

## SUPPORTING INFORMATION:

### GENERATION OF MULTIPLE TRIPLET STATES IN AN ORTHOGONAL BODIPY DIMER: A BREAKTHROUGH SPECTROSCOPIC AND THEORETICAL APPROACH

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## ELECTRONIC STRUCTURE CALCULATIONS

### Correction of singlet and triplet excitation energies

In a recent study [J. Chem. Theory Comput. 2021. DOI: 10.1021/acs.jctc.1c00544] we have rationalized the errors of TDDFT approximations in the calculation of transition energies to the lowest excited triplet ( $T_1$ ) and singlet ( $S_1$ ) states of BODIPY. TDDFT systematically overestimates (underestimates) the  $S_1$  ( $T_1$ ) energies, with the magnitude of the errors depending on the employed exchange-correlation functional. Interestingly, in our study, we concluded that despite the inaccuracy of TDDFT in the excitation energies, the electronic character of singlet and triplet states can be well described with TDDFT calculations. These results allow us to study the present molecules (PM546, PM567 and dimer **1**) with TDDFT. Obtained energies are corrected upon the expected errors (Table S1).

We foresee that charge transfer (CT) states, that is, excitations with weak electron/hole overlap, can play a role in the BODIPY dimer studied here. Therefore, in our TDDFT calculations we have chosen to use a range-separated functional, CAM-B3LYP [Chem. Phys. Lett. 2004, 393, 51], which is able to properly deal with CT states and has shown excellent results in the characterization of electronic states in organic systems. Comparison between CAM-B3LYP energies and highly accurate CASPT2 results for the BODIPY monomer (Figure S1), allows to quantify the errors in the low-lying excitations (Table S1). The active space in CASPT2 calculations comprises 12 electrons in 11 orbitals, amounting to the complete set of  $\pi$  valence orbitals, as recommended in references [J. Chem. Theory Comput. 2015, 11, 2619-2632] and [J. Phys. Chem. A 2013, 117, 1665-1669].

Table S1. Vertical excitation energies (in eV) to the lowest singlet and triplet excited states of BODIPY (Figure S1) computed with the CAM-B3LYP functional and CASPT2. All calculations were done with the cc-pVTZ basis set. CAM-B3LYP  $T_1$  energies were obtained with the TDA, while  $S_1$  with full TDDFT.

state	CAM-B3LYP	CASPT2	error
$T_1$	1.56	1.86	-0.30
$T_2$	3.20	3.20	0.00
$T_3$	3.40	3.42	-0.02
$S_1$	2.99	2.48	0.51
$S_2$	4.10	3.84	0.26

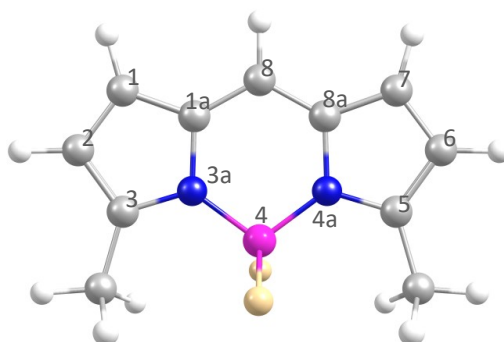


Figure S1. Molecular structure of the employed BODIPY monomer to evaluate the CAM-B3LYP  $S_1$  and  $T_1$  errors with respect to CASPT2.

## Ground state vertical excitations

Table S2. Vertical excitation energies (in eV) to the lowest singlet and triplet excited states of monomer PM546 computed at the ground state geometry.  $\Delta E$  and  $\Delta E_{\text{corr}}$  indicate row TDDFT and corrected energies, respectively. Oscillator strength in parenthesis. Triplet energies from TDA.

state	$\Delta E$	$\Delta E_{\text{corr}}$	contribution
T <sub>1</sub>	1.71	2.01	H→L
T <sub>2</sub>	3.19	3.19	H-1→L
T <sub>3</sub>	3.33	3.35	H-2→L
S <sub>1</sub>	3.06 (0.549)	2.55	H→L
S <sub>2</sub>	3.99 (0.063)	3.73	H-1→L
S <sub>3</sub>	4.27 (0.042)		H-2→L

Table S3. Vertical excitation energies (in eV) to the lowest singlet and triplet excited states of monomer PM567 computed at the ground state geometry.  $\Delta E$  and  $\Delta E_{\text{corr}}$  indicate row TDDFT and corrected energies, respectively. Oscillator strength in parenthesis. Triplet energies from TDA.

state	$\Delta E$	$\Delta E_{\text{corr}}$	contribution
T <sub>1</sub>	1.64	1.94	H→L
T <sub>2</sub>	3.01	3.01	H-1→L
T <sub>3</sub>	3.22	3.24	H-2→L
S <sub>1</sub>	2.93 (0.614)	2.42	H→L
S <sub>2</sub>	3.85 (0.100)	3.59	H-1→L
S <sub>3</sub>	4.10 (0.051)		H-2→L

Table S4. Vertical excitation energies (in eV) to the lowest singlet and triplet excited states of dimer **1** computed at the ground state geometry.  $\Delta E$  and  $\Delta E_{\text{corr}}$  indicate row TDDFT and corrected energies, respectively. Oscillator strength in parenthesis. Triplet energies from TDA.

state	$\Delta E$	$\Delta E_{\text{corr}}$	contribution	character
T <sub>1</sub>	1.61	1.91	H→L	LE (8')
T <sub>1</sub> '	1.72	2.02	H-1→L	LE (2')
T <sub>2</sub>	3.11	3.11	H-2→L	LE (8')
S <sub>1</sub>	2.99 (0.614)	2.48	H→L	LE (8'+2')
S <sub>1</sub> '	3.00 (0.100)	2.49	H-1→L	LE (8'+2')
S <sub>2</sub>	3.33 (0.051)		H-2→L	CT (8'→2')

## Vertical de-excitations

Table S5. Vertical energy gaps (in eV) computed at the lowest singlet excited states geometry of monomers PM546, PM567 and dimer **1**.  $\Delta E$  and  $\Delta E_{\text{corr}}$  indicate row TDDFT and corrected energies, respectively.

molecule	state	$\Delta E$	$\Delta E_{\text{corr}}$
PM546	T <sub>1</sub>	1.48	1.78
	S <sub>1</sub>	2.92	2.41
PM567	T <sub>1</sub>	1.44	1.74
	S <sub>1</sub>	2.79	2.28
dimer <b>1</b>	T <sub>1</sub>	1.38	1.68
	T <sub>1</sub> '	1.48	1.78
	<sup>3</sup> CT	2.19	
	S <sub>1</sub>	2.84	2.31

## Spin orbit couplings

Table S6. SOCs (in cm<sup>-1</sup>) between singlet and triplet excited states of monomer PM546 computed at the ground state geometry.

	S1	S2	S3	S4	S5
T1	0.047	0.066	0.224	1.714	5.143
T2	0.014	0.020	6.182	2.605	5.698
T3	1.879	5.757	0.159	0.560	9.682
T4	0.704	0.168	0.285	0.048	1.145
T5	1.940	0.977	0.080	0.050	1.448

Table S7. SOCs (in cm<sup>-1</sup>) between singlet and triplet excited states of monomer PM567 computed at the ground state geometry.

	S1	S2	S3	S4	S5
T1	0.059	0.098	0.160	1.502	5.016
T2	0.021	0.080	5.359	3.245	5.173
T3	2.198	4.879	0.170	0.725	9.072
T4	0.092	1.343	0.443	0.085	2.111
T5	1.837	0.988	0.096	0.023	1.472

Table S8. SOCs (in cm<sup>-1</sup>) between singlet and triplet excited states of dimer **1** computed at the ground state geometry. Note that state labelling have been done according to the singlet and triplet energy order.

	S1	S2	S3	S4	S5
T1	0.158	0.120	1.826	1.386	0.279
T2	0.135	0.060	0.636	1.656	0.103
T3	0.255	0.251	0.186	1.568	0.489
T4	0.484	0.135	0.682	0.652	0.372
T5	0.879	1.829	0.340	0.969	5.526

Table S9. SOCs (in  $\text{cm}^{-1}$ ) between singlet and triplet excited states of dimer **1** computed at the  $S_1$  state geometry. Note that state labelling have been done according to the singlet and triplet energy order.

	S1	S2	S3	S4	S5
<b>T1</b>	0.536	0.432	1.801	1.265	0.311
<b>T2</b>	0.269	0.274	0.589	1.617	0.307
<b>T3</b>	0.704	0.215	0.650	1.051	1.294
<b>T4</b>	0.250	0.595	0.272	1.435	0.636
<b>T5</b>	1.466	1.120	0.769	0.429	4.846

Table S10. SOCs (in  $\text{cm}^{-1}$ ) between singlet and triplet excited states of dimer **1** computed at the  $^3\text{CT}$  state geometry. Note that state labelling have been done according to the singlet and triplet energy order.

	S1	S2	S3	S4	S5
<b>T1</b>	0.813	1.501	1.109	0.101	1.806
<b>T2</b>	0.148	0.415	0.285	0.349	0.890
<b>T3</b>	0.457	1.489	0.773	0.376	2.302
<b>T4</b>	2.882	1.289	0.263	5.248	0.342
<b>T5</b>	1.009	1.121	1.650	0.558	0.227

## Reduction of the $S_0$ - $T_1$ energy gap

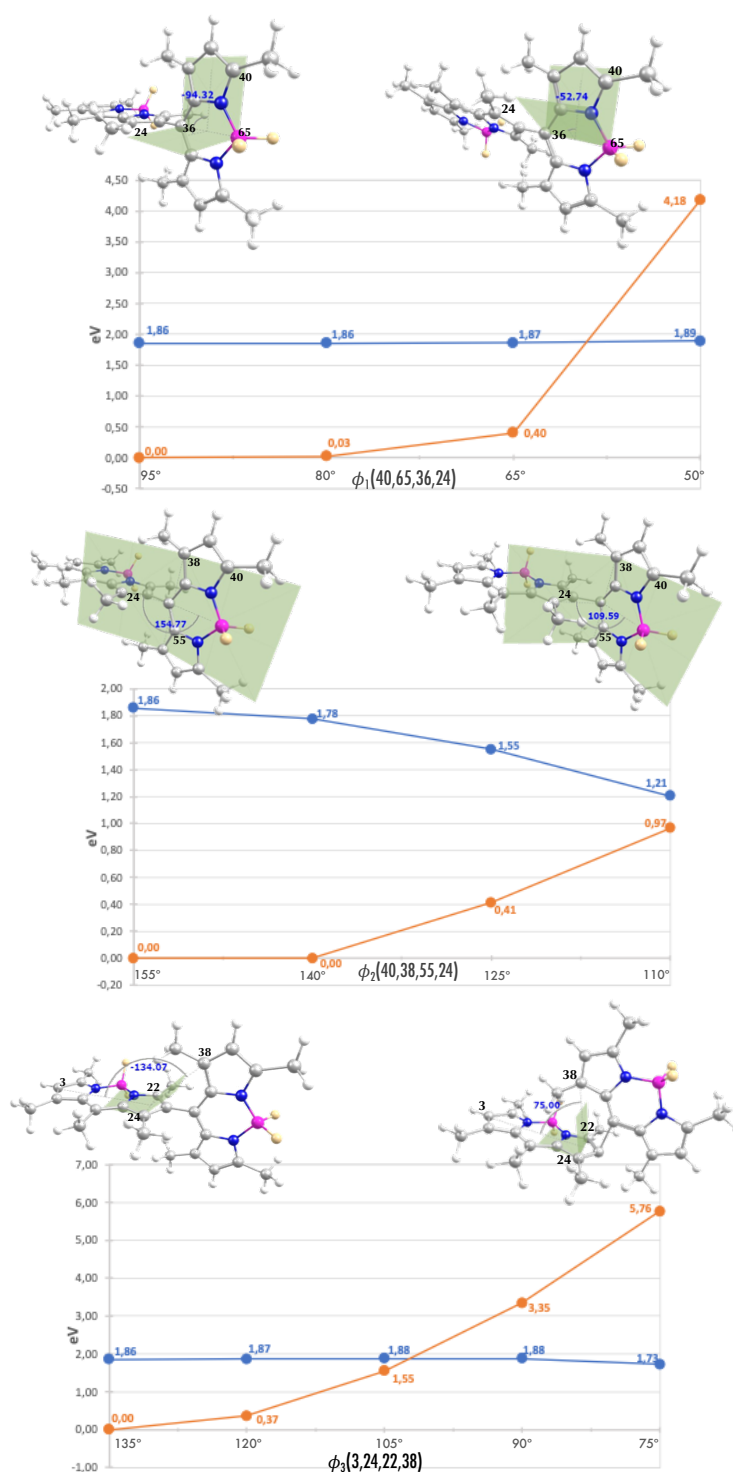


Figure S2. Evolution of the  $S_0$ - $T_1$  energy gap (in blue) and the energy change of the  $T_1$  electronic state,  $T_1$ - $T_1$ (initial), (in orange,) along with three different distortions computed at the TDA/CAM-B3LYP/cc-pVTZ level. Distortions account for bendings of BDP8' on top of BDP2' and vice versa. For each bending (i.e.,  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$ ) the non-distorted geometry ( $S_0$  optimized geometry) and the most distorted one are displayed for comprehensive reasons. We identify  $\phi_2$ -bending as a low-energy intra-monomer distortion able to decrease the  $S_0$ - $T_1$  energy gap.

## Evaluation of the $S_0 \leftarrow T_1$ radiative decay

The optical transition between singlet and triplet states is forbidden unless the spin-orbit coupling is considered. Following the procedure described in ref. [J. Chem. Theory Comput., 2013, 9, 1132-1143], first-order perturbation theory is used to describe new mixed singlet and triplet electronic states.

$$|S'\rangle = |S\rangle + \sum_n^{\{triplets\}} \sum_{m=-1}^1 \frac{\langle {}^3n_m | \hat{H}^{SO} | S \rangle}{{}^1E_S - {}^3E_n} | {}^3n_m \rangle$$

$$|T'_m\rangle = |T_m\rangle + \sum_k^{\{singlets\}} \frac{\langle {}^1k | \hat{H}^{SO} | T_m \rangle}{{}^3E_T - {}^1E_k} | {}^1k \rangle$$

Here, n and k are intermediate triplet and singlet electronic states, respectively; m is the magnetic quantum number ( $m = \{-1, 0, 1\}$ ).

Then, the transition dipolar moment between singlet and triplet electronic states becomes allowed and can be expressed as:

$$\mu_{S \leftarrow T_m} \equiv \langle S' | \hat{\mu} | T'_m \rangle$$

$$= \sum_n^{\{triplets\}} \sum_{m'=-1}^1 \frac{\langle S | \hat{H}^{SO} | {}^3n_{m'} \rangle \langle {}^3n_{m'} | \hat{\mu} | T_m \rangle}{{}^1E_S - {}^3E_n} + \sum_k^{\{singlets\}} \frac{\langle S | \hat{\mu} | {}^1k \rangle \langle {}^1k | \hat{H}^{SO} | T_m \rangle}{{}^3E_T - {}^1E_k}$$

The total transition dipolar moment is the average of the three components:

$$|\mu_{S \leftarrow T}|^2 = \frac{1}{3} \sum_m |\mu_{S \leftarrow T_m}|^2$$

Table S11. Oscillator strength (in a.u.) and dipole strength of the  $S_0 \leftarrow T_1$  transition of the monomer PM567.

	$ \mu_{S \leftarrow T} ^2$	f (Oscillator strength) (a.u.)
From S0 geom	$5.06 \cdot 10^{-10}$	$1.76 \cdot 10^{-11}$
From T1 geom	$1.54 \cdot 10^{-9}$	$4.06 \cdot 10^{-11}$

Table S12. Oscillator strength (in a.u.) and dipole strength of the  $S_0 \leftarrow T_1$  transition of the dimer **1**.

	$ \mu_{S \leftarrow T} ^2$	f (Oscillator strength) (a.u.)
From S0 geom	$8.56 \cdot 10^{-10}$	$2.69 \cdot 10^{-11}$
From T1 geom	$1.41 \cdot 10^{-9}$	$2.90 \cdot 10^{-11}$

## EXPERIMENTAL CHARACTERIZATION

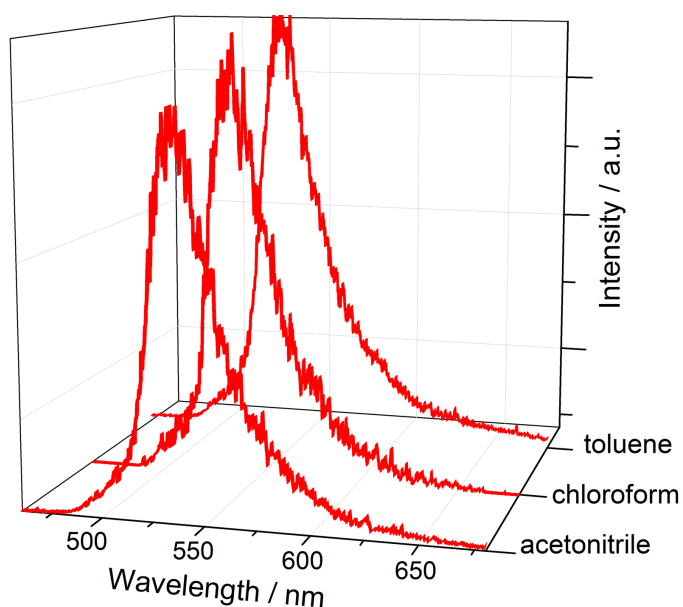


Figure S3. Fluorescence spectral profile of PM546 is not dependent on the solvent polarity.

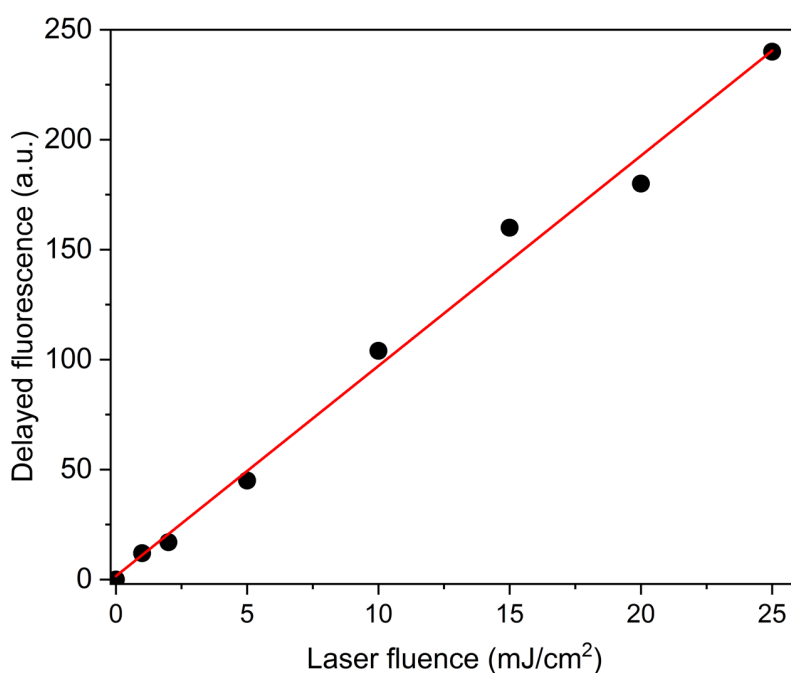


Figure S4. Dependence on the laser fluence at 532 nm of the delayed fluorescence of PM546 in aerated chloroform solution at room temperature recorded at a delay time of 10  $\mu$ s. The solid line is the best fit of the data points (fit parameters: slope: 0.99517,  $\chi^2 < 0.0001$ ). It should be noted that all monomeric BODIPYs herein selected as well as dimr **1** follow similar dependence on laser fluence.



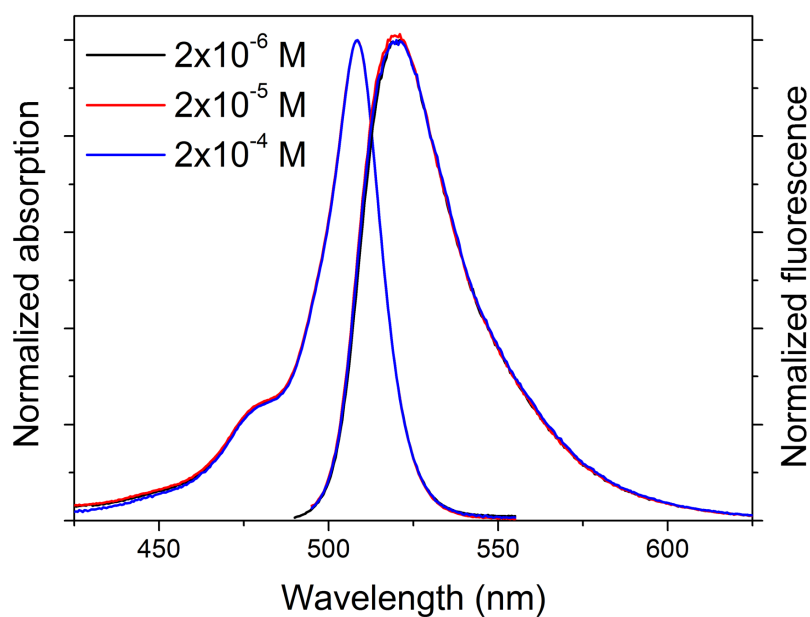


Figure S5. Absorption and fluorescence spectra of BODIPY dimer **1** in cyclohexane as a function of dye concentration.

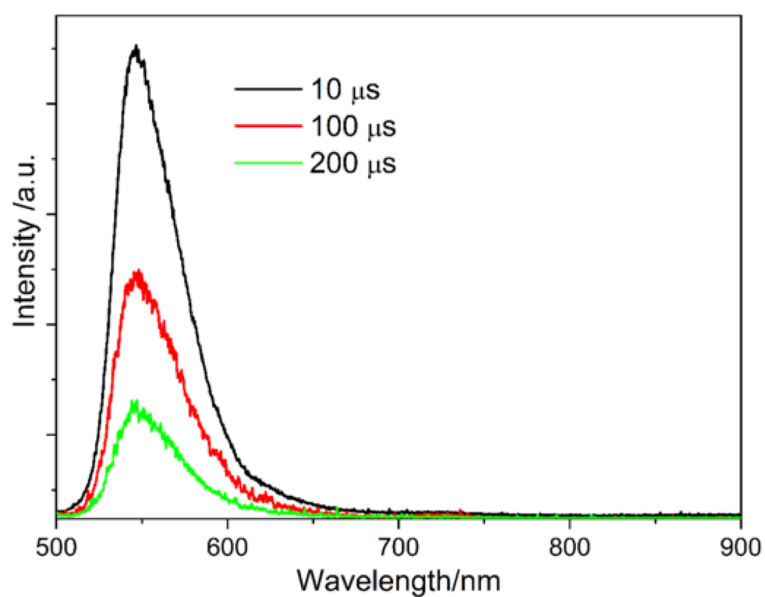


Figure S6. Time-dependent emission spectra of PM567 in glycerin measured under ambient conditions after laser photoexcitation at 532 nm. Dye concentration:  $5 \times 10^{-5}$  M.

### Spectral response at 900-1200 nm

The spectral response of the employed detection system (monochromator grating and CCD) at the 900-1200 nm spectral region results in a rather irregular emission profile. Details of the employed instrumentation can be found at the Andor website, accessed on September 2, 2021:

<https://andor.oxinst.com/assets/uploads/products/andor/documents/andor-kymera-193-specifications.pdf>

<https://andor.oxinst.com/assets/uploads/products/andor/documents/andor-istar-ccd-imaging-specifications.pdf>