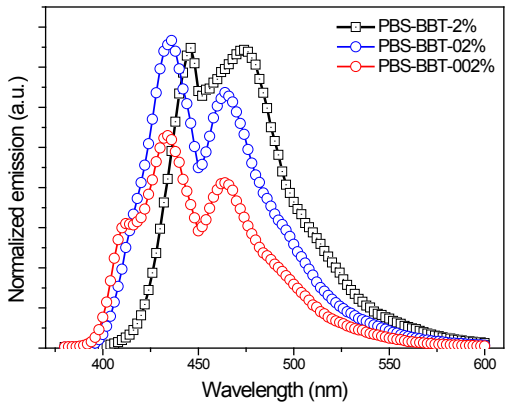

Figure 2. Fluorescence spectra of BBT molecules dispersed at various concentrations in polybutylene succinate films.

BBT Quenching Mechanism. BBT was found to fluoresce strongly with an average fluorescence quantum yield of 75% independently of solvent polarity and proticity (tested in a dozen different solvents). As a consequence, BBT can be used as a universal fluorophore and sensor, and, in particular, as a reference for fluorescence actinometric studies. However, it is noteworthy that the measured quantum yields are less than unity, implying the presence of deactivation modes other than fluorescence, such as nonradiative, internal conversion (IC) and intersystem crossing (ISC). At 77 K, deactivation modes by bond rotations are normally suppressed, allowing the determination of the IC quantum yield. Indeed, the fluorescence quantum yield increases by 9% at 77 K relative to that at room temperature. The observed increase confirms that deactivation by IC occurs, albeit only by a minor energy dissipation pathway, namely via the thiophene–oxazole bond.

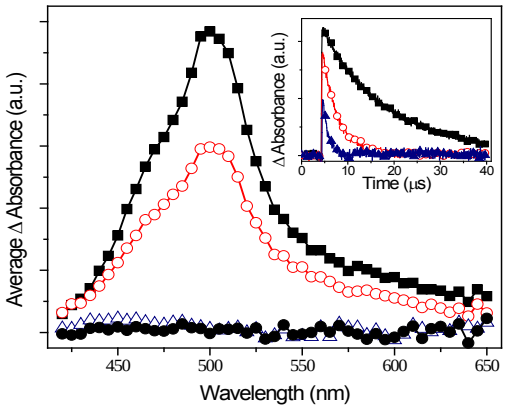

Figure 3. Transient absorption spectra of BBT recorded in acetonitrile at 5.9 (■) and 9.8 μs (○) after a laser pulse at 355 nm before and after adding 60 μL of 1,3-cyclohexadiene (CHD) at 5.9 (Δ) and 9.8 μs (◆). Inset: Decay kinetics of BBT monitored at 500 nm before (■) and after adding 20 (○) and 60 μL (▲) of 1,3-cyclohexadiene as a triplet state quencher.

Figure 3 shows that direct excitation of BBT at 355 nm by laser flash photolysis produces a visible strong transient at 500 nm. To assign this transient, BBT was quenched with successive additions of 1,3-cyclohexadiene (CHD), resulting in a decrease of the transient intensity and a shortening of the lifetime, as evidenced in Figure 3 and its inset, respectively. Since it is quenched with the known triplet quencher (CHD) and given its first-order kinetics (t_o = 14.4 μs), it can be concluded that the observed transient is a triplet. The triplet nature is further confirmed by the phosphorescence emission measured at 77 K. The singlet deactivation by intersystem crossing (ISC) to the triplet state can be approximated according to the energy conservation principle. It can be calculated from the combined temperature dependent fluorescence measurements that the triplet state is formed to ca. 16%, showing that BBT undergoes singlet deactivation by ISC. The collective steady-state and time resolved measurements indicate that both nonradiative pathways, IC and ISC, are minor deactivation processes, relative to fluorescence.

CONCLUSION

The BBT fluorophore was found to exhibit spectroscopic and photophysical properties that are of interest for its potential use as a fluorescent probe. BBT is advantageous because of its photochemical and thermal inertness. Its high fluorescence yield in organic solvents and polymer films further makes BBT a suitable fluorescence reference for actinometric fluorescence studies. Although the primary deactivation mode of the singlet excited state is by fluorescence, BBT also deactivates to a minor extent by both IC and ISC. The bent nature of the BBT molecule, due to the 1,4-di-functionalization of the central thiophene ring, limits the number of possible intermolecular interactions making it inherently soluble in most organic solvents. Indeed, the solvent independent and high fluorescence of BBT, taken together with its high solubility in common organic solvents, make it a viable sensor for polymeric and solution studies. Finally, BBT can form aggregates between molecules in the ground state and this aggregate formation is relatively independent of the BBT concentration.

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