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Toward Benzobis(thiadiazole)-based Diradicaloids

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Abstract: We theoretically predicted that acetylene-bridged benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (BBT) oligomers would show a quick increase of diradical character with extension of chain length. To validate the hypothesis, six stable BBT-based diradicaloids were synthesized and fully characterized by X-ray crystallographic analysis and various spectroscopic measurements. Three of them showed prominent paramagnetic activity at elevated temperatures due to thermal population from the open-shell singlet ground state to triplet excited state. It was also found that substitution by electron-donating triphenylamine groups at the termini promoted the diradical character and reduced the singlet-triplet energy gap, and at the same time, resulted in intense near-infrared absorption.

Recently, *π*-conjugated molecules with an open-shell singlet diradical ground state have attracted a lot of attention due to their unique electronic, optical and magnetic properties, and promising applications in materials science.1 Most of the currently investigated systems are based on pro-aromatic or anti-aromatic π -conjugated polycyclic hydrocarbons (PHs), and these studies have revealed that the number of aromatic sextet ring,² strain release³ and spatial distribution of frontier molecular orbitals⁴ all played important roles in determining the diradical character and singlet-triplet energy gap. By applying these fundamental rules, even polyradicaloids can be synthesized.⁵ However, a general problem for the PH-based diradicaloids and polyradicaloids is their intrinsic high reactivity. Thus, chemists also looked for heteroatom-containing open-shell singlet thienoacene⁷ diradicaloids. Indeed, oligothiophene, and have porphyrinoid⁸ based diradicaloids demonstrated reasonably good stability. Herein, we would like to exploit the potential diradical character of another hetero-aromatic molecule, benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (BBT) (Figure 1a).

BBT is a well-known building block for the construction of organic conductors, donor-acceptor type low band gap polymers, and near-infrared (NIR) dyes due to their strong electronwithdrawing nature.⁹ However, another feature of this unique molecule, that is, its diradical character, was not well investigated. BBT can be drawn in a closed-shell form with a hypervalent sulfur atom and an open-shell diradical form with one additional aromatic thiadiazole ring (the pentagon shaded in blue colour, Figure 1a). Therefore, BBT in principle has intrinsic tendency to be diradicals. Such simple analysis was further supported by theoretical calculations that BBT derivatives with various substituents could show tunable diradical character.¹⁰ However, experimentally, these hypothesises were not well validated because the target compounds usually have a small diradical character and a large singlet-triplet energy gap, making

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magnetic measurements difficult. Wudl *et al* first reported the experimental observation of paramagnetic activity of BBT-based donor-acceptor polymers and ascribed the magnetic property to the intrinsic diradical character of BBT.¹¹ To deep understand the origins, oligomer approach is more desirable. The electron-deficiency also implies that BBT-based compounds will have a low-lying HOMO and thus are stable. Therefore, BBT-based diradicaloids could be stable functional materials.



Figure 1. (a) Resonance structures of BBT and acetylene-bridged BBT oligomers **BBT-n**; (b) chain length dependence of the calculated diradical character (y_0) and singlet-triplet energy gap ($\Delta E_{\text{S-T}}$) of **BBT-n** (n=1-6).

In this context, we first calculated the diradical characters (y_0) and the tetraradical characters (y_1) of a series of acetylenebridged BBT oligomers (BBT-n) (Figure 1a). Our spinunrestricted calculations (UCAM-B3LYP/6-31G(d,p)) clearly predict that with increase of repeat unit number of BBT (n), the diradical character index (y_0) quickly increases from 0.025 for BBT-1, 0.30 for BBT-2, 0.63 for BBT-3, 0.82 for BBT-4, 0.92 for BBT-5, to 0.96 for BBT-6 (Figure 1b and Supporting Information (SI)), which can be simply explained by the recovery of one more aromatic thiadiazole sextet ring in each BBT unit in the diradical form. However, the calculated tetraradical characters (y_1) are negligible for all BBT oligomers (Table S1 in SI). At the same time, the singlet-triplet energy gap (ΔE_{S-T}) rapidly decreases from 12.36 kcal/mol for BBT-1, 6.44 kcal/mol for BBT-2, 3.35 kcal/mol for BBT-3, 2.24 kcal/mol for BBT-4, 1.65 kcal/mol for BBT-5, to 1.37 kcal/mol for BBT-6 (Figure 1b). This interesting theoretical result inspired us to synthesize their derivatives and analogues, and experimentally probe their diradical character and magnetic activity. To make soluble compounds, 3,5-di-tert-butylphenyl groups are attached to the termini of BBT units, and the BBT monomer BBT-BP-1 and dimer BBT-BP-2 were successfully synthesized (Scheme 1). During the synthesis, the directly linked BBT dimer BBT-BP-3 was occasionally obtained. To investigate the effect of substituent, electron-donating triphenylamine (TPA) terminated

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analogues **BBT-TPA-1** – **BBT-TPA-3** were also synthesized (Scheme 1). These molecules are supposed to be NIR dyes due to intramolecular charge transfer.



Scheme 1. Synthesis of two series of BBT derivatives: (a) $Pd(PPh_3)_2CI_2$, toluene, 80-100 °C; (b) bis(tributylstannyl)acetylene (0.5 equiv), $Pd(PPh_3)_2CI_2$, toluene, 90-100 °C.

Compound BBT-BP-1 was simply synthesized in 78% yield by Pd-catalysed Stille coupling reaction between the commercially available dibromo- BBT 1 and 2.2 equiv tributyl(3,5-di-tertbutylphenyl)stannane 2 (Scheme 1). When the ratio of 2 to 1 was set to 6:5, the monobromo- BBT intermediate 3 was isolated in 26% yield. Stille coupling reaction of 3 with 0.5 equiv bis(tributylstannyl)acetylene afforded the acetylene-bridged BBT dimer BBT-BP-2 in 19% yield. Prolonging the reaction time (24 h) resulted in the unexpected BBT dimer BBT-BP-3 in 10% yield. Since no reductive species is involved in the reaction, we suppose that the formation of BBT-BP-3 is due to the debromination of 2 followed by homo-coupling of the asgenerated radicals, which is reasonable considering of the intrinsic radical character of BBT. Both compounds BBT-BP-2 and BBT-BP-3 are reasonably stable and can be purified by silica gel column chromatography in air. However, attempted synthesis of longer acetylene-bridged BBT oligomers suffered from their inherent instability associated with their larger diradical character (Scheme S1 in SI). The TPA-substituted BBT analogues BBT-TPA-1 - BBT-TPA-3 were synthesized by using а similar strategy starting from 4-(N,N-di-(4methoxy)phenyl)aminophenyl-tributylstannane 4. By controlling the ratio of 4 to 1, BBT-TPA-1 and the intermediate 5 were obtained in 30% and 13% yield, respectively. Interestingly, during the synthesis of 5, prolonging the reaction time from 12 h to 24 h gave the homo-coupled product BBT-TPA-3 in 54% yield, implying a larger radical character of 5 compared to 3. Compound BBT-TPA-2 were obtained in 26% yield by Stille coupling between 5 and bis(tributylstannyl)acetylene.

Single crystals suitable for X-ray crystallographic analysis were obtained for **BBT-BP-1**, **BBT-BP-2** and **BBT-TPA-3**

(Figure 2).12 Both BBT-BP-1 and BBT-BP-2 form a closely stacked dimeric structure, with a face-to-face distance of about 3.634 Å and 3.341 Å, respectively. A number of [S ···· N] short contacts (2.977 ~ 3.221 Å) are observed between two neighboring BBT-BP-2 molecules lying in the same plane (Figure 2b). Interestingly, the backbone of BBT-BP-2 is bended and approaches to each other in the stacked dimer (Figure 2b) presumably due to the strong intermolecular spin-spin interactions as well as the steric repulsion between the bulky 3,5-di-tert-butylphenyl substituents. The dihedral angle between the two BBT planes is very small, indicating a good πconjugation between the two BBT units. BBT-TPA-3 adopts a twisted structure with a large distortional angle of about 56°, and there are neither close π-stacking between the molecules nor regular [S•••N] close contacts (Figure 2c). Since the highest spin density is expected to locate on the C4 and C8 sites of the BBT unit (Figure 1a), bond length analysis of their neighboring C-C bonds will be valuable for evaluating the relative contribution of the diradical form. In BBT-BP-1, the bonds a and b are 1.413 Å and 1.404 Å, shorter than a typical C(sp²)-C(sp²) bond (~1.47 Å), but much longer than a typical double bond (1.33-1.34 Å), suggesting that the bonds a and b have a certain single bond character and that the thiadiazole ring partially recovers its aromaticity. In BBT-BP-2, the corresponding bonds, d and e (1.420 Å and 1.424 Å) are significantly longer than a and b. indicating a larger diradical contribution, which is further supported by a shortened bond f (1.446 Å) compared to bond c(1.457 Å). The length of the central C(sp)-C(sp) triple bond (1.212 Å) is longer than that in the diphenylacetylene (1.205 Å), in accordance with the cumulenic contribution in the diradical form (Figure 1a). In BBT-TPA-3, the bond length pattern on BBT is comparable with BBT-BP-1, but the bond between the BBT units is very long (1.475 Å) due to large strain. FR-IR measurement (Figure S1 in SI) show that the vibrational band of the C-C triple bond is shifted to lower frequency from BBT-BP-2 (2153 cm⁻¹) to **BBT-TPA-2** (2126 cm⁻¹), indicating a larger diradical character for the latter.

No significant ESR signals were observed for compounds BBT-BP-1, BBT-BP-3, and BBT-TPA-1 at room temperature, suggesting that they have a small diradical character. Indeed, DFT calculations predicted a negligible diradical radical character ($y_0 < 10\%$) and a large singlet-triplet gap for these three molecules (Table 1 and Table S1 in SI). Broad ESR signals for the solid sample were observed for BBT-TPA-2 and BBT-TPA-3 with ge value of 2.0038, 2.0039. Similar calculations predict that BBT-TPA-2 and BBT-TPA-3 have a diradical character of 35.5% and 11.4%, respectively. In both cases, the spins are delocalized throughout the whole π -conjugated skeleton (Figure 3c), which explains the broad feature of the ESR spectrum. Superconducting quantum interference device (SQUID) measurements were also performed on the freshly prepared powder samples and it is found that both BBT-TPA-2 and BBT-TPA-3 have a singlet ground state which can be thermally populated to the paramagnetic triplet excited state. Fitting of the data by Bleaney-Bowers equation gave a singlettriplet gap (ΔE_{S-T}) of -3.2 and -3.66 kcal/mol for BBT-TPA-2 and BBT-TPA-3. Compound BBT-BP-2 respectively. was theoretically calculated to have a moderate diradical character $(y_0 = 30.4\%)$ which is slightly smaller than its counterpart **BBT-**TPA-2. However, the solid sample of BBT-BP-2 only showed very weak ESR and SQUID signals at room temperature. Such

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Figure 2. X-ray structures, molecular packing and selected bond lengths (in Å) for BBT-BP-1 (a), BBT-BP-2 (b) and BBT-TPA-3 (c). Hydrogen atoms are omitted for clarity.



Figure 3. (a) ESR spectra of **BBT-TPA-2** and **BBT-TPA-3** in solid at room temperature. (b) $\chi_M T$ -T curves in the SQUID measurements for **BBT-TPA-2** and **BBT-TPA-3**. (c) Calculated spin density distribution of the singlet biradicals of **BBT-TPA-2** and **BBT-TPA-3**.

phenomenon could be ascribed to strong intermolecular antiferromagnetic coupling *via* π - π interaction and short [S•••N] contacts as revealed by X-ray crystallographic analysis. Heating the solid sample to higher temperatures (from 323 K to 410 K) led to continuous increase of ESR signal and fitting the data by Bleaney-Bows equation gave an estimated singlet-triplet gap of 12.0 kcal/mol (Figure S2 in SI), which can be correlated to an overall effect and is much larger than that in **BBT-TPA-2**. By comparison this two series of compounds, it is clear that extension of π -conjugation length or introduction of electrondonating TPA groups both lead to increased diradical character and decreased singlet-triplet gap. The UV-vis-NIR absorption spectra of all compounds were recorded in DCM solution (Figure 4a and Table 1). Compound **BBT-BP-1** shows a broad absorption with $\lambda_{max} = 572$ nm ($\varepsilon_{max} = 14200 \text{ M}^{-1}\text{cm}^{-1}$). The absorption spectrum of **BBT-BP-2** exhibits a similar band structure but is significantly red-shifted ($\lambda_{max} =$



Figure 4. (a) UV-vis-NIR absorption spectra of BBT-BP-1 – BBT-BP-3 and BBT-TPA-1 – BBT-TPA-3 in DCM; (b) cyclic voltammograms of BBT-BP-1 – BBT-BP-3 and BBT-TPA-1 – BBT-TPA-3 in DCM.

Table 1. Optical and electrochemical data, calculated diradical character	(\underline{v}_0) and measured singlet-triplet gap (ΔE_{S-T}) of the BBT derivatives. ^a
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Comp.	λ_{\max} (nm)	ε _{max} (M⁻¹ cm⁻¹)	E _{1/2} ^{ox1} (eV)	E _{1/2} ^{ox2} (eV)	E _{1/2} ^{red1} (eV)	E _{1/2} ^{red2} (eV)	E _{1/2} ^{red3} (eV)	E _{1/2} ^{red4} (eV)	HOMO (eV)	LUMO (eV)	Eg ^{EC} (eV)	E ^{opt} (eV)	y 0	Δ <i>E</i> _{S-T} (kcal/mol)
BBT-BP-1	572	14200	0.92	1.23	-1.24	-	-	-	-5.70	-3.57	1.95	1.90	0.026	-
BBT-BP-2	700	26900	0.82	1.00	-0.88	-1.15	-1.83	-2.01	-5.64	-4.08	1.56	1.57	0.304	-12.0
BBT-BP-3	587	25700	0.99	-	-1.09	-1.27	-	-	-5.74	-3.86	1.88	1.83	0.081	-
BBT-TPA-1	754	22300	0.24	0.90	-1.08	-1.26	-1.96	-2.19	-4.98	-3.78	1.20	1.36	0.050	-
BBT-TPA-2	892	41700	0.18	0.98	-0.94	-1.17	-1.80	-2.05	-4.92	-3.95	0.97	1.11	0.355	-3.20
BBT-TPA-3	754	42800	0.13	0.79	-1.20	-1.39	-2.06	-2.25	-4.83	-3.69	1.14	1.38	0.114	-3.66

^aHOMO and LUMO levels were esimated according to the equations: HOMO=-($4.8+E_{ox}^{onset}$) eV and LUMO=-($4.8+E_{red}^{onset}$) eV, where E_{ox}^{onset} and E_{red}^{onset} are the onset potential (*vs* Fc⁺/Fc) of the first oxidative and reductive redox wave, respectively. E_g^{Ec} is electrochemical energy gap calculated from LUMO-HOMO. E_g^{opt} is optical energy gap derived from lowest energy absorption onset in the electronic absorption spectra.

700 nm, $\varepsilon_{max} = 26900 \text{ M}^{-1}\text{cm}^{-1}$) due to more extended π conjugation. However, **BBT-BP-3** just displays a slight red shift ($\lambda_{max} = 587 \text{ nm}, \varepsilon_{max} = 25700 \text{ M}^{-1}\text{cm}^{-1}$) due to its twisted structure. With the incorporation of electron-donating groups, the absorption spectra of **BBT-TPA-1**, **BBT-TPA-2** and **BBT-TPA-3** are dramatically red shifted into the NIR region, with λ_{max} apearing at 754, 892 and 754 nm respectively, owing to intramolecular charge transfer characcter. At the same time, the intensity increases.

Cyclic voltammetry measurements were also performed for the two series of BBT derivatives in anhydrous DCM and they all showed amphoteric redox behavior (Figure 4b and Table 1). For BBT-BP-1, two quasi-reversible oxidation waves and one reversible reduction wave were observed. Passing to BBT-BP-2, however, four reversible reduction waves were observed, indicating strong electronic interactions between the BBT units. The LUMO level is also dramtically decreased from -3.57 eV for BBT-BP-1 to -4.08 eV for BBT-BP-2 while the HOMO is slightly lifted up. For the twisted dimer BBT-BP-3, two reversible reduction waves can be determined, implying a moderate coupling between two BBT units, and the LUMO (-3.86 eV) lies between those of BBT-BP-1 and BBT-BP-2. The TPAsubstituted compounds BBT-TPA-1 - BBT-TPA-3 exhibit significantly lowed first oxidation potentials correlated to the oxidation of the TPA unit. Three (quasi)reversible reduction waves are observed for BBT-TPA-1, and its LUMO level (-3.78 eV) is lower than that BBT-BP-1, presumably due to its larger diradcial character. Compounds BBT-TPA-2 and BBT-TPA-3 show four and three reversible reduction waves, respectively, and the LUMO level is slightly lifted up due to the electrondonating effect of TPA. Due to the intramolecular charge transfer, the electrochemical energy gaps (E_g^{EC}) of BBT-TPA-1 – BBT-TPA-3 are significantly smaller than the corresponding compounds BBT-BP-1 - BBT-BP-3, in accordance with the measured optical energy gaps (E_g^{Opt}) (Table 1).

In summary, we have theoretically and experimentally deomonstrated that BBT could be used as a useful building block for construction of stable open-shell diradcialoids. It is found that by increasing the π -conjugation length or introduction of electron-donating groups to the termini, the diradical character increases, leading to prominent paramagnetic activity and small energy gap. The intensive NIR absorption of the TPA-substituted BBTs **BBT-TPA-1** – **BBT-TPA-3** implies their potential applications in bio-imaging. Our studies provided rational design principle and synthetic strategy toward BBT-based diradicaloids and NIR dyes.

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COMMUNICATION

BBT-based diradicaloids! We theoretically and experimentally investigated the potential of using BBT as a general building block for stable open-shell singlet diradicaloids. Extension of π -conjugation and substitution by electron-donating groups result in an increase of diradical character and decrease of singlet-triplet energy gap.



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diphenylacetylene was downloaded from CCDC (no. 853113) for

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