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Confinement of the Triplet States in π-Conjugated BODIPY Dimers Linked with Ethynylene or Butadiynylene Bridges: A Different View on the Effect of Symmetry

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Abstract: Understanding the impact of the excited state wavefunction confinement is crucial for the engineering of the photophysical properties and applications of organic chromophores. In the present contribution, the localization of the triplet state wavefunctions of some symmetric ethyne / butadiyne bridged BODIPY dimers and asymmetric BODIPY derivatives presenting extended π-conjugation frameworks is studied with time-resolved electron paramagnetic resonance spectroscopy and time-dependent density functional theory computations. Based on the Zero Field Splitting *D* parameters, we conclude that the triplet state wavefunctions are highly *localized* on one BODIPY unit in the symmetric dimers, which is consistent with the *ab initio* modelling that finds delocalized triplet state destabilized by 12 ~ 14 kcal mol^{-1} as compared to its localized counterpart. The result provides a new insight into the study of triplet excited state confinement and the design of molecular wires or photosensitizers for photovoltaics and photocatalysis.

Introduction

The localization of the electronic excited state wave functions in π–conjugated organic oligomers and polymers plays a paramount role in their photophysical processes,[1] such as energy transfer,[2] electron transfer,[3] and electron spin transport,[4] and can consequently be tuned to optimize applications of these materials in photovoltaics,[5] photocatalysis,[6] molecular electronics, as well as molecular probes,[7] etc. The fundamental understanding of the triplet state formation (through intersystem crossing, ISC), together with the control of both the triplet state lifetimes[8] and delocalization are undoubtedly important tasks.[9] While the energy of the electronically excited states can be well characterized by steady state and time-resolved transient optical absorption/emission spectroscopies, their spatial confinement on the molecular skeleton is hardly estimated by above methods.

In this context, the pulsed laser excited time-resolved electron paramagnetic resonance (TREPR) spectroscopy stands as a powerful tool to quantify the spatial confinement of the triplet state wave function.[5b,10] The distance between the two unpaired electrons in the triplet state can be well characterized by the zero-field splitting (ZFS) parameters of the triplet state, *i.e.*, the *D* parameter, in a point-dipole approximation.[11] In general, the relative magnitude of the *D* parameter can be used to compare the degree of delocalization of the triplet excited state. And the symmetry of the triplet state wavefunction (*e.g.,* oblate or prolate) can be deduced by the sign and magnitude of the ZFS *D* and *E* parameters.[10a]

Although the effect of molecular and orbital symmetries on the radiative transitions of the electronically excited states for organic molecules are well known, explaining for instance the weak absorption and long fluorescence lifetimes of benzene and pyrene,[12] the impact of molecular symmetry on the spatial confinement of the triplet state wavefunction remains underexplored. Previously it was found that the spatial confinements differ for the S_1 and T_1 states of a twisted [28]hexaphyrin.[13] Likewise, the triplet state delocalization in *meso*-to-*meso* ethyne or butadiyne-bridged porphyrin oligomers was studied, and it was found that the spatial confinement of the triplet state depends on the symmetry of the units in the oligomer, *i.e.*, when the porphyrin units in the dimer are chemically equivalent, the T_1 state is highly *delocalized* on both units, but the T_1 state becomes *confined* on one unit of the dimer otherwise.[9d] TREPR studies on *β*, *meso*, and *β*-fused porphyrin oligomers indicated that the triplet excited states delocalize on more than two porphyrin macrocycles.[1a] In oligo(*p*-phenyleneethynylene)s (OPEs) the singlet state wave function is believed to be delocalized, whereas the triplet state wave function appears more confined.[1b] Similar results were reported for oligothiophenes.[14]

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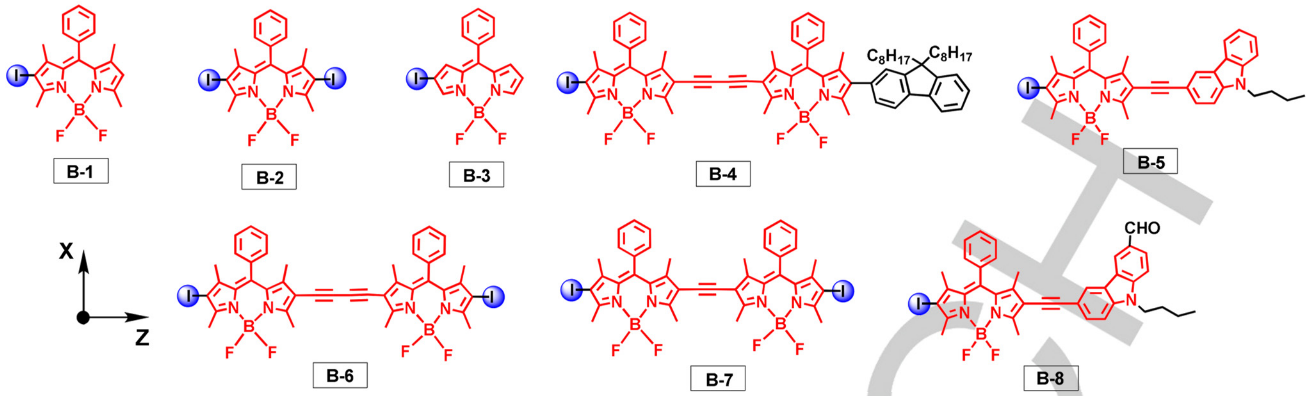

Scheme 1. Molecular structures of the compounds investigated in this work. The calculated Zero Field Splitting (ZFS) principal axes are shown.

Previously, we prepared a series of iodo-BODIPYs, including the ethyne/butadiyne linked BODIPY dimers, as triplet photosensitizer for triplet-triplet annihilation upconversion.[15] The absorption and fluorescence wavelengths of the BODIPY derivatives with the largest π-conjugation are redshifted by up to ~100 nm as compared to those of the BODIPY monomer, indicating that the singlet excited state wavefunction is delocalized. However, preliminary computations indicated that the spin density distribution of the T_1 state is mainly localized on a single BODIPY unit. In other words, the confinement of the singlet and triplet excited state wave functions do differ in these BODIPY derivatives. However, as stated above, it is not straightforward to study the spatial extent of the triplet state wave function with standard optical spectroscopy techniques.

Herein, we use TREPR spectroscopy to probe the spatial confinement of the triplet excited state wavefunction in iodo-BODIPY derivatives. Our study demonstrates that the conclusion previously obtained for linear porphyrin oligomers,[9d] does not necessarily stand as a general rule. As detailed below, we indeed obtained very different results as compared with previous studies focused on macrocyclic chains.[9b,9d]

Results and Discussion

Following our previous work,[15] we study several BODIPY dimers bearing a ethyne/butadiyne π-conjugation linker (see **B-6** and **B-7** in Scheme 1). To evaluate the impact of symmetry which was reported to be crucial, on the spatial confinement of the triplet state wave function, we also investigate an asymmetric BODIPY dimer (**B-4** in Scheme 1), as well as the iodo-BODIPY monomers **B-1**, **B-2**, and **B-3**, and the π-extended BODIPY monomers (**B-5** and **B-8**), that can be used as reference compounds.

The UV/Vis absorption spectra of all compounds were measured (Figure 1). Interestingly, for **B-7**, two absorption bands centered at 575 nm and 618 nm are observed, which clearly departs from the expected “cyanine” band shape of BODIPY derivatives. We therefore explored the ground state potential energy surface of **B-7** (see computational details in the Supporting Information), and several isonergetical ground state (GS) conformers were found (energy difference : ΔG ~ 0.2 kcal mol^{-1} between the most stable ones, Figure 2). The main geometrical difference between the two conformers is the dihedral angle (Φ) between the two BODIPY units.

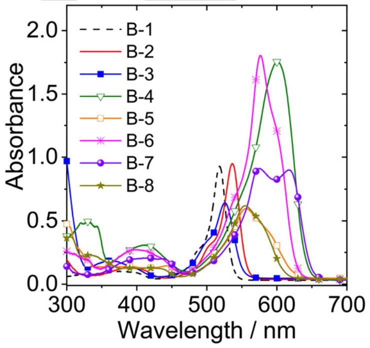

Figure 1. UV/Vis absorption spectra of the compounds in toluene, $c = 1.0 \times 10^{-5}$ M, 25 °C.

The maximal absorption wavelength difference between the two conformers, as obtained by vertical time-dependent density functional theory (TD-DFT) computations is 29 nm (M06-2X) or 70 nm (PBE0), the most coplanar structure logically leading to the redshifted absorption. We note that the measured separation between the two absorption bands is 43 nm. To go further we simulated Boltzmann-weighted vibrationally-resolved spectra for **B-7** considering all found conformers and the fit with experiment is fine with the presence of two clear peaks of similar heights (Figure S29), confirming that it is not unreasonable to ascribe the two experimentally observed absorption bands to the presence of several conformers. Similar results are observed for **B-4** and **B-6** (Supporting Information, Figures S24-S29). This result is interesting, and it goes against the common intuition that π–conjugation extension systematically stabilizes a molecule.

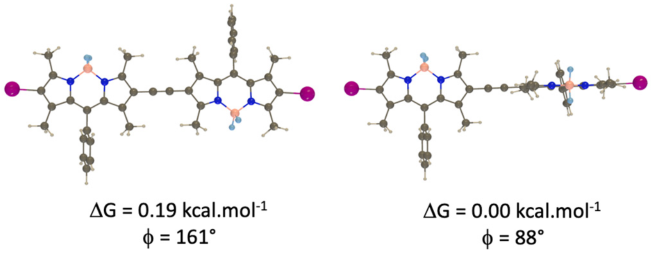

Figure 2. Two most stable conformers (M06-2X/6-31G(d) and LanL2DZ for I) of **B-7**. The relative free energies of the two conformers as well as the dihedral angle between the two BODIPY units in the conformers are given. See also Figure S26.

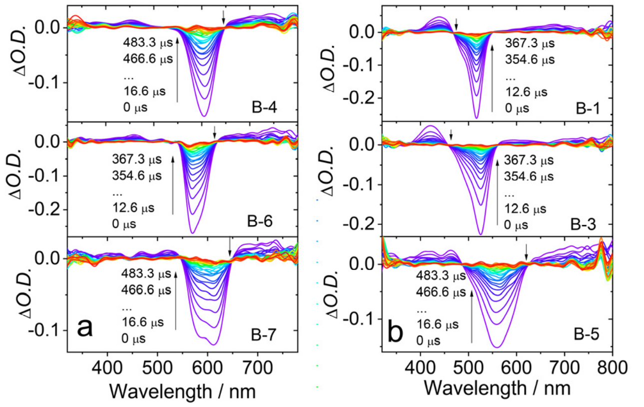

Figure 3. Nanosecond transient absorption spectra of the a) BODIPY dimers **B-4**, **B-6** and **B-7** and the b) BODIPY monomers **B-1**, **B-3** and **B-5**. $c = 1.0 \times 10^{-5}$ M in deaerated toluene, $\lambda_{ex} = 532$ nm, 20 °C.

The triplet excited states of the monomers and the dimers were studied with nanosecond transient absorption (ns-TA) spectra (Figure 3). For the monomers, significant ground state bleaching (GSB) bands are observed in the 500–600 nm range, and weaker excited state absorption (ESA) bands are found in the range of 400 – 500 nm and beyond 600 nm. These results show that for these BODIPY derivatives, the $T_1 \rightarrow T_n$ transition probability is much lower than the $S_0 \rightarrow S_1$ transition. Red-shifted GSB bands are observed for the dimers (Figure 3a) and in this case the ESA bands are also weak. The theoretical calculations were performed to identify positions of $T_1 \rightarrow T_n$ transition (Figures S31, S32 and Table S1). The ESA peaks recorded in the ns-TA spectrum (Figure 3) can be well assigned. Clearly, from these ns-TA spectra, no information on the spatial confinement of the triplet state wave function can be derived. The triplet state lifetimes of the compounds in fluid solution at room temperature are in the 143 – 225 μs range. In solid matrix (poly(methylmethacrylate), *i.e.*, PMMA, film), the triplet state lifetimes are 0.7 – 1.4 ms. We also used triplet sensitization experiments (anthracene as triplet energy donor and BODIPY derivative as triplet energy acceptors) to observe the energy transfer process from anthracene to the BODIPY derivatives (Figures S10–S17). In addition, in order to study the ISC process, we also measured the femtosecond transient absorption spectrum, and obtained the time constant of the ISC (75 ps–575 ps, Table 1) to ensure high triplet state quantum yield. The triplet signals of BODIPY derivatives obtained in above experiments well match with these observed in ns-TA.

Long triplet state lifetimes, together with the efficient ISC, and the high T_1 state energy (despite of the decreased S_1 state energy due to the extended π-conjugation frameworks in the dimers, thus red-shifted absorption), make the dimers as ideal triplet photosensitizers. The photophysical parameters are summarized in Table 1.

We do not observe any significant effect of the methyl groups on the photophysical property of the BODIPY core of **B-1**, **B-2**; and **B-3**, the absorption/emission wavelengths and the ISC efficiency are all similar (Table 1). However, different ZFS parameters ($|D|$ and $|E|$ values) are obtained in the TREPR spectra (Figure 4). For instance, **B-3**, which does not bear methyl groups on the BODIPY core, shows a larger $|D|$ value (3089 MHz) than both **B-1** (2623 MHz) and **B-2** (2948 MHz, see Table 2). Interestingly, the experimental values do not follow the generally accepted statement that larger π-systems are associated with reduced ZFS parameters. Indeed, in **B-3** there is a larger density of the two Singly Occupied Molecular Orbitals (SOMO) on the (less twisted) *meso*-phenyl group than in **B-1** (see Figure 5), whereas the $|D|$ value of **B-3** is larger than its **B-1** counterpart.

The inability of the ZFS D parameter alone to reveal in some cases the spatial delocalization of the triplet state wave function was demonstrated for oligo(*p*-phenylenethynylene)s (OPEs),[1b] as well as for the zinc porphyrin monomer and the *meso*-to-*meso* ethyne or butadiyne-linked oligomers.[9b,9d] Indeed, it was shown that the triplet state delocalization in the zinc porphyrin dimer can be underestimated if the ZFS D value is the only parameter considered.[9a,9d] Clearly, the confinement of the triplet excited states in other chromophores needs to be studied with the TREPR spectral technique, so as to verify the relationship between the molecular structure and confinement of the triplet state wavefunction. In a simplified view, the ZFS D value gives information about the distance between the two unpaired electrons of the triplet state. This is a reasonable approximation

Table 1. Photophysical properties of the compounds [a]

	λ_{abs} [b] [nm]	ε [c]	λ_{em} [d] [nm]	τ_F [e] [ns]	Φ_F [f] [%]	τ_T [g] [μs]	τ_T [h] [ms]	Φ_Δ [i] [%]	τ_{ISC} [j] [ps]
B-1	518	0.93	533	0.46	6.2	225	1.3	69	249
B-2	536	0.95	554	0.32	3.6	153	0.9	75	198
B-3	526	0.64	551	0.23	1.2	146	0.7	56	75
B-4	601	1.76	639	1.24	29.7	188	2.0	21	–[k]
B-5	557	0.59	630	0.58	7.6	159	1.4	30	351
B-6	576	1.80	623	0.53	13.0	143	1.4	39	382
B-7	575/618	0.91/0.90	642	0.68	13.5	145	0.9	37	575
B-8	555	0.62	612	0.70	11.0	184	1.4	35	–[k]

[a] In toluene (1.0×10^{-5} M). [b] UV/Vis absorption maximum. [c] Molar absorption coefficient, ε: 10^5 M^{-1} cm^{-1}. [d] Fluorescence emission maximum. [e] Fluorescence lifetimes. [f] Absolute fluorescence quantum yields, determined with optical integration sphere. [g] Intrinsic triplet state lifetime in toluene eliminates the self-quenching effect of TTA (see Supporting Information for details). [h] Triplet state lifetime in PMMA polymer film. [i] Singlet oxygen quantum yield ($^1O_2$) with **B-2** as standard ($\Phi_\Delta = 0.87$ in DCM). [j] Time constant of the ISC obtained by femtosecond transient absorption spectra processed by global fitting. [k] Not measured.

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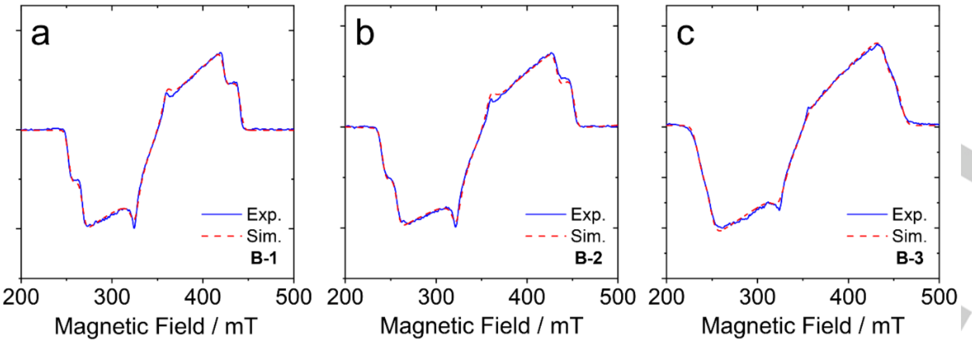

Figure 4. TREPR spectra of the BODIPY monomers a) **B-1**, b) **B-2**, c) **B-3.** The spectra were collected at *ca.* 3 μs after laser flash (532 nm, 10 mJ per pulse, 10 Hz repetition rate) in frozen toluene at 85 K. The red curves are computer simulations of the spectra of the triplet states with parameters given in Table 2.

as long as the two electrons are localized in different regions of the molecule. The *E* parameter, instead, measures the rhombicity or the non-axiality of the triplet state wavefunction.[10a–c,16] The TREPR spectral results therefore indicate that the shape of the T_1 wavefunction differs for the three monomeric dyes. Another difference is that, although the general electron spin polarization (ESP) phase pattern of the TREPR spectra of the triplet excited states of the three dyes is the same i.e. (*e*, *e*, *e*, *a*, *a*, *a*), where '*e*' stands for emission and '*a*' stands for enhanced absorption, the population rates (ΔP) of the spin sublevels of T_1 state are different for **B-1**, **B-2**, and **B-3** (Table 2). Based on these results, it seems that the methyl groups at 1,3,5,7-positions play a role in determining the triplet wavefunction extension and the population rates of the triplet sublevels.

The spin density difference plots of **B-1**, **B-2**, and **B-3** (Figure 5), show triplet states localized on the BODIPY core without significant contribution on the iodine atom(s). As noted above, the spin distributions are similar for **B-1** and **B-2**, but obviously differ in **B-3** with a small contribution from the *meso*-phenyl ring and a significant contribution on the C2 position bearing the iodine atom.

We have previously shown that with the extension of the π-conjugation framework of the BODIPYs (*e.g.*, in **B-4**, **B-5**, **B-6**, and **B-7**), the steady state UV/Vis absorption maxima redshift as compared to the monomer (e.g., **B-2**).[15] These results point to a more delocalized S_1 state in the former compounds.

The TREPR spectra of T_1 of all BODIPY dimers were measured (Figure 6). Interestingly, the ESP pattern of the TREPR spectra of the triplet excited states of the dimers **B-4**, **B-6**, and **B-7** are (*e*, *e*, *e*, *a*, *a*, *a*), which are exactly the same as the monomers (**B-1**, **B-2**, and **B-3**). These findings are different from the zinc porphyrin monomer and its butadiyne-linked dimer, for which the ESP pattern of the T_1 state TREPR spectrum of the dimer (*a*, *a*, *e*, *a*, *e*, *e*) differs from that of the monomer (*a*, *a*, *a*, *e*, *e*, *e*).[9b]

Importantly, the ZFS |*D*| parameter of the dimers (2535 MHz for **B-7** and 2700 MHz for **B-6**, respectively) are almost the same as in the corresponding monomers (2623 MHz ~ 3089 MHz). For the zinc porphyrin complexes, the ZFS |*D*| parameter of the butadiyne-linked dimer (1125 ± 5 MHz) was found significantly larger than that of the of monomer (895 ± 5 MHz).[9b] However, the hyperfine coupling constants clearly pointed to a fully delocalized triplet state wavefunction for the porphyrin dimer, which does not fit the |*D*| values. The reason for this apparent contradiction is the different ZFS principal axes orientation for the triplet states of the monomer and the dimer.[9b] Indeed, the larger ZFS |*D*| parameter of the butadiyne-linked porphyrin dimer with respect to the monomer was attributed to the spin alignment in the dimer.[9a] The ZFS *E* parameter of the dimers are also similar to those of the monomers, and this indicates that the T_1 wavefunction of the dimers is similar to that of the monomers.[9a] For our systems, the ESP and the population rates of the spin sublevels of the BODIPY dimers and monomers are similar, which is a different trend from that reported in zinc porphyrin systems.[9b,9d,17]

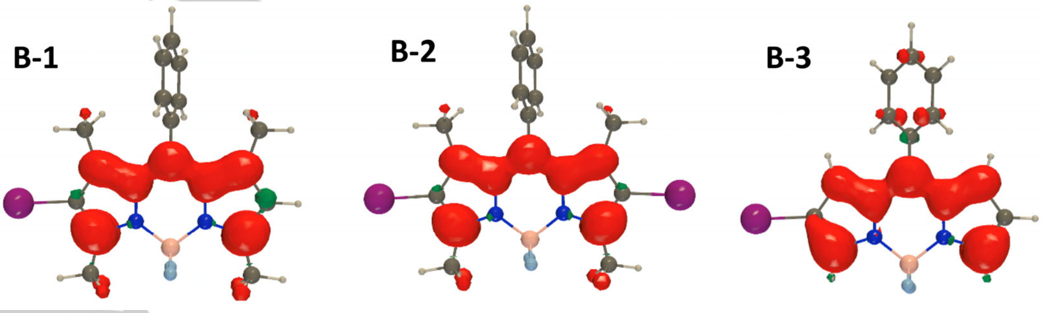

Figure 5. Spin density surfaces of the triplet excited states of **B-1**, **B-2**, and **B-3**. The spin densities were calculated at the PBE0/6-311+G(2d,p) level [LanL08(d) for I] on the M06-2X/6-31G(d) [LanL2DZ for I] structures, considering the minimal T_1 geometry as given by unrestricted DFT. Contour threshold: 0.004 au.

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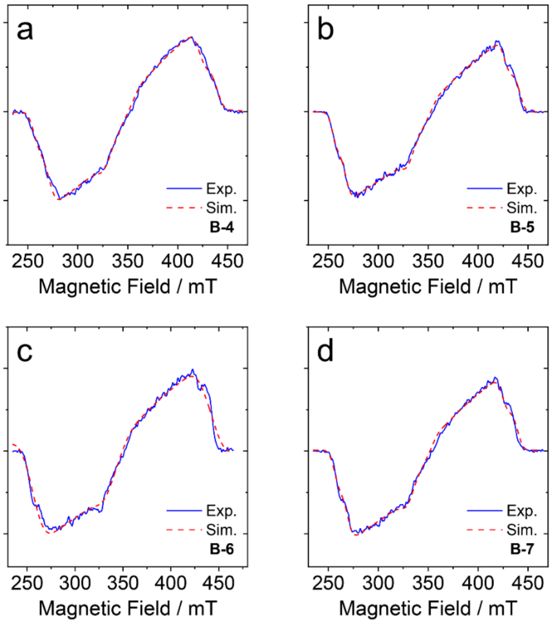

Figure 6. TREPR spectra of a) **B-4**, b) **B-5**, c) **B-6** and d) **B-7**. The spectra were collected at ca. 3 μs after laser flash (532 nm, 10 mJ per pulse, 10 Hz repetition rate) in frozen toluene at 85 K. The red curves are computer simulations of the spectra of the triplet states with parameters given in Table 2.

In order to rule out the same situation for our BODIPY monomers and the dimers, *i.e.*, different orientations of the ZFS principal axes in the BODIPY monomers and dimers, we carried out computation of the ZFS principal axes of the monomers and dimers, to confirm that the ZFS principal axes orientation is the same in monomers and dimers. Table 2 provides the computed ZFS parameters and compared them to the experimental values. Note that the calculation of ZFS parameters with DFT or complete active space self-consistent field (CASSCF) is not a simple task and significant errors are not uncommon.[10b,18,19]

For distributed wavefunctions in organic radicals, point dipole approximation emerges to be a simple method that generally provides reasonable results.[10a,20] Here, we adopted a modified point dipole approximation, assuming that molecular orbitals (MO) of the unpaired electrons are all π orbitals. An AM1 electronic distribution determined on DFT optimized geometries was used, after checking that. AM1 and DFT spin densities are comparable. The selected model accounts for the dependence of the interaction between the two charge densities localized over two *p*-orbitals on the relative orientation of the *p*-axis, using a phenomenologically cosine dependence for the elements in the normal calculation of the ZFS parameters by point dipole approximation (see the Supporting Information for details).[21] The results of Table 2 show that the difference between the calculated and the experimental *D*-value is between *ca.* 10 and 20%. The anisotropy of the X/Y components is larger for the calculated values than the experimental one, and it is around 200 MHz in terms of the $E = (Y-X) / 2$ values for both monomers and dimers. In all the calculation, the Z-value is along the direction of major extension of the molecule. In dimers, the direction is not much changed from that of isolated BODIPY units, confirming that no change in principal axis occurs.

Previously, the study on the cyclic porphyrin nanorings and butadiyne-linked linear porphyrin oligomers[9d] showed that in the symmetric case, the orientation of the ZFS principal axes changed from the monomer to the ethyne-linked dimer, thus the degree of the T_1 delocalization was assessed based on the hyperfine coupling constants (which are determined with electron nuclear double resonance, ENDOR experiments), not the ZFS *D* parameters.[9d] Our results for the ethyne-linked BODIPY dimers show that the previous conclusions do not hold in the present case, as the T_1 state wavefunction is localized on one BODIPY moiety even in the case of a fully symmetric structure, *e.g.*, **B-6** and **B-7** (see below for DFT results). We have treated artificially planar/delocalized **B-6** and **B-7** systems (relatively high in energy, *vide infra*) and the ZFS parameters are very small in these cases. Indeed, for **B-6** with dihedral angle of 180.0° geometry, for which the T_1 state wave function is rather distributed throughout the whole molecule (see below), small ZFS values are computed ($D = -352.0$ MHz and $E = -32.3$ MHz), almost one order of magnitude smaller with respect to experimental values, clearly confirming the above analysis.

Table 2. *D* and *E* ZFS parameters and relative population rates of the zero-field spin states. The calculated ZFS principal values X, Y and Z are also given.

	Calc./ MHz [a]					Exp. [b]		
	X	Y	Z	*D*	*E*	|*D*| / MHz	|*E*| / MHz	Δ*P* [c]
B-1	−265	−1855	2120	−3180	−795	2623	558	0.46
B-2	−264	−1874	2138	−3207	−805	2948	637	0.46
B-3	−225	−2081	2306	−3459	−928	3089	745	0.28
B-4	−222	−1813	2035	−3053	−796	2587	545	0.46
B-5	– [d]	– [d]	– [d]	– [d]	– [d]	2587	585	0.46
B-6	−247	−1858	2105	−3158	−806	2700	600	0.40
B-7	−222	−1821	2043	−3065	−799	2535	587	0.46
B-8	−231	−1835	2066	−3100	−802	2652	610	0.46

[a] Modified point dipole approximation, assuming that MO of the unpaired electrons are all π orbitals in MHz. [b] Measured in frozen toluene solution at 85 K with excitation at 532 nm, 10 mJ per pulse, 10 Hz repetition rate. [c] $\Delta P = |P_X - P_Y| / |P_Z - P_Y|$. [d] Not calculated.

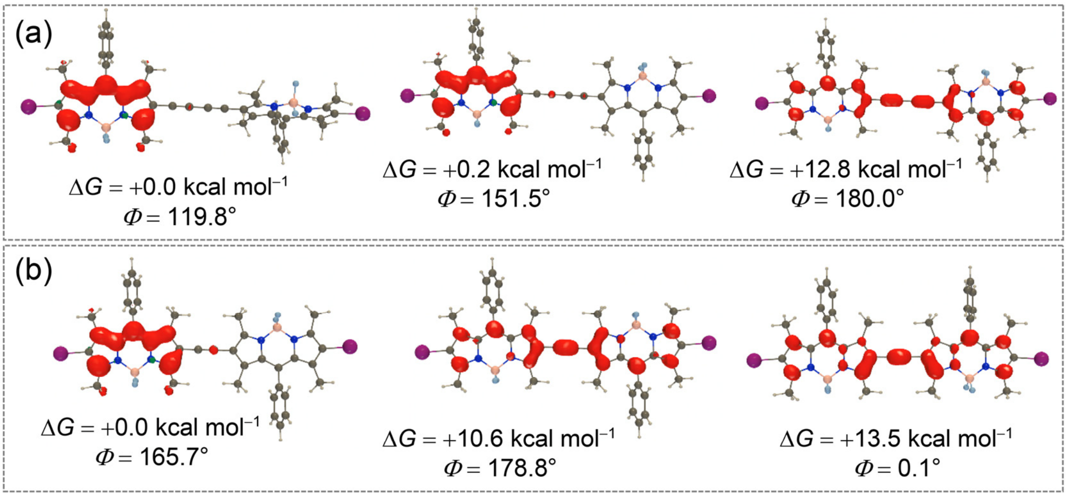

Figure 7. Electron spin density surfaces of the different conformers at the lowest adiabatic triplet excited state potential energy surfaces of a) **B-6** and b) **B-7**. See caption of Figures. 2 and 5 for more details.

In the porphyrins, it was demonstrated that although the T_1 character drastically changes from the monomers to the dimers, the *D* magnitude does not vary significantly.[9d] In order to verify this, we computed the ZFS principal axes and the results show that for the ethyn-linked BODIPY dimers, the ZFS principal axes are the same to the BODIPY monomers.

To attain further insights into the triplet excited states of the dimers, their lowest adiabatic triplet excited state potential energy surfaces were explored with theory. In the case of the asymmetric **B-5** only one conformer bearing the spin density localized on the BODIPY moiety could be located (Figure S30). Indeed, a geometry optimization starting from an optimized carbazole triplet led back to a triplet centered on the BODIPY core. For the symmetric **B-6** and **B-7** dimers, different conformers on the T_1 potential energy surface could be located (Figure 7). For **B-6** three different conformers were obtained. The conformers bearing the spin density localized only in one BODIPY unit are clearly the most favored ones energetically, with small variations depending on the relative orientations of the two BODIPY units. Interestingly, the conformer showing delocalized spin density between the two BODIPY units is highly destabilized (*i.e.*, +12.8 kcal/mol above the lowest energy conformer). Similar conclusions are obtained for **B-7**, where the lowest energy conformer also corresponds to the one confining the spin density on only one BODIPY unit. These DFT results indicate that the triplet state localized on one BODIPY moiety is very stable, supporting the results observed in the above experiments.

The experiments show that the width of the TREPR spectra for the monomers and the dimers are similar, and also confirmed that the orientation of the ZFS tensors does not change from the monomer to the dimer. This was assessed thanks to measurements in liquid crystals (LC's. Figure 8). Indeed, the rod-like **B-6** or **B-7** molecules were dissolved in nematic LC E7. Subsequently the sample was oriented in a high magnetic field (B = 500 mT) at room temperature, where the LC is nematic, and then cooled below the nematic/crystalline transition temperature in order to have a macroscopic orientation of the nematic directors, and, consequently, of long molecular axes of **B-6** and **B-7**. The TREPR spectra were acquired with the orientation vector parallel or perpendicular to the magnetic field.

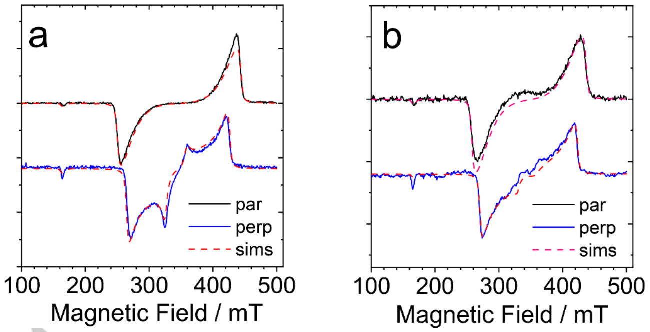

Figure 8. TREPR spectra of a) **B-6** and b) **B-7** in liquid crystal E7 at 100 K with macroscopic orientation of the nematic directors parallel (par) and perpendicular (perp) to the magnetic field. The solution of liquid crystal E7 with corresponding compound has been heated up to ~50 ºC and placed in cryostat at room temperature, than it was gradually cooled down to 100 K with static magnetic field 500 mT being applied. The spectra were collected at *ca.* 3 µs after laser flash (532 nm, 10 mJ per pulse, 10 Hz repetition rate).

The simulations were obtained by assuming an orienting potential with an energy barrier of 5–6 kT. As clearly visible from the spectra, and confirmed by the simulation, the strongest signal on both sides of the spectrum correspond the ESP of the Z-axis, this means the Z-axis is oriented parallel to the nematic director (and therefore to the long molecular axis). As for the monomer it was already established that the Z-axis of the dipolar tensor is along the major extension direction of the BODIPY monomer (parallel to the nitrogen-nitrogen direction), there is no change in direction orientation of the ZFS principal axes in going from the monomer to the dimers.

Conclusion

In summary, we studied the triplet state wave function confinement in selected BODIPY dimers, in which the two BODIPY units are connected by ethynyl or butadiyne linkers, with pulsed laser excited time-resolved electron paramagnetic resonance (TREPR) spectroscopy and theoretical calculations. Although the singlet exciton is delocalized in the dimers as demonstrated by the redshifted absorption and emission as compared to the monomer, the triplet state wave function is highly localized on one unit in these molecules with large π-conjugation framework, based on the Zero Field Splitting (ZFS) parameter *D* values and the analysis of the ZFS principal axes. This differs from the common intuition that large π-conjugation system leads to delocalized excitons. These results are also different from the previously reported TREPR spectral study of the *meso*-to-*meso* porphyrin oligomers, where it was proposed that the triplet state wave function is delocalized for the dimers with symmetric molecular structures, but localized for asymmetric dimers. The DFT analyses indicate that the delocalized triplet state in the current dimers is destabilized by 12 ~ 14 kcal mol^{-1} as compared to its localized counterpart, which fully fits the experimental findings. The results show that π-conjugation does not systematically stabilize the excited state of a molecule, at least in the case of the T_1 states investigated here, and that symmetry is not the sole parameter explaining this effect. Our studies not only provides a new idea for the in-depth understanding of the excited states of organic chromophores, but also facilitates the design and development of molecular wires, organic photovoltaics materials, and high-performance photosensitizers. Further study on other molecular systems is in progress in our laboratory.

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Conflict of interest

The authors declare no competing financial interests.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Electron Paramagnetic Resonance • Electron Spin • Intersystem Crossing • Triplet State • Zero Field Splitting

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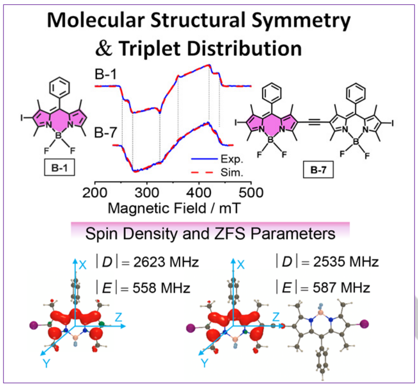
Entry for the Table of Contents

RESEARCH ARTICLE

Text for Table of Contents

The triplet wave functions of BODIPY dimers with symmetrically structured ethynylene or butadienylene linker are highly localized on one BODIPY moiety, which differs from previous findings for *meso*-to-*meso* porphyrin oligomers. This study provides a new understanding of triplet state confinement and molecular symmetry.



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Confinement of the Triplet States in π-Conjugated BODIPY Dimers Linked with Ethynylene or Butadiynylene Bridges: A Different View on the Effect of Symmetry