

## Supporting information for : Investigation of excited states of BODIPY derivatives and non-orthogonal dimers in the perspective of singlet fission

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The BODIPY monomer (A), its derivatives (A-1 to A-35), dimers (B[1,1], B[1,3], B[3,3], B[2,2], B[2,8]), derivatives of dimers (B-1, B-3), azaBODIPY (C) and its dimer derivatives (D-1 to D-4) are optimized by resolution identity coupled cluster (RICC2)<sup>48,49</sup> method and second definition polarized valence triple zeta (def2-TZVP)<sup>50</sup> basis set. Five lowest lying singlet and triplet states are also calculated at RICC2/def2-TZVP level of theory. The dynamic correlations are incorporated by calculating the singlet and triplet states by employing state averaged extended multi-configuration quasi-degenerate perturbation theory (SA-XMCQDPT)<sup>51</sup> level theory. The number of states included in the state average and the active space are varied to better suite the problem (See Sec. 3.5-3.2). Dunning's correlation consistent polarized double zeta (cc-pVDZ) basis set<sup>52</sup> is used for XMCQDPT calculations. To understand the effect of torsional angle on the electronic states of the dimers B[3,3] and B[2,8] we performed relaxed scan (See Sec. 3.4) by density functional theory (DFT) by using B3LYP hybrid functional.<sup>53,54</sup> Grimme dispersion corrections are included during the optimizations.<sup>55</sup> The geometry optimizations (DFT and RICC2) and RICC2 excitation energies are performed by using Turbomole electronic structure package.<sup>56</sup> The XMCQDPT and diabaticization calculations are performed by using GAMESS electronic structure program package.<sup>57</sup>

We have performed several exploratory calculations for the BODIPY monomer in order to choose optimal active space and basis set for XMCQDPT calculations (See Table S1-S2). We choose SA8-XMCQDPT(8,8)/cc-pVDZ level of theory to study the excited states of monomer. Table S4 and Fig. S1 provide the excited characterization and pictures of molecular orbitals (MOs) included in the active space. To calculate the vertical excited states of the dimers, we have employed SA15-XMCQDPT(8,8), SA8-XMCQDPT(8,8) and SA8-XMCQDPT(4,4) method with cc-pVDZ basis set. Table S6-S10 provide comparison of the excitation energies from the three levels of theories. The optimized orbitals are delocalized. We have localized the (4,4) active space to characterize the electronic states (See Figs. S3-S7). To access the quality of (8,8) active space, we have also employed (12,10) active space (See Table S16). The  $S_1$ ,  $S_2$ ,  $T_1$  and  $T_2$  are very close in both the active spaces. The remaining singlet and triplet state energies slightly stabilized by 0.3 eV with that of an active space (8,8).

To investigate the mechanism of intramolecular singlet fission (iSF) in the dimers B[1,1], B[1,3], B[3,3], B[2,2] and B[2,8], we have calculated 8 lowest lying adiabatic states by using SA8-XMCQDPT(4,4)/cc-pVDZ level of theory. Intruder avoidance shift 0.02 is used in the calculations. Eight relevant diabatic electronic states were derived from eight adiabatic states by using Nakamura and Truhlar's fourfold diabaticization method.<sup>61,62</sup> The diabaticization procedure comprised all configuration state functions (CSFs) with coefficients greater than 0.20 in any of the adiabatic electronic states. After applying the so-called three-fold density criterion and MORMO conditions, diabatic molecular orbitals (DMOs) were derived from the adiabatic (canonical) ones. Ultimately, a unitary transformation was employed to convert the adiabatic states represented in the DMOs bases into diabatic states.

For each of these five conformers, we selected CSFs with coefficients greater than 0.20. The weights of the dominant CSFs obtained from the DMOs in the adiabatic states  $S_0$ ,  $S_1$ ,  $S_2$ ,  $S_3$ ,  $S_4$ ,  $S_5$ ,  $S_6$  and  $S_7$  for B[1,1] are 99.9%, 98.3%, 98.0%, 93.4%, 98.2%, 95.9%, 100.0% and 94.0% respectively. For B[1,3], these weights are 99.8%, 96.8%, 94.0%, 93.8%, 92.7%, 97.9%, 87.9% and 94.1%. Similarly, for B[3,3] these weights are 100.0%, 96.7%, 94.4%, 93.0%, 92.1%, 97.3%, 91.6% and 95.9%. For B[2,2] these weights are 99.9%, 96.0%, 93.8%, 92.3%, 91.1%, 98.6%, 85.6% and 89.1% and for B[2,8] these weights are 100.0%, 97.4%, 97.2%, 98.5%, 98.4%, 98.7%, 94.6% and 96.0%. The results indicate that for each of the five regioisomers, the contributions from the dominating CSFs are 94% or higher.

The diabatic electronic states obtained include the electronic ground state  $|^1(S_0S_0)\rangle$ , the correlated triplet pair state  $|^1(T_1T_1)\rangle$  (ME state), the locally excited (LE) states  $|^1(S_1S_0)\rangle$  and  $|^1(S_0S_1)\rangle$  where the excitation ( $S_1$ ) is localized in one of the bodipy moieties, and the charge transfer (CT) states  $|^1(CA)\rangle$  and  $|^1(AC)\rangle$ , where C and A denote the radical cation and radical anion forms of the bodipy moiety, respectively. Additionally, two doubly excited (DE) diabatic states  $|^1(DE)_1\rangle$  and  $|^1(DE)_2\rangle$  were included due to energy considerations. The electronic Hamiltonian ( $HeI$ ) in the diabatic basis defined by these states can be found in Tables S11-S15 of the main text. Eqs. S1-S5 contain the diabatic to adiabatic transformation matrix for the systems B[1,1], B[1,3], B[3,3], B[2,2] and B[2,8].

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \end{pmatrix} = \begin{pmatrix} 0.98 & 0.01 & 0.01 & -0.07 & 0.07 & 0.02 & -0.11 & 0.11 \\ -0.00 & 0.59 & -0.59 & -0.39 & -0.38 & -0.00 & 0.04 & 0.04 \\ 0.00 & 0.49 & 0.49 & 0.35 & -0.35 & 0.51 & -0.08 & 0.09 \\ 0.06 & -0.49 & -0.49 & 0.46 & -0.46 & 0.27 & -0.08 & 0.08 \\ -0.00 & 0.39 & -0.39 & 0.59 & 0.59 & 0.00 & -0.04 & -0.04 \\ -0.08 & -0.14 & -0.14 & -0.39 & 0.39 & 0.79 & -0.06 & 0.06 \\ 0.16 & -0.01 & -0.01 & 0.05 & -0.05 & 0.18 & 0.69 & -0.68 \\ -0.00 & -0.01 & 0.01 & 0.06 & 0.06 & -0.00 & 0.70 & 0.70 \end{pmatrix} \begin{pmatrix} |^1(S_0S_0)\rangle \\ |^1(S_1S_0)\rangle \\ |^1(S_0S_1)\rangle \\ |^1(CA)\rangle \\ |^1(AC)\rangle \\ |^1(T_1T_1)\rangle \\ |^1(DE)_1\rangle \\ |^1(DE)_2\rangle \end{pmatrix} \quad (S1)$$

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \end{pmatrix} = \begin{pmatrix} 0.98 & 0.00 & 0.02 & 0.05 & -0.07 & 0.01 & -0.10 & -0.09 \\ 0.01 & 0.63 & -0.55 & -0.44 & -0.32 & -0.01 & 0.04 & -0.04 \\ 0.01 & 0.48 & 0.56 & -0.31 & 0.42 & 0.39 & -0.12 & -0.08 \\ -0.04 & 0.46 & 0.48 & 0.43 & -0.49 & -0.33 & 0.07 & 0.11 \\ 0.02 & 0.38 & -0.35 & 0.53 & 0.62 & -0.23 & -0.10 & 0.06 \\ -0.07 & 0.06 & -0.18 & 0.49 & -0.26 & 0.79 & -0.09 & -0.145 \\ 0.11 & 0.05 & 0.00 & 0.04 & 0.14 & 0.15 & 0.97 & 0.08 \\ 0.08 & -0.00 & -0.03 & -0.06 & -0.02 & 0.19 & -0.11 & 0.97 \end{pmatrix} \begin{pmatrix} |^1(S_0S_0)\rangle \\ |^1(S_1S_0)\rangle \\ |^1(S_0S_1)\rangle \\ |^1(CA)\rangle \\ |^1(AC)\rangle \\ |^1(T_1T_1)\rangle \\ |^1(DE)_1\rangle \\ |^1(DE)_2\rangle \end{pmatrix} \quad (S2)$$

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \end{pmatrix} = \begin{pmatrix} 0.98 & -0.00 & 0.00 & 0.05 & -0.06 & -0.04 & -0.12 & -0.12 \\ -0.00 & 0.57 & 0.57 & 0.43 & 0.42 & -0.00 & -0.00 & -0.01 \\ -0.00 & -0.71 & 0.71 & 0.03 & -0.03 & 0.05 & 0.01 & 0.01 \\ -0.01 & -0.04 & 0.04 & -0.54 & 0.55 & -0.58 & -0.17 & -0.19 \\ -0.00 & -0.42 & -0.42 & 0.58 & 0.56 & -0.00 & 0.00 & -0.02 \\ 0.14 & 0.01 & -0.01 & -0.43 & 0.46 & 0.67 & 0.26 & 0.26 \\ 0.00 & 0.00 & 0.00 & 0.00 & -0.02 & 0.00 & 0.72 & -0.69 \\ 0.13 & -0.01 & 0.01 & 0.05 & -0.03 & -0.46 & 0.61 & 0.63 \end{pmatrix} \begin{pmatrix} |^1(S_0S_0)\rangle \\ |^1(S_1S_0)\rangle \\ |^1(S_0S_1)\rangle \\ |^1(CA)\rangle \\ |^1(AC)\rangle \\ |^1(T_1T_1)\rangle \\ |^1(DE)_1\rangle \\ |^1(DE)_2\rangle \end{pmatrix} \quad (S3)$$

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \end{pmatrix} = \begin{pmatrix} 0.99 & -0.01 & 0.01 & 0.03 & -0.03 & 0.00 & 0.09 & 0.09 \\ 0.00 & 0.63 & 0.63 & 0.32 & 0.32 & -0.00 & -0.04 & 0.04 \\ -0.00 & -0.63 & 0.63 & -0.29 & 0.29 & 0.15 & 0.05 & 0.05 \\ -0.00 & -0.33 & -0.33 & 0.62 & 0.62 & 0.00 & -0.06 & 0.05 \\ 0.04 & 0.12 & -0.12 & -0.47 & 0.47 & -0.72 & -0.04 & -0.04 \\ 0.01 & 0.28 & -0.28 & -0.44 & 0.44 & 0.661 & 0.09 & 0.09 \\ -0.13 & 0.02 & -0.02 & 0.04 & -0.04 & -0.14 & 0.69 & 0.69 \\ 0.00 & -0.01 & -0.01 & -0.07 & -0.07 & 0.00 & -0.70 & 0.70 \end{pmatrix} \begin{pmatrix} |^1(S_0S_0)\rangle \\ |^1(S_1S_0)\rangle \\ |^1(S_0S_1)\rangle \\ |^1(CA)\rangle \\ |^1(AC)\rangle \\ |^1(T_1T_1)\rangle \\ |^1(DE)_1\rangle \\ |^1(DE)_2\rangle \end{pmatrix} \quad (S4)$$

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \end{pmatrix} = \begin{pmatrix} 0.99 & -0.02 & -0.09 & -0.00 & -0.01 & -0.00 & 0.09 & -0.09 \\ 0.01 & 0.82 & 0.36 & 0.03 & -0.43 & -0.07 & 0.00 & -0.03 \\ -0.00 & -0.36 & 0.78 & -0.49 & -0.04 & -0.13 & 0.00 & 0.02 \\ -0.00 & -0.26 & 0.42 & 0.77 & -0.16 & 0.35 & -0.00 & -0.00 \\ 0.04 & 0.33 & 0.29 & 0.15 & 0.88 & -0.021 & -0.03 & 0.08 \\ 0.00 & 0.12 & -0.02 & -0.36 & 0.04 & 0.92 & -0.00 & 0.01 \\ -0.10 & 0.01 & 0.01 & 0.01 & 0.05 & 0.00 & 0.97 & -0.16 \\ 0.07 & 0.00 & -0.02 & 0.00 & -0.09 & -0.00 & 0.17 & 0.98 \end{pmatrix} \begin{pmatrix} |^1(S_0S_0)\rangle \\ |^1(S_1S_0)\rangle \\ |^1(S_0S_1)\rangle \\ |^1(CA)\rangle \\ |^1(AC)\rangle \\ |^1(T_1T_1)\rangle \\ |^1(DE)_1\rangle \\ |^1(DE)_2\rangle \end{pmatrix} \quad (S5)$$

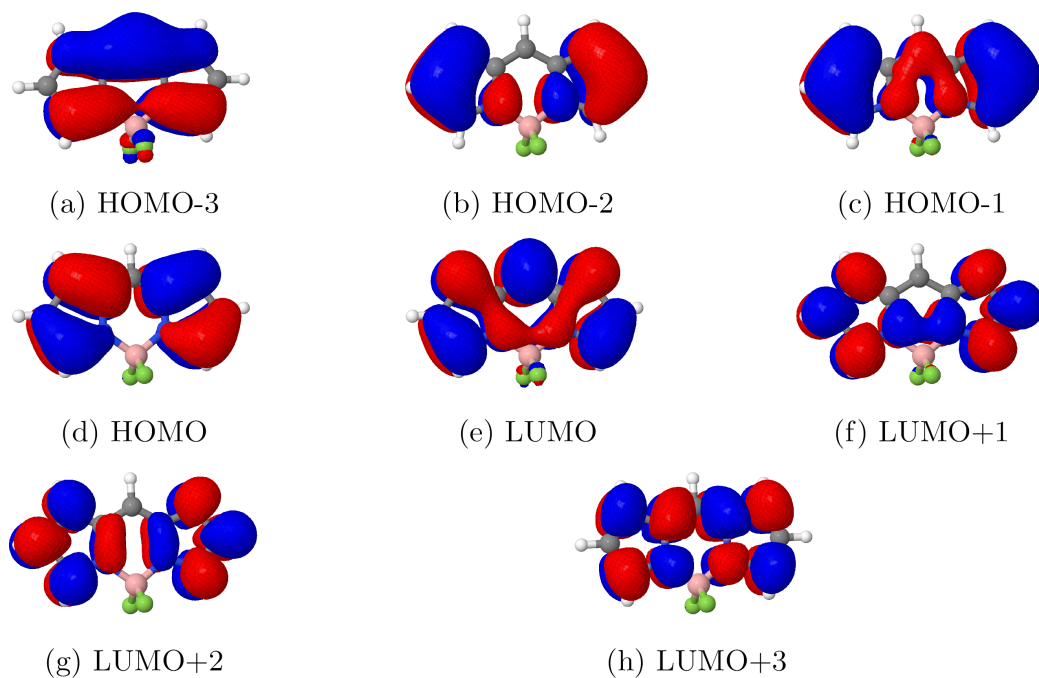
In order to understand the effect of substitution on the singlet and triplet state energies, a variety of substitutions ( $\pi$  accepting and  $\pi$  donating groups) have been tried on the BODIPY core at  $\alpha$  (3<sup>rd</sup> and 5<sup>th</sup>),  $\beta$  (2<sup>nd</sup> and 6<sup>th</sup>), and meso (8<sup>th</sup>) positions. We choose the substituents BH<sub>2</sub>, NO<sub>2</sub>, CN, CF<sub>3</sub>, H, Me, Cl, OH, OCH<sub>3</sub> and NH<sub>2</sub> according to their pEDA parameter proposed by Dobrowilski.<sup>75</sup> The optimized coordinates in angstrom units are provided at the end of this document. The ball and stick representation of the optimized geometries (A-1 to A-35) are given in Fig. S10-S13. The energies of HOMO ( $E(H)$ ), LUMO ( $E(L)$ ) and their differences  $E(H) - E(L)$  are given in Table S17. The variation of HOMO and LUMO energies for substitutions are  $\alpha$ ,  $\beta$  and meso positions are shown in Figs. S19, S20 and S21 respectively. The ball and stick representation of the BODIPY dimers B[1,1], B[1,3], B[3,3], B[2,2] and B[2,8] are shown in Fig. S15. Further we studied the effect of substitution on the BODIPY dimers. The ball and stick representation of the dimers are shown in Fig. S16. The variation of energies of S<sub>1</sub>, T<sub>1</sub> states and the thermodynamic condition  $\Delta_{SF}$  for the substitutions  $\alpha$  and  $\beta$  substitutions are shown in Figs. S17-S18.

For an efficient singlet fission from the BODIPY dimers designed, near degeneracy of the ME and quintet is desirable.<sup>34</sup> For BODIPY dimers linked by one C-C single bond, the quintet state is high in energy than the ME state (See Fig. 2) at non-orthogonal geometry. The

quintet state may be stabilized by linking dimers covalently with long spacers (chain of three phenyl groups)<sup>25,27</sup> or non-conjugated (1,3-diethynyladamantyl) spacer.<sup>26</sup> Alternatively, the  $\pi$  stacking of the monomers also shown to stabilize the quintet states and make the singlet fission efficient.<sup>33-35</sup> To understand, the SF energetics, we have designed two dimers (a) covalently coupled dimers (B-4) and (b)  $\pi$  stacked (B-5) from A-29. The geometries of the dimers are shown in Fig. S22. The energies of singlet, multi-excitonic and quintet states are tabulated in Table S23. The energy of quintet state is closer to the multiexcitonic state in  $\pi$  stacked dimer while the gap is large for covalently bonded non-orthogonal dimer B-4. It is to be noted that the ME and quintet states are close in energy at the orthogonal conformation of B[3,3]. However due to the availability of torsional motion, quintet state is destabilized than the ME state. In the  $\pi$  stacked dimer, due to the lack of torsional motions, we propose the ME and quintet states will be near degenerate. If formed through a suitable mechanism, the ME state convert into a quintet state in a  $\pi$  stacked dimer readily than the covalently bonded dimer.

Long spacers such as three phenyls<sup>27</sup> or non-conjugated 1,3-diethynyladamantyl<sup>26</sup> are shown to stabilize the quintet states. In the bodipy dimers B[3,3] and B[1,3] the monomers are linked by only one single bond. As a result, the quintet state is destabilized than the ME state. We have performed a rigid calculation of the  $\pi$  stacked dimer B-5 to variation of quintet state energy versus interchromophoric distance. We have increased the distance between the center of mass of each monomer from 4.0 Angstrom to 9.0 Angstrom. The result of rigid scan is shown in Fig. S23. A Lennard-Jones type of potential is seen for all electronic states. All PES of  $S_0$  (GS),  $S_1$  (LE),  $S_3$  (ME) and  $Q_1$  show minimum between 4.5 – 5.0 Angstrom. Each state converge to energies 1.0, 2.8, 3.5 and 4.0 eV respectively denoting the dissociative region. The ME and  $Q_1$  are near degenerate in the region 4.5 – 5.0 eV. As the interchromophoric distance is increasing, the quintet state get destabilize and the difference between ME and  $Q_1$  increased to 0.5 eV. These results correlate well to the observations of Tsuneda et. al. where they proposed the moderate  $\pi$  stacking (not too close not too far, in both cases the quintet is destabilized than the ME state) for efficient singlet fission.<sup>34,35</sup>

**Figure S1** The molecular orbitals of the active space (8,8) of BODIPY.



**Table S1** The VEEs of BODIPY calculated using various active spaces.

	State	(4, 4)	(8, 8)	(12, 11)
This Work	S <sub>1</sub>	2.82	2.64	2.55
	T <sub>1</sub>	1.88	1.87	1.85
Ref. 67 <sup>a</sup>	S <sub>1</sub>	2.13	2.42	2.45

<sup>a</sup> VEEs for triplet states are reported.

**Table S2** The VEEs of BODIPY calculated using various active spaces.

	State	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ
This Work	S <sub>1</sub>	2.64	2.61	2.62
	T <sub>1</sub>	1.87	1.87	1.88
Ref. 67 <sup>a</sup>	S <sub>1</sub>	2.539	2.452	2.441

<sup>a</sup> VEEs for triplet states are reported.



**Table S3** The vertical excitation energies (VEEs in eV units)<sup>a</sup>, oscillator strengths ( $f$ , in dimensionless units)<sup>b</sup> and dipole moments ( $\mu$ , in Debye units)<sup>b</sup> of BODIPY monomer.

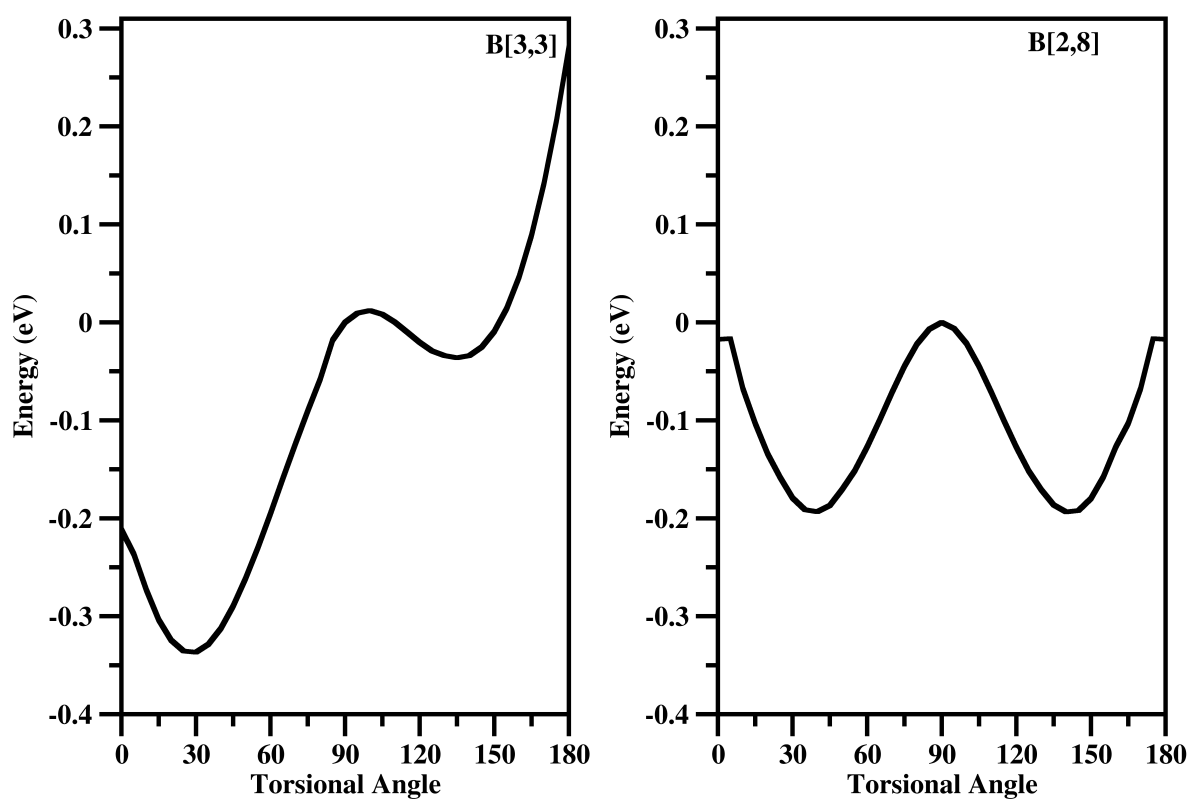
State	This work			CASPT2			LC-TDDFT	Experiment
	VEE	$f$	$\mu$	Ref. 19	Ref. 68	Ref. 32	Ref. 34	
S <sub>0</sub>	0.000	-	4.76	—	—	—		
T <sub>1</sub>	1.808	-	4.72	1.86	1.56	1.84	1.62	1.82 <sup>19</sup>
S <sub>1</sub>	2.616	0.810	8.21	2.48	2.99	2.55	2.27	2.46 <sup>70</sup>
T <sub>2</sub>	2.901	-	1.33	3.20	3.20	3.28		—
S <sub>2</sub>	3.513	0.160	3.14	3.84	4.10	3.66		—
T <sub>3</sub>	3.356	-	1.84	—	—			—
T <sub>4</sub>	3.914	-	5.72	—	—			—
S <sub>3</sub>	3.930	0.160	3.08	—	—			—
S <sub>4</sub>	4.528	0.007	0.65	—	—			—
T <sub>5</sub>	5.243	-	3.87	—	—			—

<sup>a</sup> Calculated at SA8-XMCQDPT(8,8)/cc-pVDZ level of theory <sup>b</sup> Calculated at SA8-CASSCF(8,8)/cc-pVDZ level of theory

**Table S4** The characterization of the vertical excited states of BODIPY. The occupations of electrons in the configuration state functions are given from HOMO-3 to LUMO+3 in the order.

State	CSF	Co-eff	Co-eff <sup>2</sup>	Char.	
S <sub>0</sub>	22220000	-0.94	0.88	GS	
S <sub>1</sub>	222+-000	0.84	0.71	SE	SE: H → L
	22+2-000	0.25	0.06	SE	
S <sub>2</sub>	222+-000	-0.24	0.06	SE	SE: H-1 → L
	22+2-000	0.71	0.50	SE	
	22+-2000	0.32	0.10	DE	
	2+22-000	-0.31	0.10	SE	
	22+2-200	-0.23	0.05	DE	
S <sub>3</sub>	22+2-000	0.31	0.10	SE	SE: H-2 → L
	22+-2000	-0.31	0.10	DE	
	2+22-000	0.70	0.49	SE	
	2+2-2000	-0.32	0.10	DE	
S <sub>4</sub>	222+0-00	0.35	0.12	SE	DE: H ⇒ L
	22202000	-0.67	0.45	DE	
	+222-000	0.23	0.48	SE	
	02222000	0.23	0.05	DE	
T <sub>1</sub>	222+ +000	-0.95	0.90	SE	
T <sub>2</sub>	22+2+000	-0.73	0.53	SE	
	2+22+000	0.51	0.26	SE	
T <sub>3</sub>	22+2+000	0.48	0.23	SE	
	22++2000	-0.24	0.06	DE	
	2+22+000	0.65	0.42	SE	
	+222+000	-0.30	0.09	SE	
T <sub>4</sub>	2+22+000	0.30	0.91	SE	
	+222+000	0.85	0.72	SE	
T <sub>5</sub>	222+0+00	0.76	0.58	SE	
	2+2+2000	-0.25	0.06	DE	

**Figure S2** The relaxed scan of the ground singlet state energy of the BODIPY dimers B[3,3] on the left and B[2,8] on the right.



**Table S5** The vertical excitation energies (VEEs in eV units)<sup>a</sup>, oscillator strengths ( $f$ , in dimensionless units)<sup>b</sup> and dipole moments ( $\mu$ , in Debye units)<sup>b</sup> and character of the electronic state <sup>c</sup> of BODIPY dimers B[1,1], B[1,3], B[3,3], B[2,2] and B[2,8].

State	B[1,1]			B[1,3]			B[3,3]			B[2,2]			B[2,8]			
	VEEs	$f$	$\mu$	Char.	VEEs	$f$	$\mu$	Char.	VEEs	$f$	$\mu$	Char.	VEEs	$f$	$\mu$	Char.
S <sub>0</sub>	0.000	—	2.48	GS	0.000	—	8.88	GS	0.000	—	0.03	GS	0.000	—	9.06	GS
S <sub>1</sub>	2.202	1.465	3.32	LE <sub>1</sub>	2.156	1.047	8.83	LE <sub>1</sub>	2.045	1.399	0.40	LE <sub>1</sub>	2.054	1.461	8.46	LE <sub>1</sub>
S <sub>2</sub>	2.485	0.212	5.54	LE <sub>1</sub>	2.489	0.024	8.01	CT <sub>1</sub>	2.444	<0.001	0.01	CT <sub>1</sub>	2.550	0.251	12.38	LE <sub>1</sub>
S <sub>3</sub>	2.830	0.070	7.21	CT <sub>1</sub>	2.740	0.060	9.19	LE <sub>1</sub>	2.923	0.003	0.82	LE <sub>1</sub>	3.039	0.042	7.74	CT <sub>1</sub>
S <sub>4</sub>	3.142	0.268	2.58	LE <sub>2</sub>	3.133	0.550	8.16	CT <sub>1</sub>	3.479	0.485	0.91	LE <sub>2</sub>	3.329	0.470	10.32	CT <sub>1</sub>
S <sub>5</sub>	3.394	0.082	2.97	CT <sub>1</sub>	3.469	0.578	8.18	ME	3.509	0.023	0.66	LE <sub>2</sub>	3.679	0.072	11.02	ME
S <sub>6</sub>	3.703	0.061	7.42	ME	3.601	0.206	5.03	LE <sub>2</sub>	3.853	0.005	1.11	ME	3.822	0.019	9.38	LE <sub>2</sub>
S <sub>7</sub>	3.890	0.285	8.88	LE <sub>2</sub>	3.797	0.131	5.92	LE <sub>2</sub>	3.914	0.250	0.26	CT <sub>1</sub>	4.228	0.308	7.47	LE <sub>2</sub>
S <sub>8</sub>	4.269	0.111	7.88	CT <sub>2</sub>	4.264	0.035	9.77	CT <sub>2</sub>	4.563	<0.001	0.14	CT <sub>2</sub>	4.342	0.030	8.82	CT <sub>2</sub>
S <sub>9</sub>	4.612	0.024	2.27	CT <sub>2</sub>	4.566	0.059	16.97	CT <sub>2</sub>	4.603	0.352	0.09	CT <sub>2</sub>	4.705	0.074	16.39	CT <sub>2</sub>
T <sub>1</sub>	1.541	0.000	3.76		1.550	0.000	7.87		1.353	0.000	0.22		1.839	0.000	9.77	
T <sub>2</sub>	1.771	0.000	3.73		1.775	0.000	7.15		1.932	0.000	0.36		1.948	0.000	8.45	
T <sub>3</sub>	2.685	0.000	5.78		2.633	0.000	8.92		3.105	0.000	0.46		3.295	0.000	8.94	
T <sub>4</sub>	2.998	0.000	4.91		2.941	0.000	6.34		3.115	0.000	0.94		3.375	0.000	10.21	
T <sub>5</sub>	3.140	0.000	1.27		3.332	0.000	9.04		3.344	0.000	1.04		3.719	0.000	9.04	
T <sub>6</sub>	3.690	0.000	1.63		3.533	0.000	7.23		3.359	0.000	0.06		4.096	0.000	8.18	
T <sub>7</sub>	3.792	0.000	3.41		3.760	0.000	8.69		4.106	0.000	0.50		4.161	0.000	10.71	
T <sub>8</sub>	4.146	0.000	2.79		4.117	0.000	6.34		4.356	0.000	0.79		4.353	0.000	7.55	
Q <sub>1</sub>	3.442	0.000	3.16		3.627	0.000	7.77		3.804	0.000	0.83		3.410	0.000	7.26	

<sup>a</sup> Calculated at SA15-XMCQDPT(8,8)/cc-pVDZ level of theory <sup>b</sup> Calculated at SA15-CASSCF(8,8)/cc-pVDZ level of theory <sup>c</sup> Character of the excited state: GS = Ground state, LE<sub>1</sub> = optically bright states that correlate with the plus and minus combinations of locally excited states of both BODIPY monomers (from HOMO of one monomer to LUMO of the same monomer), LE<sub>2</sub> = optically bright states that correlate with the plus and minus combinations of locally excited states of both BODIPY monomers (from HOMO-1 of one monomer to LUMO of the same monomer), ME = multiexcitonic state, CT<sub>1</sub> = charge transfer states (from HOMO of one monomer to LUMO of the another monomer) and CT<sub>2</sub> = charge transfer states (from HOMO-1 of one monomer to LUMO of the another monomer)

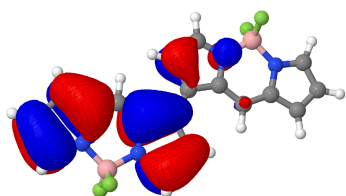
**Table S6** The excitation energy (in eV units), oscillator strength (in dimensionless) and dipole moment (in Debye units) and electronic configuration of the dimer B[1,1] calculated by using SA15-XMCQDPT(8,8), SA8-XMCQDPT(8,8) and SA8-XMCQDPT(4,4) level of theory.

S. No.	SA15-XMCQDPT(8,8)				SA8-XMCQDPT(8,8)		SA8-XMCQDPT(4,4)		Char. <sup>a</sup>
	$\Delta E$	$f$	$\mu$	config <sup>a</sup>	$\Delta E$	config <sup>a</sup>	$\Delta E$	config <sup>a</sup>	
S <sub>0</sub>	0.0	0.0	2.48	22220000	0.0	22220000	0.0	2200	GS
S <sub>1</sub>	2.202	1.465	3.32	222+-000 22+20-00	2.19	222+-000 22+20-00	2.13	2+-0 +20-	LE <sub>1</sub>
S <sub>2</sub>	2.485	0.212	5.54	22+2-000 22202000	2.50	22+2-000 22202000	2.47	+2-0 2020	LE <sub>1</sub>
S <sub>3</sub>	2.830	0.070	7.21	222+0-00 22202000	2.82	222+0-00 22202000	2.84	2+0- 2020 ++-	CT <sub>1</sub>
S <sub>4</sub>	3.142	0.268	2.58	2+22-000 22202000 2+2+-00 2+-22000	3.23	2+22-000 2+220-00 22202000 22+20-00 2+-22000			LE <sub>2</sub>
S <sub>5</sub>	3.394	0.082	2.97	22+20-00 2+22-000 22+-2000	3.53	22+20-00 2+22-000 22+-22000	3.20	+20-	CT <sub>1</sub>
S <sub>6</sub>	3.703	0.061	7.42	22022000 22202000 2+220-00 222+0-00 22200200 22+-0-00 22020200 2+22-000	3.82	22022000 22+-0-00 222+0-00 22020200 22200200 22202000 2+2-2000	3.53	0220 2+0- 2020 2002 0202 ++- +2-0	ME
S <sub>7</sub>	3.890	0.285	8.88	2+220-00 222+0-00 22202000 22+2-000 22+-+00 2+2-2000	4.29	22202000 2220+-00 22+-2000 22+-+00			LE <sub>2</sub>
S <sub>8</sub>	4.269	0.111	7.88	+222-000 22+-2000					CT <sub>2</sub>
S <sub>9</sub>	4.612	0.024	2.27	2+2-2000 2+2-0200 2+220-00 +222-000					CT <sub>2</sub>

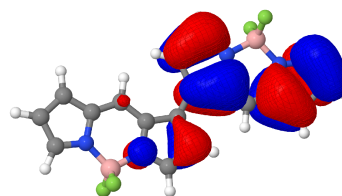
<sup>a</sup> In the localised orbitals. Please see Fig. S3 <sup>b</sup> In the delocalised orbitals

**Figure S3** The characterization of the excited states of dimer B[1,1] by using the localised HOMO-1 (a), HOMO (b), LUMO (c) and LUMO+1 (d) orbitals. Single and double arrows represents single and double excitations. The value on top of the arrow represent the % of the particular excitation to the total wavefunction. The black and blue boxes represent the constructive and destructive combinations.

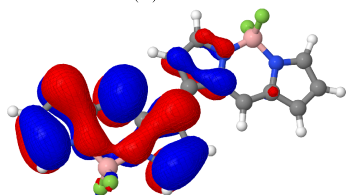
State	Orbital transition		Weight	Character
S <sub>1</sub>	(b) $\xrightarrow{0.13}$ (c)	(a) $\xrightarrow{0.13}$ (d)	0.26	CT
	(b) $\xrightarrow{0.34}$ (d)	(a) $\xrightarrow{0.34}$ (c)	0.68	LE
S <sub>2</sub>	(b) $\xrightarrow{0.19}$ (c)	(a) $\xrightarrow{0.19}$ (d)	0.38	CT
	(b) $\xrightarrow{0.23}$ (d)	(a) $\xrightarrow{0.23}$ (c)	0.46	LE
	(a),(b) $\xrightarrow{0.05}$ (c),(d)		0.05	ME
S <sub>3</sub>	(b) $\xrightarrow{0.11}$ (c)	(a) $\xrightarrow{0.11}$ (d)	0.22	CT
	(b) $\xrightarrow{0.23}$ (d)	(a) $\xrightarrow{0.23}$ (c)	0.46	LE
	(a),(b) $\xrightarrow{0.19}$ (c),(d)	(a),(b) $\xrightarrow{0.04}$ (c),(d)	0.23	ME
S <sub>4</sub>	(b) $\xrightarrow{0.29}$ (c)	(a) $\xrightarrow{0.29}$ (d)	0.58	CT
	(b) $\xrightarrow{0.15}$ (d)	(a) $\xrightarrow{0.15}$ (c)	0.30	LE
S <sub>5</sub>	(b) $\xrightarrow{0.15}$ (d)	(a) $\xrightarrow{0.15}$ (c)	0.30	CT
	(a),(b) $\xrightarrow{0.54}$ (c),(d)	(a),(b) $\xrightarrow{0.08}$ (c),(d)	0.62	ME
S <sub>6</sub>	(b) $\xrightarrow{0.32}$ (d)	(a) $\xrightarrow{0.32}$ (c)	0.64	DE
	(b) $\xrightarrow{0.07}$ (c),(d)	(a) $\xrightarrow{0.07}$ (c),(d)	0.14	DE
	(a),(b) $\xrightarrow{0.11}$ (c),(d)		0.11	ME
S <sub>7</sub>	(b) $\xrightarrow{0.39}$ (d)	(a) $\xrightarrow{0.39}$ (c)	0.78	DE
	(b) $\xrightarrow{0.08}$ (c),(d)	(a) $\xrightarrow{0.08}$ (c),(d)	0.16	DE



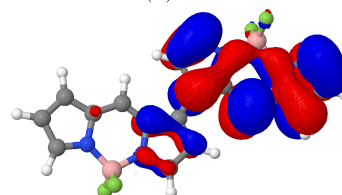
(a) HOMO-1



(b) HOMO



(c) LUMO



(d) LUMO+1

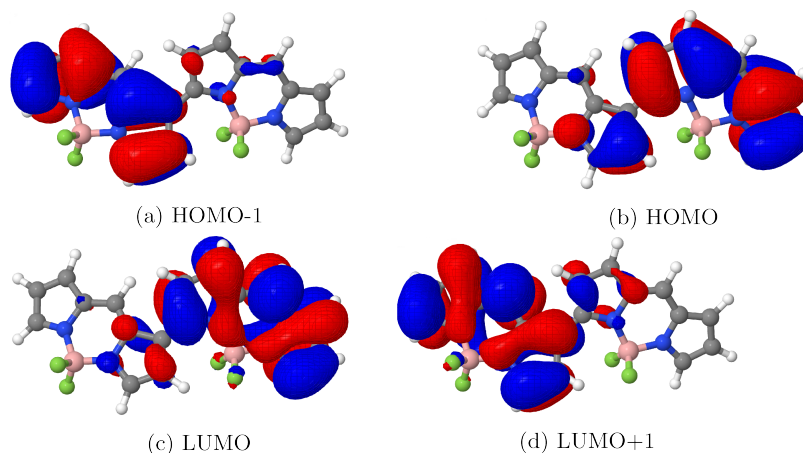
**Table S7** The excitation energy (in eV units), oscillator strength (in dimensionless) and dipole moment (in Debye units) and electronic configuration of the dimer B[1,3] calculated by using SA15-XMCQDPT(8,8), SA8-XMCQDPT(8,8) and SA8-XMCQDPT(4,4) level of theory.

S. No.	SA15-XMCQDPT(8,8)				SA8-XMCQDPT(8,8)		SA8-XMCQDPT(4,4)		Char. <sup>a</sup>
	$\Delta E$	$f$	$\mu$	config <sup>b</sup>	$\Delta E$	config <sup>b</sup>	$\Delta E$	config <sup>b</sup>	
S <sub>0</sub>	0.0	0.0	8.88	22220000	0.0	22220000	0.0	2200	GS
S <sub>1</sub>	2.156	1.047	8.83	222+-000 22+20-00	2.21	222+-000	2.09	2+-0 +20-	LE <sub>1</sub>
S <sub>2</sub>	2.489	0.024	8.01	22+2-000 22202000 22+20-00	2.64	22+2-000 22202000 22+20-00	2.54	+2-0 2020	CT <sub>1</sub>
S <sub>3</sub>	2.740	0.060	9.19	222+0-00 22202000	2.83	222+0-00 22202000 22+2-000	2.76	2+0- 2020	LE <sub>1</sub>
S <sub>4</sub>	3.133	0.550	8.16	22+20-00 22202000 22+2-000			3.15	+20- +-20 2+-0	CT <sub>1</sub>
S <sub>5</sub>	3.469	0.578	8.18	2+22-000 22202000 22+20-00	3.38	2+22-000 22202000 22+ +-00 22+20-00 22200200 +2220-00	3.62	2020 0220 2+0- ++-	ME
S <sub>6</sub>	3.601	0.206	5.03	+222-000 2+220-00 2+-22000 22202000	3.53	+222-000 2+220-00 2+22-000 +22-2000			LE <sub>2</sub>
S <sub>7</sub>	3.797	0.131	5.92	22022000 22+2-000 22+ +-00 22020200 2+22-000 +222-000 222+0-00 22202000	3.74	+222-000 22+-2000 22022000 2+22-000 2+2-2000 22+20-00			LE <sub>2</sub>
S <sub>8</sub>	4.264	0.035	9.77	2+220-00 2+2-2000 22202000					CT <sub>2</sub>
S <sub>9</sub>	4.566	0.059	16.97	2+220-00 2+22-000 22+-2000					CT <sub>2</sub>

<sup>a</sup> In the localised orbitals. Please see Fig. S4 <sup>b</sup> In the delocalised orbitals

**Figure S4** The characterization of the excited states of dimer B[1,3] by using the localised HOMO-1 (a), HOMO (b), LUMO (c) and LUMO+1 (d) orbitals. Single and double arrows represents single and double excitations. The value on top of the arrow represent the % of the particular excitation to the total wavefunction. The black and blue boxes represent the constructive and destructive combinations.

State	Orbital transition	Weight	Character
S <sub>1</sub>	(b) $\xrightarrow{0.39}$ (c)   (a) $\xrightarrow{0.29}$ (d)	0.68	LE
	(b) $\xrightarrow{0.08}$ (d)   (a) $\xrightarrow{0.17}$ (c)	0.25	CT
S <sub>2</sub>	(b) $\xrightarrow{0.19}$ (c)   (a) $\xrightarrow{0.22}$ (d)	0.41	LE
	(b) $\xrightarrow{0.23}$ (d)   (a) $\xrightarrow{0.16}$ (c)	0.39	CT
	(a),(b) $\xrightarrow{0.08}$ (c),(d)	0.08	ME
S <sub>3</sub>	(b) $\xrightarrow{0.22}$ (c)   (a) $\xrightarrow{0.30}$ (d)	0.52	LE
	(b) $\xrightarrow{0.16}$ (d)   (a) $\xrightarrow{0.09}$ (c)	0.25	CT
	(a),(b) $\xrightarrow{0.12}$ (c),(d)	0.12	ME
S <sub>4</sub>	(b) $\xrightarrow{0.14}$ (c)   (a) $\xrightarrow{0.12}$ (d)	0.26	LE
	(b) $\xrightarrow{0.32}$ (d)   (a) $\xrightarrow{0.23}$ (c)	0.55	CT
S <sub>5</sub>	(b) $\xrightarrow{0.06}$ (d)   (a) $\xrightarrow{0.24}$ (c)	0.30	CT
	(a),(b) $\xrightarrow{0.51}$ (c),(d)   (a),(b) $\xrightarrow{0.09}$ (c),(d)	0.60	ME
S <sub>6</sub>	(b) $\xrightarrow{0.63}$ (c)	0.63	DE
	(b) $\xrightarrow{0.13}$ (c),(d)	0.13	DE
	(a),(b) $\xrightarrow{0.09}$ (c)	0.09	DE
	(a),(b) $\xrightarrow{0.08}$ (c),(d)	0.08	ME
S <sub>7</sub>	(a) $\xrightarrow{0.75}$ (d)	0.75	DE
	(a) $\xrightarrow{0.10}$ (c),(d)	0.10	DE
	(a),(b) $\xrightarrow{0.05}$ (c),(d)	0.05	ME



**Table S8** The excitation energy (in eV units), oscillator strength (in dimensionless) and dipole moment (in Debye units) and electronic configuration of the dimer B[3,3] calculated by using SA15-XMCQDPT(8,8), SA8-XMCQDPT(8,8) and SA8-XMCQDPT(4,4) level of theory.

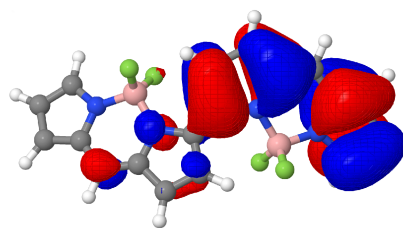
S. No.	SA15-XMCQDPT(8,8)				SA8-XMCQDPT(8,8)		SA8-XMCQDPT(4,4)		Char. <sup>a</sup>
	$\Delta E$	$f$	$\mu$	config <sup>b</sup>	$\Delta E$	config <sup>b</sup>	$\Delta E$	config <sup>b</sup>	
S <sub>0</sub>	0.0	0.0	0.028	22220000	0.0	22220000	0.0	2200	GS
S <sub>1</sub>	2.046	<0.001	0.01	222+-000	2.17	222+-000	1.94	2+-0	LE <sub>1</sub>
S <sub>2</sub>	2.445	1.399	0.40	222+0-00	2.56	222+0-00	2.52	2+0-	CT <sub>1</sub>
				22202000		22202000		2020	
S <sub>3</sub>	2.929	0.003	0.82	22+2-000	3.26	22+2-000	2.75	2+0-	LE <sub>1</sub>
				22+-+00		22202000		+2-0	
S <sub>4</sub>	3.480	0.485	0.91	2+22-000	3.66	2+22-000 +2220-00			LE <sub>2</sub>
S <sub>5</sub>	3.509	0.023	0.66	+222-000	3.76	+222-000 222+0-00			LE <sub>2</sub>
S <sub>6</sub>	3.853	0.005	1.11	22202000			3.74	2+0-	ME
				222+0-00				2020	
S <sub>7</sub>	3.913	0.250	0.26	22+20-00			3.61	+20-	CT <sub>1</sub>
				+22-2000					
S <sub>8</sub>	4.563	<0.001	0.14	2+22-000					CT <sub>2</sub>
				2+-20200					
				2+-22000					
S <sub>9</sub>	4.603	0.352	0.09	2+220-00					CT <sub>2</sub>
				2+2-2000					
				+2-20200					

<sup>a</sup> In the localised orbitals. Please see Fig. S5 <sup>b</sup> In the delocalised orbitals.

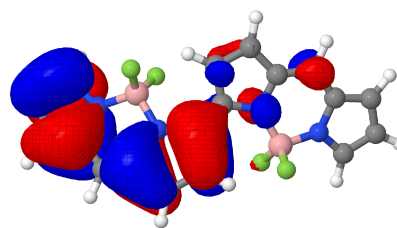


**Figure S5** The characterization of the excited states of dimer B[3,3] by using the localised HOMO-1 (a), HOMO (b), LUMO (c) and LUMO+1 (d) orbitals. Single and double arrows represents single and double excitations. The value on top of the arrow represent the % of the particular excitation to the total wavefunction. The black and blue boxes represent the constructive and destructive combinations.

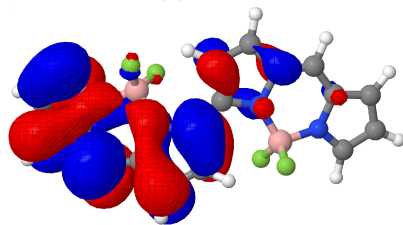
State	Orbital transition		Weight	Character
S <sub>1</sub>	(b) $\xrightarrow{0.32}$ (c)	(a) $\xrightarrow{0.32}$ (d)	0.64	LE
	(b) $\xrightarrow{0.15}$ (d)	(a) $\xrightarrow{0.15}$ (c)	0.29	CT
S <sub>2</sub>	(b) $\xrightarrow{0.26}$ (d)	(a) $\xrightarrow{0.26}$ (c)	0.51	CT
	(a),(b) $\xrightarrow{0.26}$ (c),(d)		0.26	ME
S <sub>3</sub>	(b) $\xrightarrow{0.46}$ (c)	(a) $\xrightarrow{0.46}$ (d)	0.93	LE
S <sub>4</sub>	(b) $\xrightarrow{0.21}$ (d)	(a) $\xrightarrow{0.21}$ (c)	0.42	CT
	(a),(b) $\xrightarrow{0.43}$ (c),(d)		0.43	ME
S <sub>5</sub>	(b) $\xrightarrow{0.17}$ (c)	(a) $\xrightarrow{0.17}$ (d)	0.35	LE
	(b) $\xrightarrow{0.25}$ (d)	(a) $\xrightarrow{0.25}$ (c)	0.50	CT
S <sub>6</sub>	(b) $\xrightarrow{0.38}$ (c)	(a) $\xrightarrow{0.38}$ (d)	0.77	DE
	(b) $\xrightarrow{0.05}$ (c),(d)	(a) $\xrightarrow{0.05}$ (c),(d)	0.11	DE
	(a),(b) $\xrightarrow{0.06}$ (c)	(a),(b) $\xrightarrow{0.05}$ (d)	0.12	DE
S <sub>7</sub>	(b) $\xrightarrow{0.25}$ (c)	(a) $\xrightarrow{0.25}$ (d)	0.50	DE
	(a),(b) $\xrightarrow{0.10}$ (c),(d)	(a),(b) $\xrightarrow{0.21}$ (c),(d)	0.32	ME



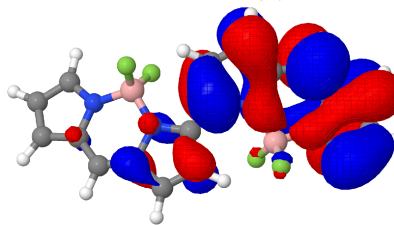
(a) HOMO-1



(b) HOMO



(c) LUMO



(d) LUMO+1

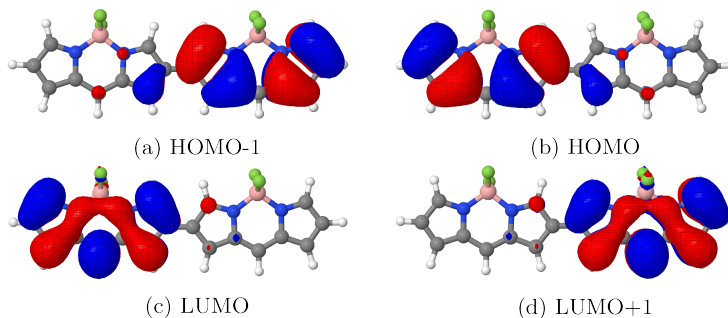
**Table S9** The excitation energy (in eV units), oscillator strength (in dimensionless) and dipole moment (in Debye units) and electronic configuration of the dimer B[2,2] calculated by using SA15-XMCQDPT(8,8), SA8-XMCQDPT(8,8) and SA8-XMCQDPT(4,4) level of theory.

S. No.	SA15-XMCQDPT(8,8)			SA8-XMCQDPT(8,8)		SA8-XMCQDPT(4,4)		Char. <sup>a</sup>	
	$\Delta E$	$f$	$\mu$	config <sup>b</sup>	$\Delta E$	config <sup>b</sup>	$\Delta E$		config <sup>b</sup>
S <sub>0</sub>	0.0	0.0	9.06	22220000	0.0	22220000	0.0	2200	GS
S <sub>1</sub>	2.054	1.461	8.46	222+-000	2.06	222+-000	2.04	2+-0	LE <sub>1</sub>
				222+0-00		22+20-00			
				22+20-00					
				22+2-000					
S <sub>2</sub>	2.550	0.251	12.38	222+0-00	2.58	222+0-00	2.57	2+0-	LE <sub>1</sub>
				22+2-000		22+2-000		+2-0	
S <sub>3</sub>	3.039	0.042	7.74	22+2-000	3.12	22+2-000	3.07	2020	CT <sub>1</sub>
				22202000		22++-00		++-	
				222+-000		222+0-00		2002	
				2+22-000				2+0-	
S <sub>4</sub>	3.329	0.470	10.32	22+20-00	3.52	22+20-00	3.44	+20-	CT <sub>1</sub>
				2+22-000		222+-000		2+-0	
				2220+-00		2220+-00			
				22202000		2+2+-00			
S <sub>5</sub>	3.679	0.072	11.02	22+20-00	3.80	22+2-000	3.66	+2-0	ME
				22200200		22202000		2002	
				22202000		22202000		2020	
				2+220-00		22022000		0202	
S <sub>6</sub>	3.822	0.019	9.38	2+22-000	4.26	22++-00		++-	LE <sub>2</sub>
				22+-2000		222+00-0			
				22+2-000					
				222+-000					
S <sub>7</sub>	4.228	0.308	7.47	2+220-00	4.26	2+22-000			LE <sub>2</sub>
				22+-+-00		2220+-00			
				2+2-+-00		22+-2000			
				22202000		22+-+-00			
S <sub>8</sub>	4.342	0.030	8.82	+222-000					CT <sub>2</sub>
				22022000					
				22+-2000					
S <sub>9</sub>	4.705	0.074	16.39	2+220-00					CT <sub>2</sub>
				2+2-0200					
				22++-00					

<sup>a</sup> In the localised orbitals. Please see Fig. S6 <sup>b</sup> In the delocalised orbitals

**Figure S6** The characterization of the excited states of dimer B[2,2] by using the localised HOMO-1 (a), HOMO (b), LUMO (c) and LUMO+1 (d) orbitals. Single and double arrows represents single and double excitations. The value on top of the arrow represent the % of the particular excitation to the total wavefunction. The black and blue boxes represent the constructive and destructive combinations.

State	Orbital transition		Weight	Character
S <sub>1</sub>	(b) $\xrightarrow{0.38}$ (c)	(a) $\xrightarrow{0.38}$ (d)	0.77	LE
	(b) $\xrightarrow{0.09}$ (d)	(a) $\xrightarrow{0.09}$ (c)	0.18	CT
S <sub>2</sub>	(b) $\xrightarrow{0.38}$ (c)	(a) $\xrightarrow{0.38}$ (d)	0.77	LE
	(b) $\xrightarrow{0.08}$ (d)	(a) $\xrightarrow{0.08}$ (c)	0.16	CT
S <sub>3</sub>	(b) $\xrightarrow{0.08}$ (c)	(a) $\xrightarrow{0.08}$ (d)	0.15	LE
	(b) $\xrightarrow{0.18}$ (d)	(a) $\xrightarrow{0.18}$ (c)	0.36	CT
	(a),(b) $\xrightarrow{0.31}$ (c),(d)	(a),(b) $\xrightarrow{0.10}$ (c),(d)	0.41	ME
S <sub>4</sub>	(b) $\xrightarrow{0.10}$ (c)	(a) $\xrightarrow{0.10}$ (d)	0.20	LE
	(b) $\xrightarrow{0.35}$ (d)	(a) $\xrightarrow{0.35}$ (c)	0.70	CT
S <sub>5</sub>	(b) $\xrightarrow{0.21}$ (d)	(a) $\xrightarrow{0.21}$ (c)	0.42	CT
	(a),(b) $\xrightarrow{0.46}$ (c),(d)	(a),(b) $\xrightarrow{0.06}$ (c),(d)	0.52	ME
S <sub>6</sub>	(b) $\xrightarrow{0.35}$ (c)	(a) $\xrightarrow{0.35}$ (d)	0.70	DE
	(a),(b) $\xrightarrow{0.13}$ (c),(d)		0.13	ME
S <sub>7</sub>	(b) $\xrightarrow{0.44}$ (c)	(a) $\xrightarrow{0.44}$ (d)	0.88	DE



**Table S10** The excitation energy (in eV units), oscillator strength (in dimensionless) and dipole moment (in Debye units) and electronic configuration of the dimer B[2,8] calculated by using SA15-XMCQDPT(8,8), SA8-XMCQDPT(8,8) and SA8-XMCQDPT(4,4) level of theory.

S. No.	SA15-XMCQDPT(8,8)				SA8-XMCQDPT(8,8)		SA8-XMCQDPT(4,4)		Char. <sup>a</sup>
	$\Delta E$	$f$	$\mu$	config <sup>b</sup>	$\Delta E$	config <sup>b</sup>	$\Delta E$	config <sup>b</sup>	
S <sub>0</sub>	0.00	0.00	6.78	22220000	0.00	22220000	0.00	2200	GS
S <sub>1</sub>	2.416	0.546	5.40	222+-000	2.42	222+-000	2.38	2+-0	LE <sub>1</sub>
				22+2-000		22+2-000		+2-0	
				22+20-00		22++-00		+20-	
				22++-00					
S <sub>2</sub>	2.553	0.021	4.71	22+2-000	2.53	22+2-000	2.42	+2-0	LE <sub>1</sub>
				222+-000		222+-000		2+-0	
				22+20-00				2+0-	
S <sub>3</sub>	2.793	0.286	5.81	222+0-00	2.75	222+0-00	2.75	2+0-	CT <sub>1</sub>
						22+20-00		+20-	
S <sub>4</sub>	3.368	0.030	6.39	22+20-00			3.24	+20-	CT <sub>1</sub>
				22+2-000				+2-0	
				2+22-000				2+0-	
								2+0	
S <sub>5</sub>	3.453	0.753	4.91	2+220-00	3.41	2+220-00			LE <sub>2</sub>
				2+22-000		2+22-000			
				22+2-000		+222-000			
				2+-20200		+2220-00			
S <sub>6</sub>	3.493	0.880	15.09	+222-000	3.40	+222-000			LE <sub>2</sub>
				2+22-000		2+22-000			
				+22-2000		2+220-00			
S <sub>7</sub>	3.840	0.036	7.32	22++-00	3.83	22++-00	3.74	++-	ME
				222+0-00		22202000		2+0-	
				22+-2000		22200200		+20	
				22+-+00				+02	
				22+-0200				2020	
S <sub>8</sub>	4.182	0.232	16.28	+2220-00				CT <sub>2</sub>	
S <sub>9</sub>	4.325	0.016	7.98	2+22-000				CT <sub>2</sub>	
				2+220-00					

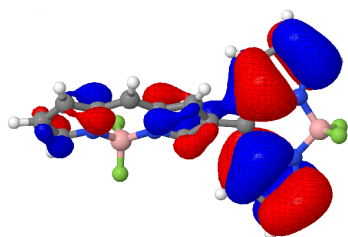
<sup>a</sup> In the localised orbitals. Please see Fig. S7 <sup>b</sup> In the delocalised orbitals

**Table S11** The diabatic electronic energies and couplings between the diabatic states  $|^1(S_0S_0)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(S_1S_0)\rangle$ ,  $|^1(S_1S_1)\rangle$ ,  $|^1(CA)\rangle$ ,  $|^1(AC)\rangle$ ,  $|^1(T_1T_1)\rangle$ ,  $|^1(DE)_1\rangle$  and  $|^1(DE)_2\rangle$  for the system B[1,1] calculated at SA8-XMCQDPT(4,4)/cc-pVDZ level of theory.

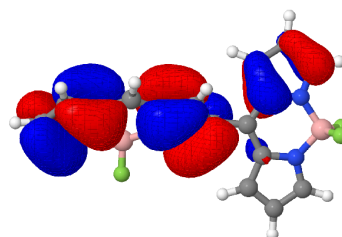
$\mathcal{H}_{el}$	$ ^1(S_0S_0)\rangle$	$ ^1(S_1S_0)\rangle$	$ ^1(S_0S_1)\rangle$	$ ^1(CA)\rangle$	$ ^1(AC)\rangle$	$ ^1(T_1T_1)\rangle$	$ ^1(DE)_1\rangle$	$ ^1(DE)_2\rangle$
$\langle^1(S_0S_0) $	0.0000	-0.0237	-0.0237	0.2228	-0.2228	-0.0664	0.5071	-0.5070
$ ^1(S_1S_0)\rangle$	-0.0237	2.3547	0.1250	-0.1582	-0.4405	-0.0301	0.0192	0.0547
$ ^1(S_0S_1)\rangle$	-0.0237	0.1250	2.3550	0.4405	0.1583	-0.0301	-0.0546	-0.0191
$ ^1(CA)\rangle$	0.2228	-0.1582	0.4405	2.7182	0.0428	-0.2610	0.1417	-0.0036
$ ^1(AC)\rangle$	-0.2228	-0.4405	0.1583	0.0428	2.7184	0.2610	-0.0035	0.1418
$\langle^1(T_1T_1) $	-0.0664	-0.0301	-0.0301	-0.2610	0.2610	3.1378	0.1808	-0.1810
$\langle^1(DE)_1 $	0.5071	0.0192	-0.0546	0.1417	-0.0035	0.1808	4.2661	0.1159
$\langle^1(DE)_2 $	-0.5070	0.0547	-0.0191	-0.0036	0.1418	-0.1810	0.1159	4.2661

**Figure S7** The characterization of the excited states of dimer B[2,8] by using the localised HOMO-1 (a), HOMO (b), LUMO (c) and LUMO+1 (d) orbitals. Single and double arrows represents single and double excitations. The value on top of the arrow represent the % of the particular excitation to the total wavefunction. The black and blue boxes represent the constructive and destructive combinations.

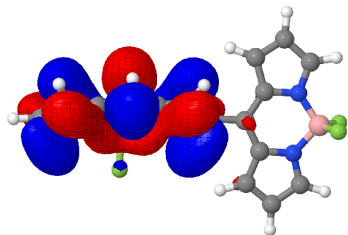
State	Orbital transition	Weight	Character
S <sub>1</sub>	(b) $\xrightarrow{0.65}$ (c)   (a) $\xrightarrow{0.13}$ (d)	0.78	LE
	(b) $\xrightarrow{0.17}$ (d)	0.17	CT
S <sub>2</sub>	(b) $\xrightarrow{0.13}$ (c)   (a) $\xrightarrow{0.58}$ (d)	0.71	LE
	(a) $\xrightarrow{0.23}$ (c)	0.23	CT
S <sub>3</sub>	(b) $\xrightarrow{0.07}$ (c)   (a) $\xrightarrow{0.17}$ (d)	0.24	LE
	(a) $\xrightarrow{0.58}$ (c)	0.58	CT
	(a),(b) $\xrightarrow{0.07}$ (c),(d)	0.07	ME
S <sub>4</sub>	(b) $\xrightarrow{0.10}$ (c)   (a) $\xrightarrow{0.08}$ (d)	0.18	LE
	(b) $\xrightarrow{0.73}$ (d)	0.73	CT
S <sub>5</sub>	(b) $\xrightarrow{0.10}$ (c),(d)   (a) $\xrightarrow{0.10}$ (c),(d)	0.20	DE
	(a),(b) $\xrightarrow{0.38}$ (c),(d)   (a),(b) $\xrightarrow{0.23}$ (c),(d)	0.61	ME
S <sub>6</sub>	(b) $\xrightarrow{0.68}$ (c)	0.68	DE
	(b) $\xrightarrow{0.09}$ L,(d)	0.09	DE
	(a),(b) $\xrightarrow{0.13}$ (c)	0.13	DE
S <sub>7</sub>	(a) $\xrightarrow{0.74}$ (d)	0.74	DE
	(a),(b) $\xrightarrow{0.16}$ (d)	0.16	DE



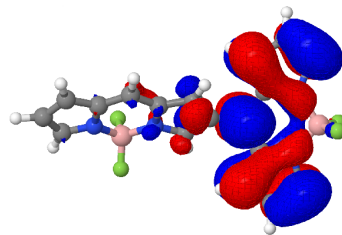
(a) HOMO-1



(b) HOMO

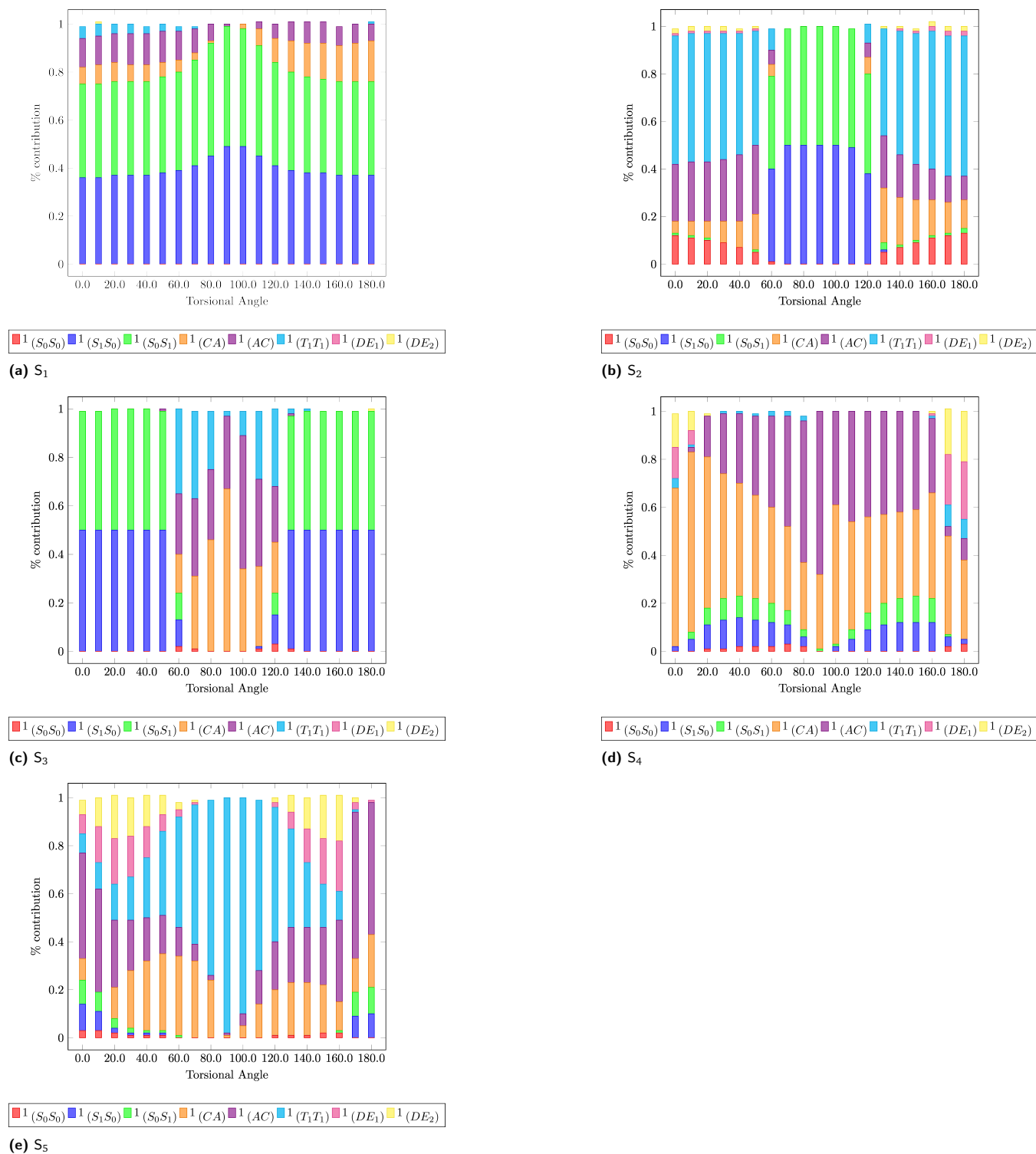


(c) LUMO

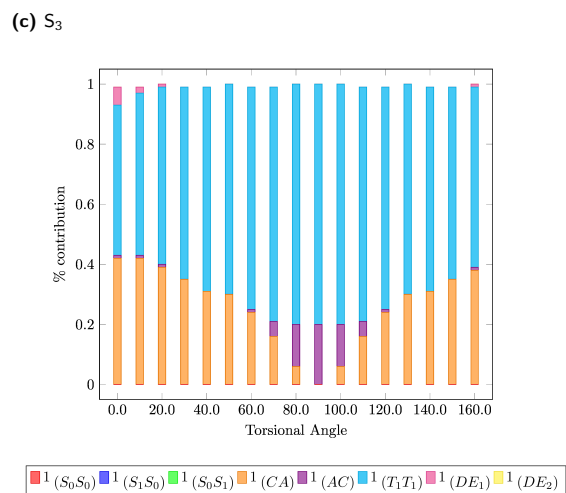
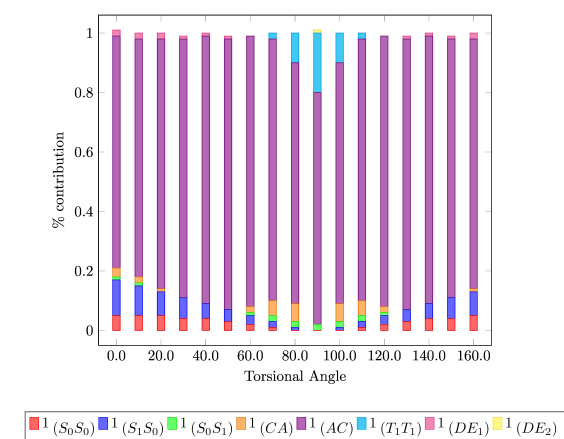
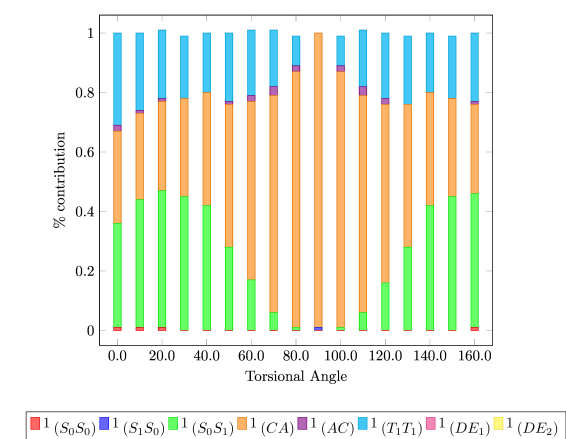
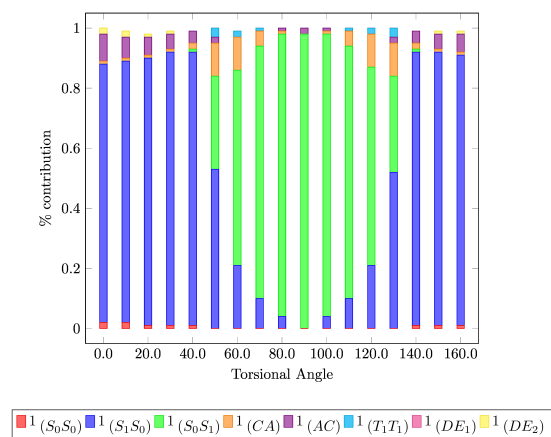
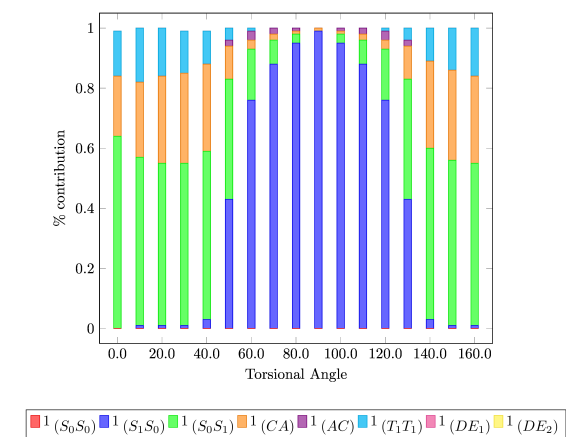


(d) LUMO+1

**Figure S8** The contribution of the diabatic states  $|^1(S_0S_0)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(T_1T_1)\rangle$ ,  $|^1(AC)\rangle$ ,  $|^1(CA)\rangle$ ,  $|^1(DE)_1\rangle$  and  $|^1(DE)_2\rangle$  to the adiabatic states ( $S_1 - S_6$ ) for dimer B[3,3].



**Figure S9** The contribution of the diabatic states  $|^1(S_0S_0)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(T_1T_1)\rangle$ ,  $|^1(AC)\rangle$ ,  $|^1(CA)\rangle$ ,  $|^1(DE)_1\rangle$  and  $|^1(DE)_2\rangle$  to the adiabatic states ( $S_1 - S_6$ ) of dimer B[2,8]



**Table S12** The diabatic electronic energies and couplings (in eVs) between the diabatic states  $|^1(S_0S_0)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(T_1T_1)\rangle$ ,  $|^1(AC)\rangle$ ,  $|^1(CA)\rangle$ ,  $|^1(DE)_1\rangle$  and  $|^1(DE)_2\rangle$  for the system B[1,3] calculated at SA8-XMCQDPT(4,4)/cc-pVDZ level of theory.

$\mathcal{H}_{el}$	$ ^1(S_0S_0)\rangle$	$ ^1(S_1S_0)\rangle$	$ ^1(S_0S_1)\rangle$	$ ^1(CA)\rangle$	$ ^1(AC)\rangle$	$ ^1(T_1T_1)\rangle$	$ ^1(DE)_1\rangle$	$ ^1(DE)_2\rangle$
$\langle^1(S_0S_0) $	0.0000	0.0014	-0.0435	0.2314	-0.1584	-0.0402	0.4241	0.4445
$ ^1(S_1S_0)\rangle$	0.0014	2.3344	0.1286	0.3331	0.2983	0.0524	0.0262	0.0164
$\langle^1(S_0S_1) $	-0.0435	0.1286	2.4168	-0.1375	-0.4078	-0.0579	0.0542	-0.0786
$ ^1(CA)\rangle$	0.2314	0.3331	-0.1375	2.7466	0.0241	-0.2722	0.2091	0.0260
$ ^1(AC)\rangle$	-0.1584	0.2983	-0.4078	0.0241	2.7800	0.3048	0.0308	-0.1623
$\langle^1(T_1T_1) $	-0.0402	0.0524	-0.0579	-0.2722	0.3048	3.2782	0.1518	0.2988
$\langle^1(DE)_1 $	0.4241	0.0262	0.0542	0.2091	0.0308	0.1518	4.1676	-0.1119
$\langle^1(DE)_2 $	0.4445	0.0164	-0.0786	0.0260	-0.1623	0.2988	-0.1119	4.4710

**Table S13** The diabatic electronic energies and couplings (in eVs) between the states  $|^1(S_0S_0)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(T_1T_1)\rangle$ ,  $|^1(AC)\rangle$ ,  $|^1(CA)\rangle$ ,  $|^1(DE)_1\rangle$  and  $|^1(DE)_2\rangle$  for the system B[3,3] calculated at SA8-XMCQDPT(4,4)/cc-pVDZ level of theory.

$\mathcal{H}_{el}$	$ ^1(S_0S_0)\rangle$	$ ^1(S_1S_0)\rangle$	$ ^1(S_0S_1)\rangle$	$ ^1(CA)\rangle$	$ ^1(AC)\rangle$	$ ^1(T_1T_1)\rangle$	$ ^1(DE)_1\rangle$	$ ^1(DE)_2\rangle$
$\langle^1(S_0S_0) $	0.0000	0.0110	-0.0072	-0.1967	0.2075	0.0796	0.5153	0.5161
$ ^1(S_1S_0)\rangle$	0.0110	2.4327	-0.1443	-0.5013	-0.4575	0.0047	-0.0001	-0.0009
$ ^1(S_0S_1)\rangle$	-0.0072	-0.1443	2.4328	-0.4742	-0.4852	0.0027	0.0160	0.0139
$ ^1(CA)\rangle$	-0.1967	-0.5013	-0.4742	2.7829	0.0695	-0.4258	-0.0839	-0.0637
$ ^1(AC)\rangle$	0.2075	-0.4575	-0.4852	0.0695	2.7910	0.4322	0.1157	0.0697
$\langle^1(T_1T_1) $	0.0796	0.0047	0.0027	-0.4258	0.4322	3.2583	-0.4239	-0.3908
$\langle^1(DE)_1 $	0.5153	-0.0001	0.0160	-0.0839	0.1157	-0.4239	4.1604	-0.1626
$\langle^1(DE)_2 $	0.5161	-0.0009	0.0139	-0.0637	0.0697	-0.3908	-0.1626	4.1785

**Table S14** The diabatic electronic energies and couplings (in eVs) between the diabatic states  $|^1(S_0S_0)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(T_1T_1)\rangle$ ,  $|^1(AC)\rangle$ ,  $|^1(CA)\rangle$ ,  $|^1(DE)_1\rangle$  and  $|^1(DE)_2\rangle$  for the system B[2,2] calculated at SA8-XMCQDPT(4,4)/cc-pVDZ level of theory.

$\mathcal{H}_{el}$	$ ^1(S_0S_0)\rangle$	$ ^1(S_1S_0)\rangle$	$ ^1(S_0S_1)\rangle$	$ ^1(CA)\rangle$	$ ^1(AC)\rangle$	$ ^1(T_1T_1)\rangle$	$ ^1(DE)_1\rangle$	$ ^1(DE)_2\rangle$
$ ^1(S_0S_0)\rangle$	0.0	0.0217	-0.0218	0.1222	-0.1222	0.0012	-0.4386	-0.4386
$ ^1(S_1S_0)\rangle$	0.0217	2.3686	-0.1813	-0.1927	-0.4496	-0.0124	0.0807	-0.0154
$ ^1(S_0S_1)\rangle$	-0.0218	-0.1813	2.3688	-0.4499	-0.1925	0.0126	0.0155	-0.0806
$ ^1(CA)\rangle$	0.1222	-0.1927	-0.4499	3.1279	-0.0223	-0.2394	0.0242	-0.1423
$ ^1(AC)\rangle$	-0.1222	-0.4496	-0.1925	-0.0223	3.1282	0.2394	0.1424	-0.0241
$\langle^1(T_1T_1) $	0.0012	-0.0124	0.0126	-0.2394	0.2394	3.3076	-0.1372	-0.1372
$ ^1(DE)_1\rangle$	-0.4386	0.0807	0.0155	0.0242	0.1424	-0.1372	4.5303	-0.1453
$\langle^1(DE)_2 $	-0.4386	-0.0154	-0.0806	-0.1423	-0.0241	-0.1372	-0.1453	4.5303

**Table S15** The diabatic electronic energies and couplings (in eVs) between the diabatic states  $|^1(S_0S_0)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(S_0S_1)\rangle$ ,  $|^1(T_1T_1)\rangle$ ,  $|^1(AC)\rangle$ ,  $|^1(CA)\rangle$ ,  $|^1(DE)_1\rangle$  and  $|^1(DE)_2\rangle$  for the system B[2,8] calculated at SA8-XMCQDPT(4,4)/cc-pVDZ level of theory.

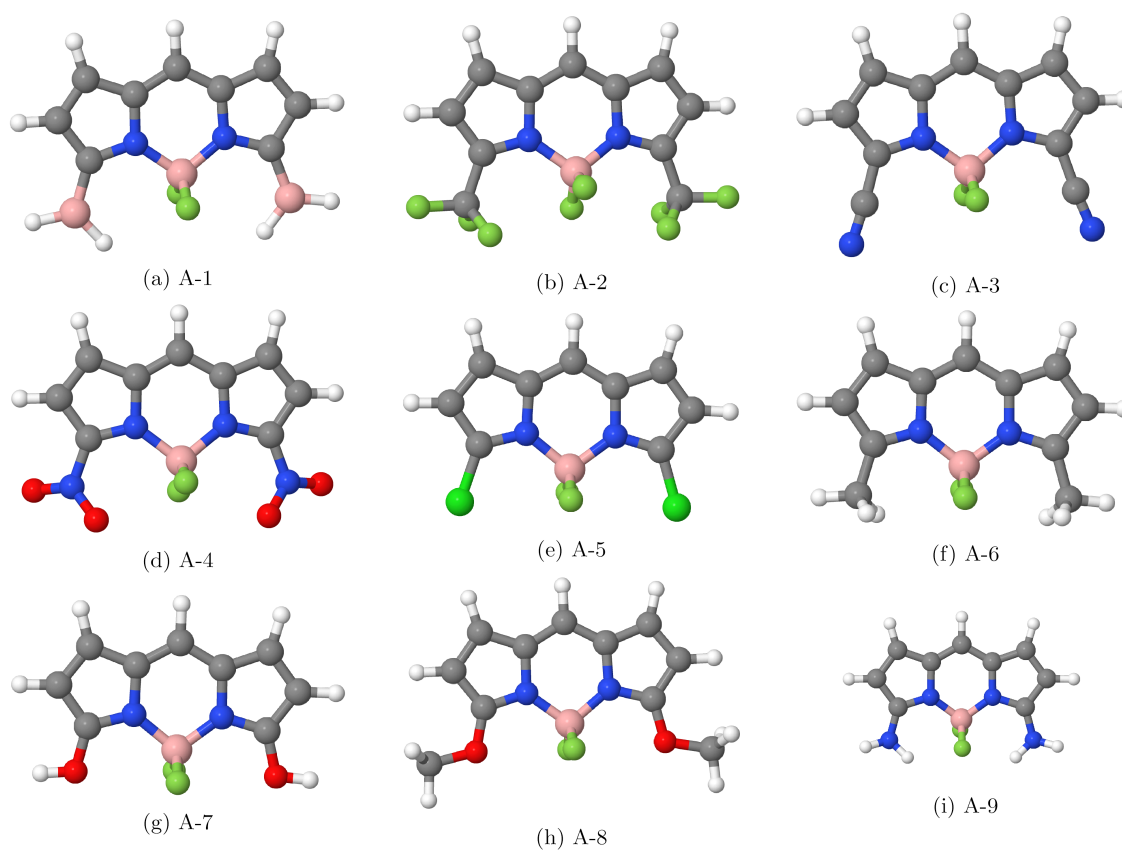
$\mathcal{H}_{el}$	$ ^1(S_0S_0)\rangle$	$ ^1(S_1S_0)\rangle$	$ ^1(S_0S_1)\rangle$	$ ^1(CA)\rangle$	$ ^1(AC)\rangle$	$ ^1(T_1T_1)\rangle$	$ ^1(DE)_1\rangle$	$ ^1(DE)_2\rangle$
$ ^1(S_0S_0)\rangle$	0.0000	0.0692	0.0206	0.0129	0.0346	0.0071	-0.4343	0.4498
$ ^1(S_1S_0)\rangle$	0.0692	2.4129	0.0239	-0.0999	0.2919	0.1167	0.0221	0.0179
$ ^1(S_0S_1)\rangle$	0.0206	0.0239	2.4382	0.1717	0.2094	0.0324	0.0115	-0.0509
$ ^1(CA)\rangle$	0.0129	-0.0999	0.1717	2.7348	0.0461	-0.3536	0.0188	0.0129
$ ^1(AC)\rangle$	0.0346	0.2919	0.2094	0.0461	3.0181	0.0127	0.0599	-0.1780
$ ^1(T_1T_1)\rangle$	0.0071	0.1167	0.0324	-0.3536	0.0127	3.5105	0.0087	-0.0005
$ ^1(DE)_1\rangle$	-0.4343	0.0221	0.0115	0.0188	0.0599	0.0087	4.8379	0.0571
$ ^1(DE)_2\rangle$	0.4498	0.0179	-0.0509	0.0129	-0.1780	-0.0005	0.0571	4.8838



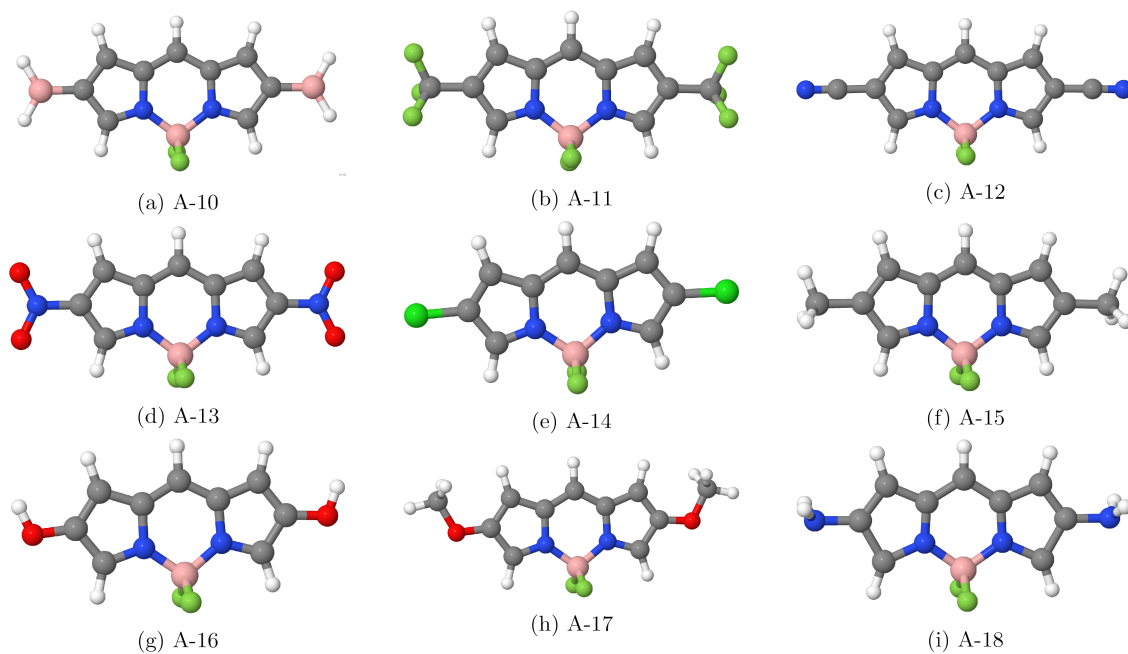
**Table S16** The excitation energy (in eV units) of the dimer B[3,3] calculated by using SA15-XMCQDPT(12,10), SA15-XMCQDPT(8,8) level of theory.

S. No.	SA15-XMCQDPT(12,10)	SA15-XMCQDPT(8,8)
	$\Delta E$	$\Delta E$
S <sub>0</sub>	0.00	0.00
S <sub>1</sub>	2.03	2.04
S <sub>2</sub>	2.53	2.44
S <sub>3</sub>	2.68	2.92
S <sub>4</sub>	3.44	3.48
S <sub>5</sub>	3.47	3.50
S <sub>6</sub>	3.69	3.85
S <sub>7</sub>	3.69	3.91
T <sub>1</sub>	1.37	1.35
T <sub>2</sub>	1.92	1.93
T <sub>3</sub>	2.70	3.10
T <sub>4</sub>	2.81	3.11
T <sub>5</sub>	3.09	3.34
T <sub>6</sub>	3.13	3.36
T <sub>7</sub>	3.60	4.10

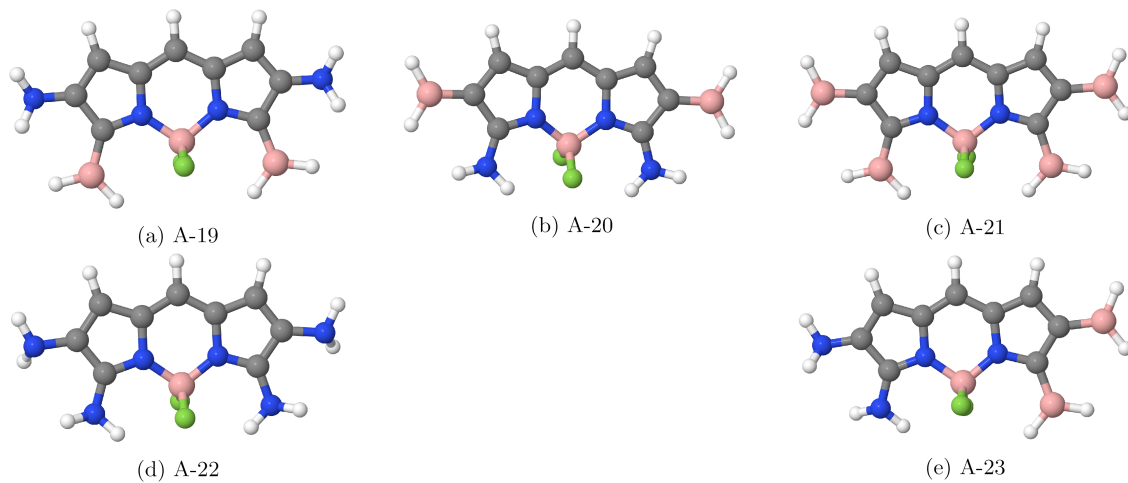
**Figure S10** The ball and stick representation of optimized geometries with substitutions at  $\alpha$  positions.



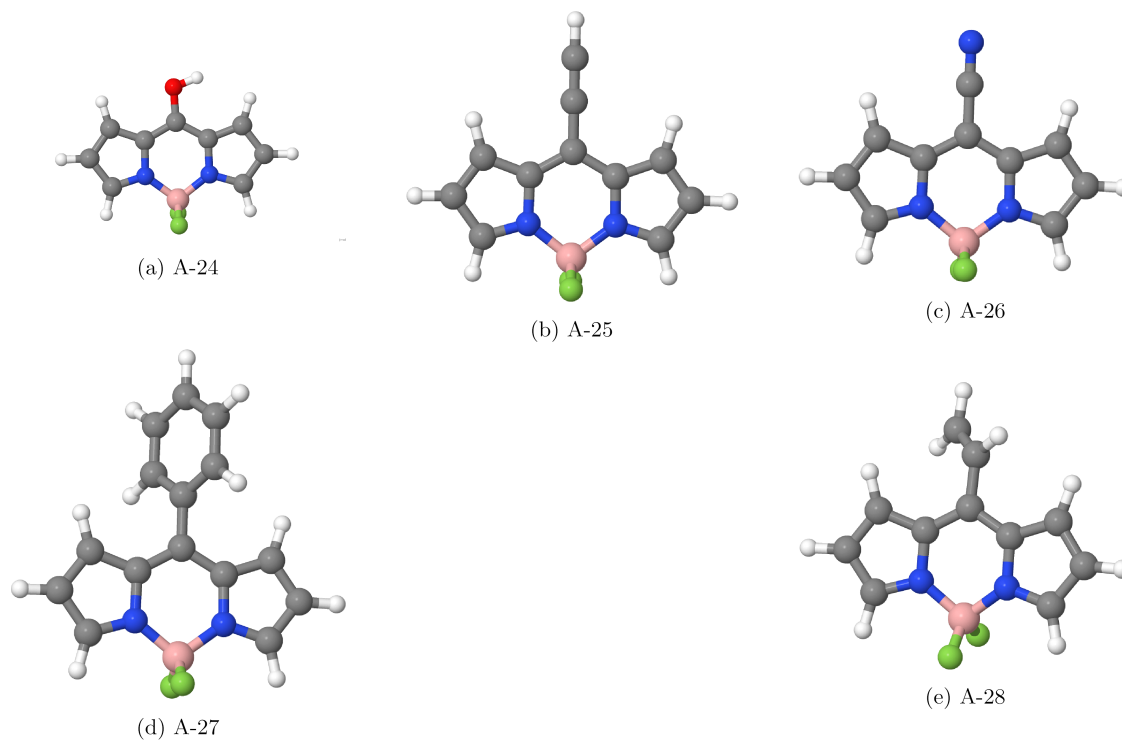
**Figure S11** The ball and stick representation of optimized geometries with substitutions at  $\beta$  positions.



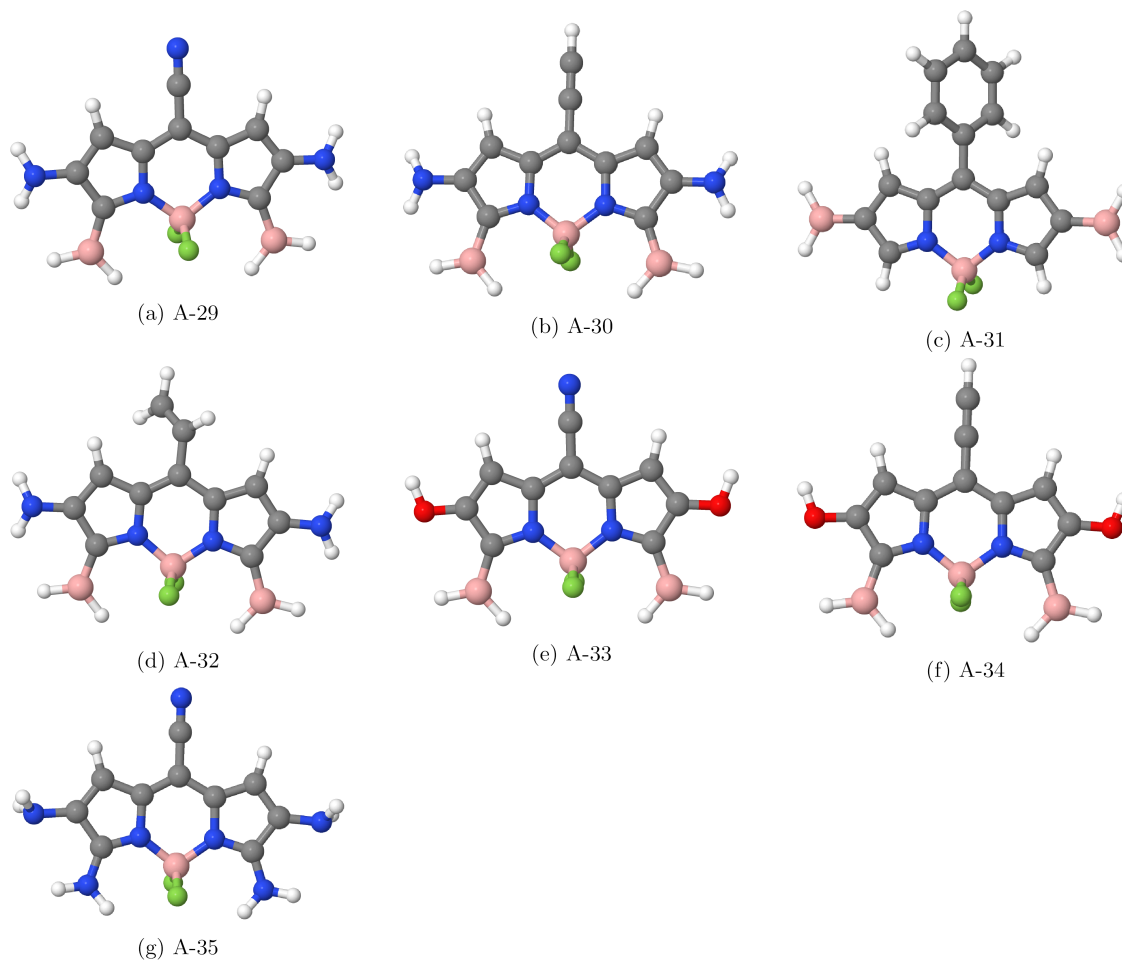
**Figure S12** The ball and stick representation of optimized geometries with substitutions at  $\alpha$  and  $\beta$  positions.



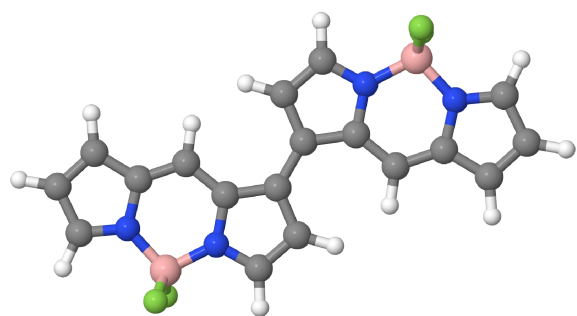
**Figure S13** The ball and stick representation of optimized geometries with substitutions at meso position.



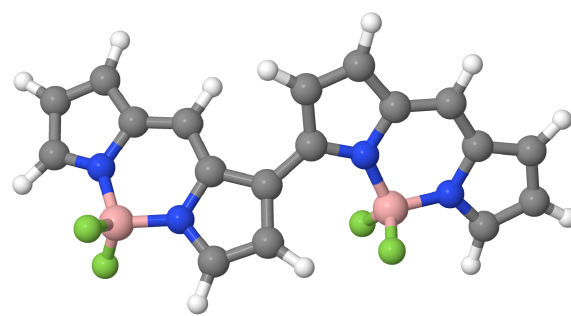
**Figure S14** The ball and stick representation of optimized geometries with substitutions at  $\alpha$ ,  $\beta$  and meso positions.



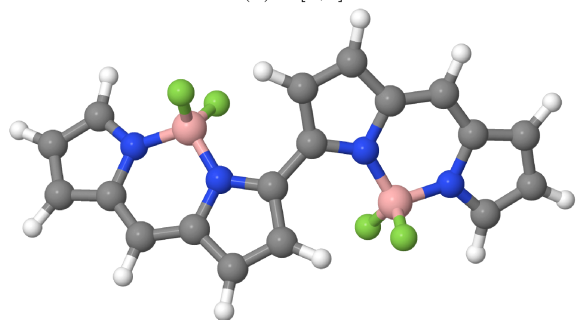
**Figure S15** The ball and stick representation of optimized geometries of BODIPY dimers B[1,1], B[1,3], B[3,3], B[2,2] and B[2,8].



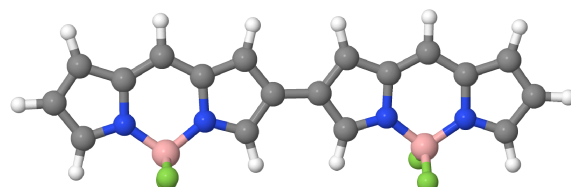
(a) B[1,1]



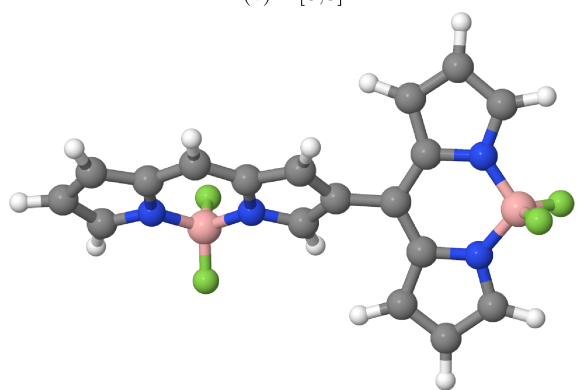
(b) B[1,3]



(c) B[3,3]

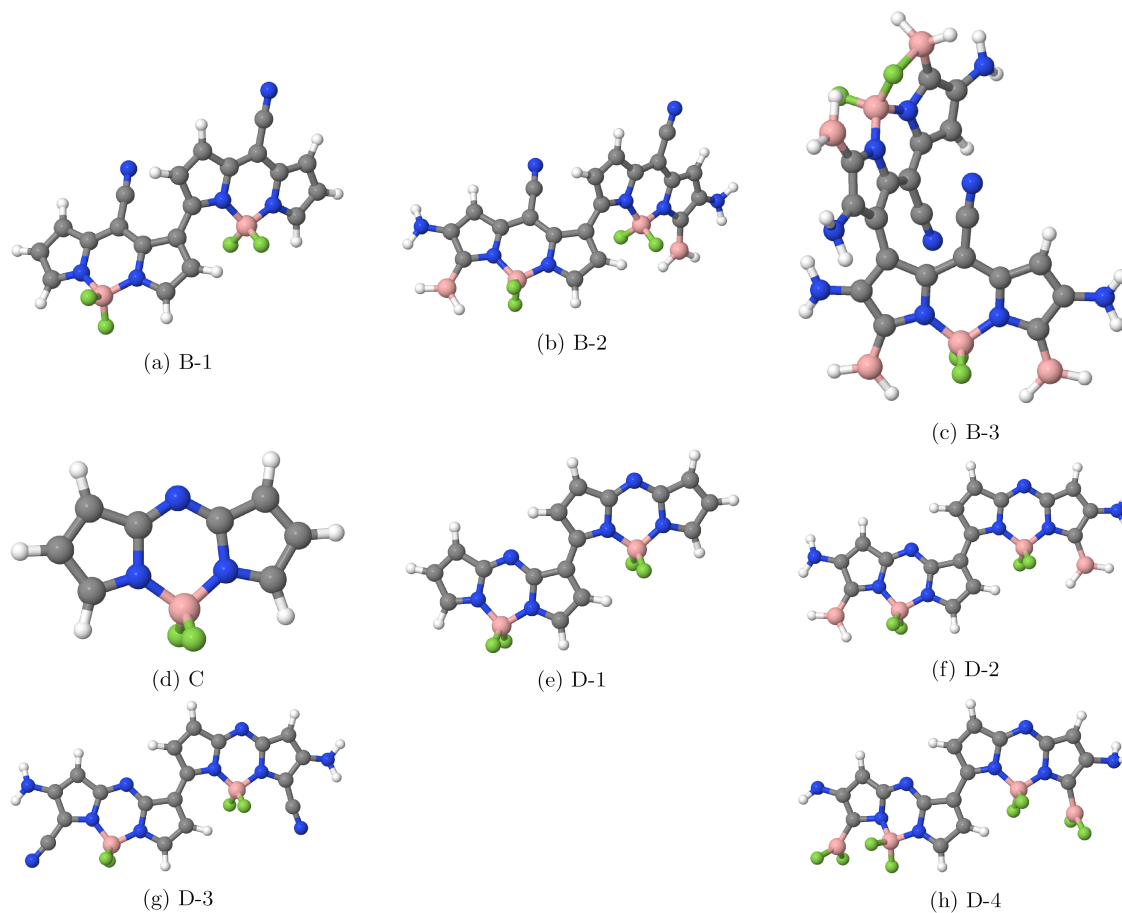


(d) B[2,2]

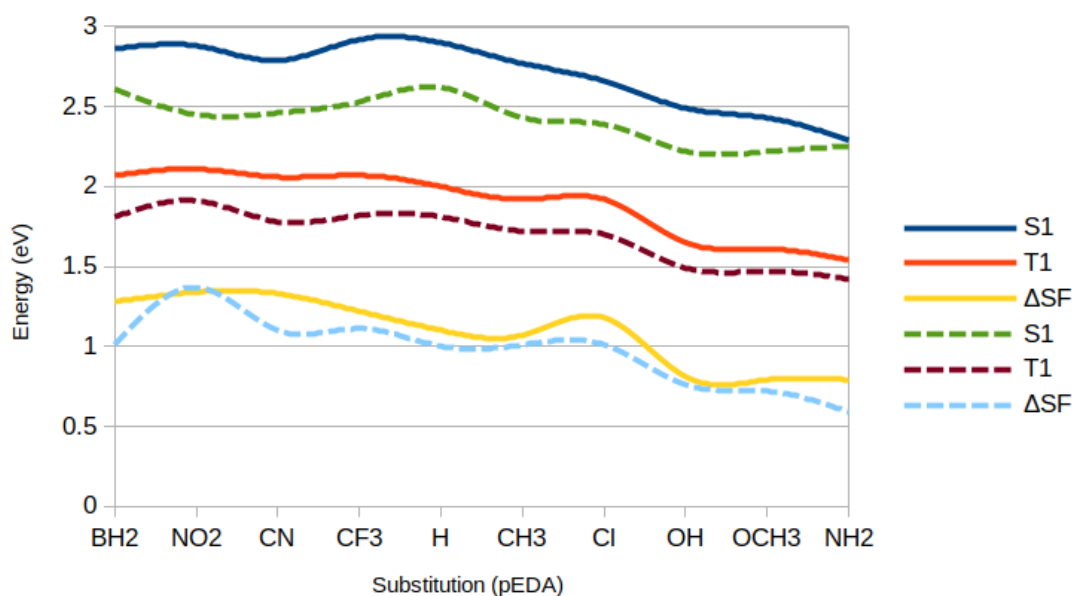


(e) B[2,8]

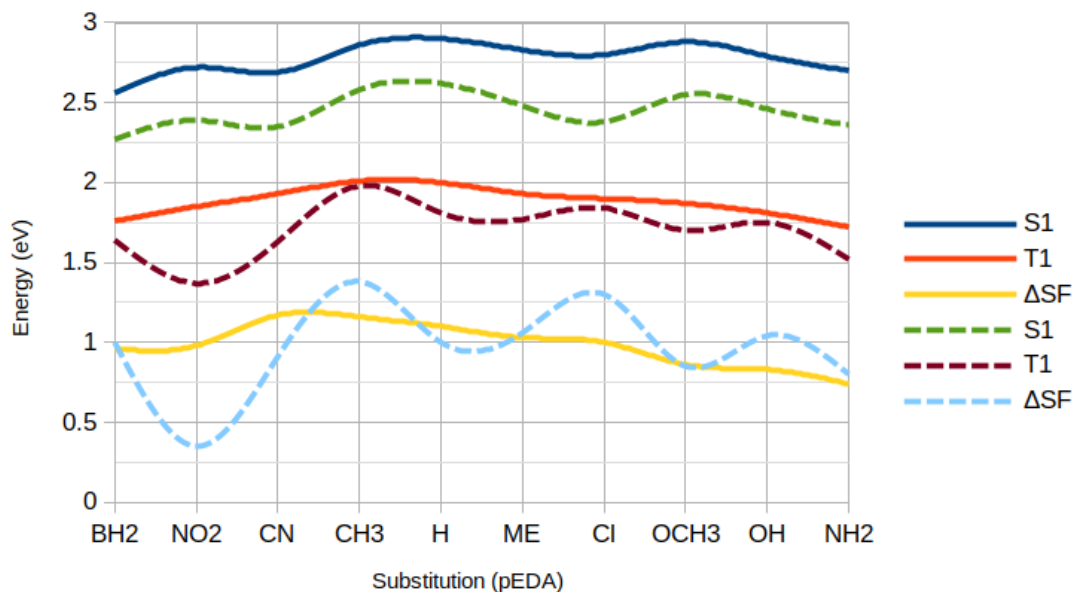
**Figure S16** The ball and stick representation of optimized geometries of BODIPY dimers with substitutions.



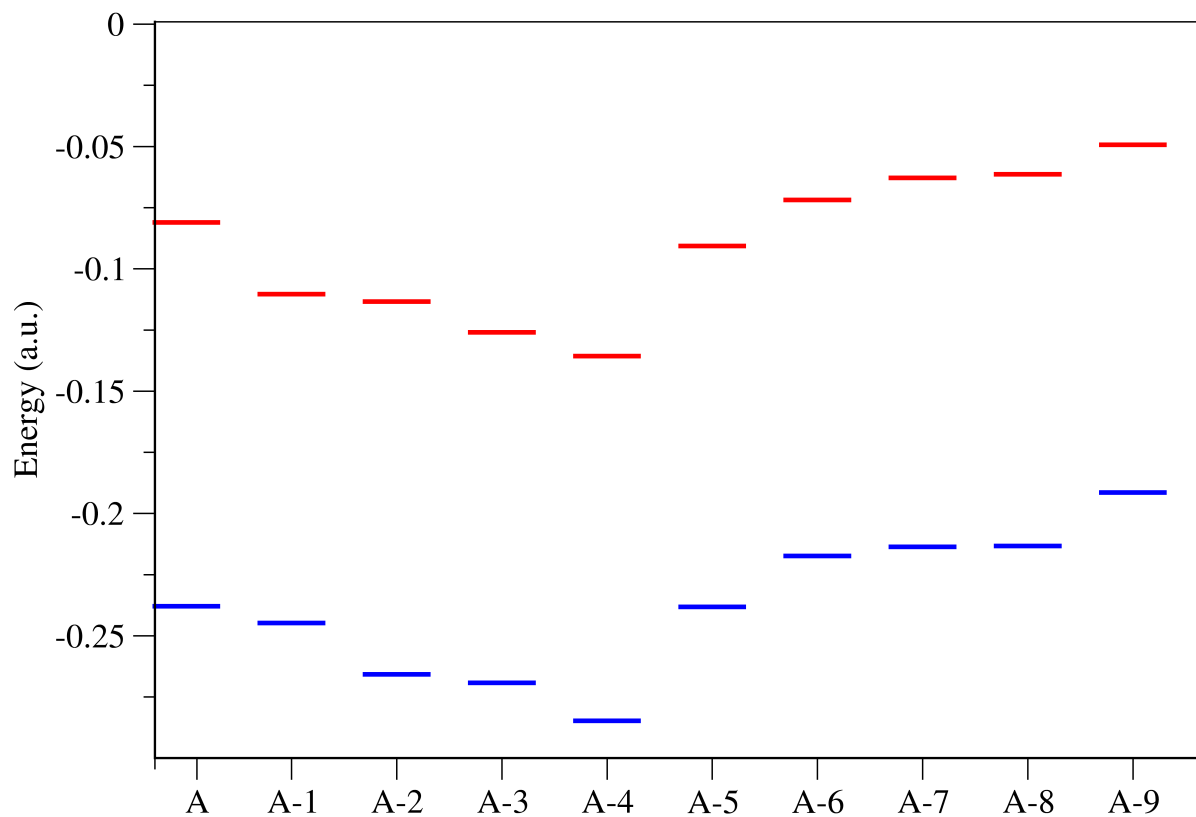
**Figure S17** The variation of vertical excitation energies (in eVs) of the lowest lying singlet excited state  $S_1$ , triplet ground state  $T_1$ ,  $\Delta_{SF}$  at RICC2 (solid) and XMCQDPT (dashed) level of theory with substitution at the  $\alpha$  position.



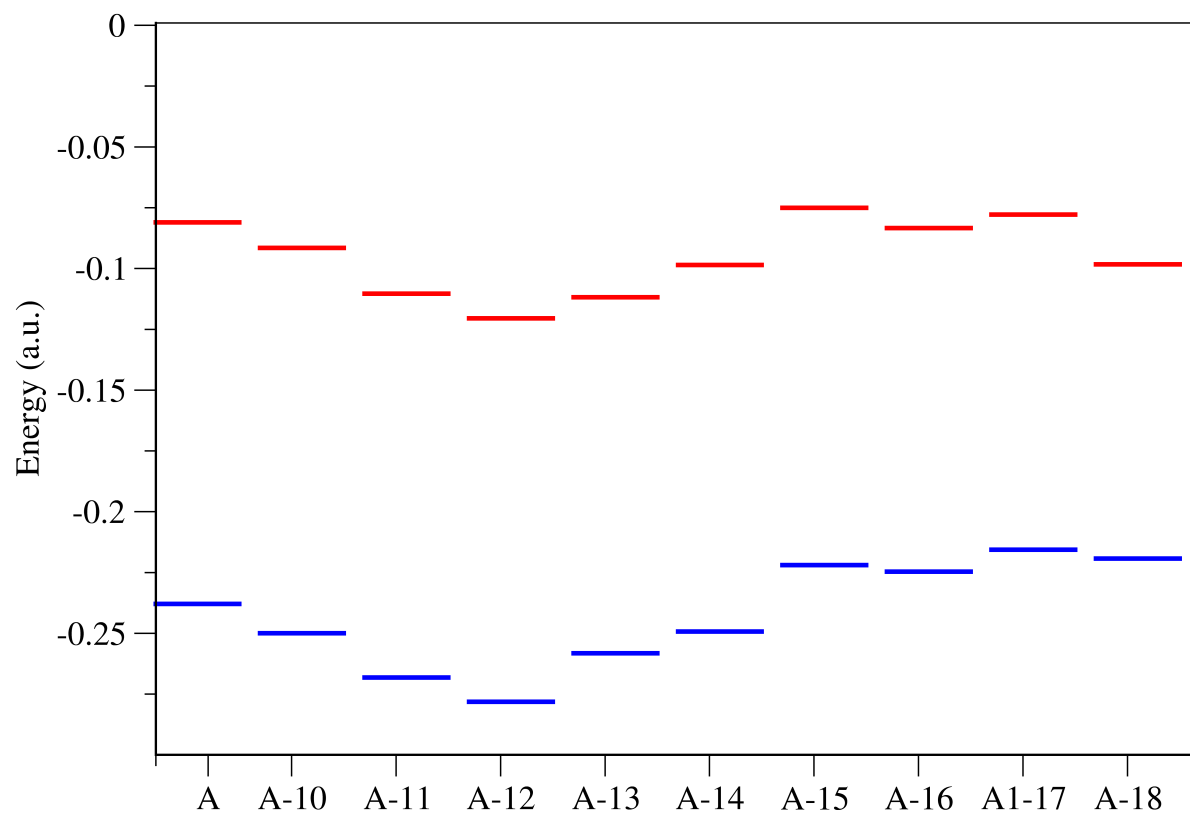
**Figure S18** The variation of vertical excitation energies (in eVs) of the lowest lying singlet excited state  $S_1$ , triplet ground state  $T_1$ ,  $\Delta_{SF}$  at RICC2 (solid) and XMCQDPT (dashed) level of theory with substitution at the  $\beta$  position.



**Figure S19** The HOMO-LUMO energy levels of the BODIPY derivatives obtained due to the substitution at position  $\alpha$ .



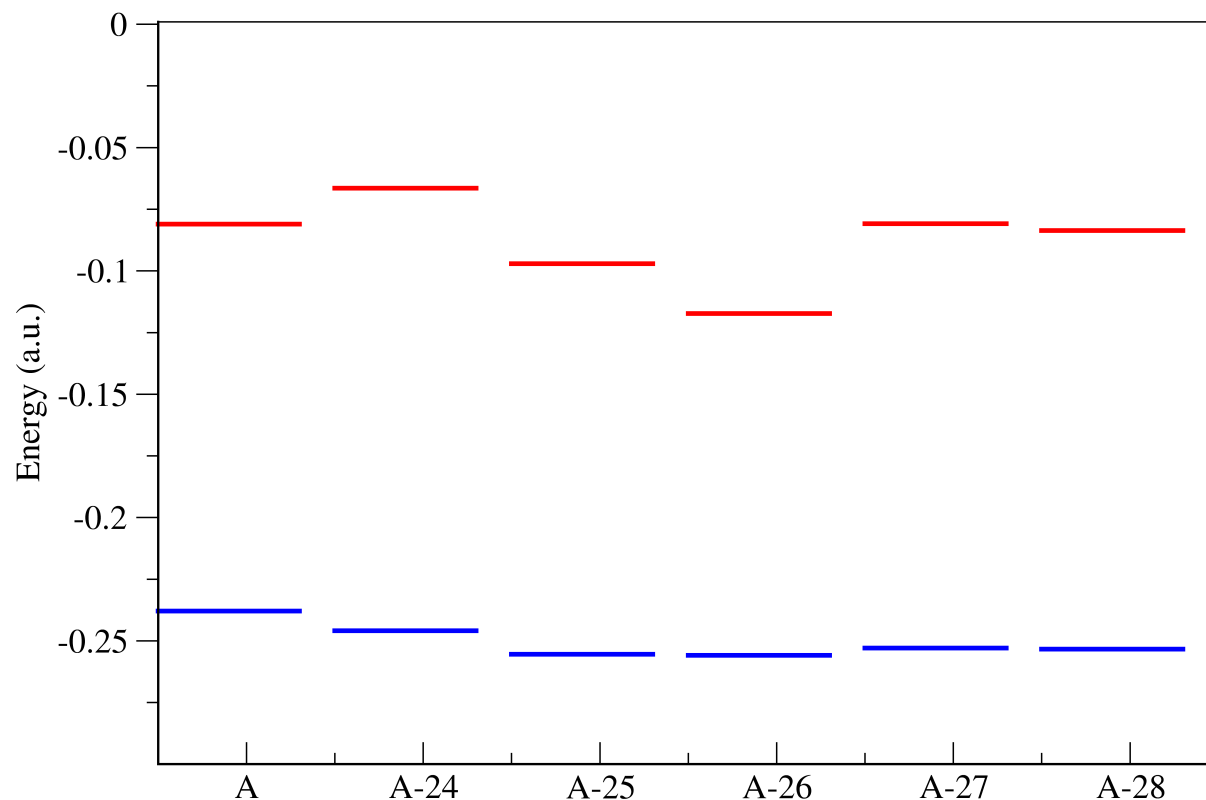
**Figure S20** The HOMO-LUMO energy levels of the BODIPY derivatives obtained due to the substitution at position  $\beta$ .



**Table S17** The energies (in eV) of highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals and the difference between the energies of HOMO and LUMO for different substitutions.

Structure	$E(H)$	$E(L)$	$E(H) - E(L)$	Structure	$E(H)$	$E(L)$	$E(H) - E(L)$
A	-0.2380	-0.0811	0.1569	A21	-0.2522	-0.1105	0.1417
A1	-0.2448	-0.1104	0.1344	A22	-0.1748	-0.0429	0.1319
A2	-0.2658	-0.1134	0.1524	A23	-0.2106	-0.0658	0.1448
A3	-0.2693	-0.1260	0.1433	A24	-0.2459	-0.0665	0.1794
A4	-0.2848	-0.1357	0.1491	A25	-0.2555	-0.0971	0.1584
A5	-0.2382	-0.0907	0.1475	A26	-0.2559	-0.1173	0.1386
A6	-0.2174	-0.0719	0.1455	A27	-0.2530	-0.0809	0.1721
A7	-0.2137	-0.0629	0.1508	A28	-0.2534	-0.0837	0.1697
A8	-0.2133	-0.0614	0.1519	A29	-0.2363	-0.1434	0.0929
A9	-0.1915	-0.0493	0.1422	A30	-0.2250	-0.1182	0.1068
A10	-0.2500	-0.0916	0.1584	A31	-0.2591	-0.0796	0.1795
A11	-0.2682	-0.1104	0.1578	A32	-0.2266	-0.1060	0.1206
A12	-0.2782	-0.1205	0.1577	A33	-0.2506	-0.1444	0.1062
A13	-0.4175	-0.2583	0.1464	A34	-0.2398	-0.1235	0.1163
A14	-0.0986	0.1619	0.1507	A35	-0.1904	-0.0645	0.1259
A15	-0.2220	-0.0751	0.1469	B	-0.2237	-0.0920	0.1317
A16	-0.2247	-0.0834	0.1413	B1	-0.2398	-0.1179	0.1219
A17	-0.2157	-0.0779	0.1378	B2	-0.2370	-0.1485	0.0885
A18	-0.2193	-0.0983	0.1210	B3	-0.2245	-0.1340	0.0905
A19	-0.2216	-0.1100	0.1116				
A20	-0.1842	-0.0439	0.1403				

**Figure S21** The HOMO-LUMO energy levels of the BODIPY derivatives obtained due to the substitution at meso position.



**Table S18** The energies of  $S_1$ ,  $T_1$  states (eVs), SF thermodynamic condition  $\Delta_{SF}$  (eVs), diradical indexes % $D$ ,  $y_0$  and  $y_1$  (dimensionless quantities) for substitutions at  $\alpha$  position of BODIPY. The ball stick representation of the optimized geometries are shown in Fig. S10. The active space used are (12,11), (8,8), (8,8), (8,10), (8,10), (10,9), (8,8), (10,10), (10,10), (10,10) from top to bottom.

System	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	RICC2 <sup>a</sup>			XMCQDPT <sup>b</sup>			Diradical indexes <sup>c</sup>		
				$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$D$ (%)	$y_0$	$y_1$
A	H	H	H	2.90	2.00	1.10	2.62	1.81	1.00	2.56	0.12	0.05
A-1	H	H	BH <sub>2</sub>	2.56	1.76	0.96	2.27	1.64	1.00	3.20	0.17	0.06
A-2	H	H	CF <sub>3</sub>	2.86	2.01	1.16	2.58	1.88	1.18	2.94	0.15	0.06
A-3	H	H	CN	2.72	1.85	0.98	2.35	1.63	0.91	3.10	0.14	0.05
A-4	H	H	NO <sub>2</sub>	2.69	1.93	1.17	2.39	1.37	0.35	2.76	0.13	0.05
A-5	H	H	Cl	2.80	1.90	1.00	2.38	1.84	1.30	2.20	0.14	0.06
A-6	H	H	CH <sub>3</sub>	2.83	1.93	1.03	2.48	1.77	1.06	3.02	0.14	0.05
A-7	H	H	OH	2.88	1.87	0.86	2.55	1.70	0.85	2.98	0.14	0.06
A-8	H	H	OCH <sub>3</sub>	2.79	1.81	0.83	2.51	1.76	1.01	2.70	0.13	0.06
A-9	H	H	NH <sub>2</sub>	2.70	1.72	0.74	2.36	1.58	0.80	3.08	0.13	0.06

<sup>a</sup> Calculated using RICC2/def2-TZVP level of theory <sup>b</sup> Calculated using SA5-XMCQDPT/cc-pVDZ level of theory. <sup>c</sup> Calculated using natural orbitals from SA5-CASSCF/cc-pVDZ level of theory



**Table S19** The energies of  $S_1$ ,  $T_1$  states (eVs), SF thermodynamic condition  $\Delta_{SF}$  (eVs), diradical indexes % $D$ ,  $y_0$  and  $y_1$  (dimensionless quantities) for substitutions at  $\beta$  position of BODIPY. The ball stick representation of the optimized geometries are shown in Fig. S11. The active space used are (12,11), (8,9), (8,11), (8,10), (12,11), (8,9), (8,12), (8,8), (8,10), (8,8) from top to bottom.

System	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	RICC2 <sup>a</sup>			XMCQDPT <sup>b</sup>			Diradical indexes <sup>c</sup>		
				$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$D$ (%)	$y_0$	$y_1$
A	H	H	H	2.90	2.00	1.10	2.62	1.81	1.00	2.56	0.12	0.05
A-10	H	BH <sub>2</sub>	H	2.86	2.07	1.28	2.61	1.81	1.01	2.20	0.12	0.05
A-11	H	CF <sub>3</sub>	H	2.92	2.07	1.22	2.62	1.83	1.04	2.76	0.12	0.05
A-12	H	CN	H	2.79	2.06	1.33	2.51	1.73	0.95	2.48	0.12	0.05
A-13	H	NO <sub>2</sub>	H	2.88	2.11	1.34	2.51	1.92	1.33	1.40	0.17	0.16
A-14	H	Cl	H	2.66	1.92	1.18	2.44	1.71	0.98	2.90	0.13	0.05
A-15	H	CH <sub>3</sub>	H	2.77	1.92	1.07	2.47	1.72	0.97	3.00	0.14	0.05
A-16	H	OH	H	2.49	1.65	0.81	2.26	1.50	0.74	3.60	0.14	0.05
A-17	H	OCH <sub>3</sub>	H	2.43	1.61	0.79	2.27	1.48	0.69	4.00	0.15	0.05
A-18	H	NH <sub>2</sub>	H	2.29	1.54	0.79	2.25	1.42	0.59	5.20	0.28	0.09

<sup>a</sup> Calculated using RICC2/def2-TZVP level of theory <sup>b</sup> Calculated using SA5-XMCQDPT/cc-pVDZ level of theory. <sup>c</sup> Calculated using natural orbitals from SA5-CASSCF/cc-pVDZ level of theory

**Table S20** The energies of  $S_1$ ,  $T_1$  states (eVs), SF thermodynamic condition  $\Delta_{SF}$  (eVs), diradical indexes % $D$ ,  $y_0$  and  $y_1$  (dimensionless quantities) for simultaneous substitutions at  $\alpha$  and  $\beta$  positions of BODIPY. The ball stick representation of the optimized geometries are shown in Fig. S12. The active space used are (8,8), (8,8), (8,8), (8,7), (8,7) from top to bottom.

System	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	RICC2 <sup>a</sup>			XMCQDPT <sup>b</sup>			Diradical indexes <sup>c</sup>		
				$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$D$ (%)	$y_0$	$y_1$
A-19	H	NH <sub>2</sub>	BH <sub>2</sub>	1.71	1.12	0.53	1.65	1.11	0.57	4.60	0.22	0.06
A-20	H	BH <sub>2</sub>	NH <sub>2</sub>	2.45	1.62	0.79	2.06	1.44	0.81	3.64	0.11	0.04
A-21	H	BH <sub>2</sub>	BH <sub>2</sub>	2.63	1.88	1.13	2.23	1.73	1.23	2.52	0.16	0.06
A-22	H	NH <sub>2</sub>	NH <sub>2</sub>	2.50	1.56	0.62	2.14	1.37	0.60	4.52	0.14	0.04
A-23	H	BH <sub>2</sub> /NH <sub>2</sub>	BH <sub>2</sub> /NH <sub>2</sub>	2.87	1.85	0.83	2.76	1.76	0.76	2.02	0.13	0.07

<sup>a</sup> Calculated using RICC2/def2-TZVP level of theory <sup>b</sup> Calculated using SA5-XMCQDPT/cc-pVDZ level of theory. <sup>c</sup> Calculated using natural orbitals from SA5-CASSCF/cc-pVDZ level of theory

**Table S21** The energies of  $S_1$ ,  $T_1$  states (eVs), SF thermodynamic condition  $\Delta_{SF}$  (eVs), diradical indexes % $D$ ,  $y_0$  and  $y_1$  (dimensionless quantities) for substitutions at meso position of BODIPY. The ball stick representation of the optimized geometries are shown in Fig. S13. The active space used are (12,11), (8,8), (12,10), (8,8), (12,10), (10,9) from top to bottom.

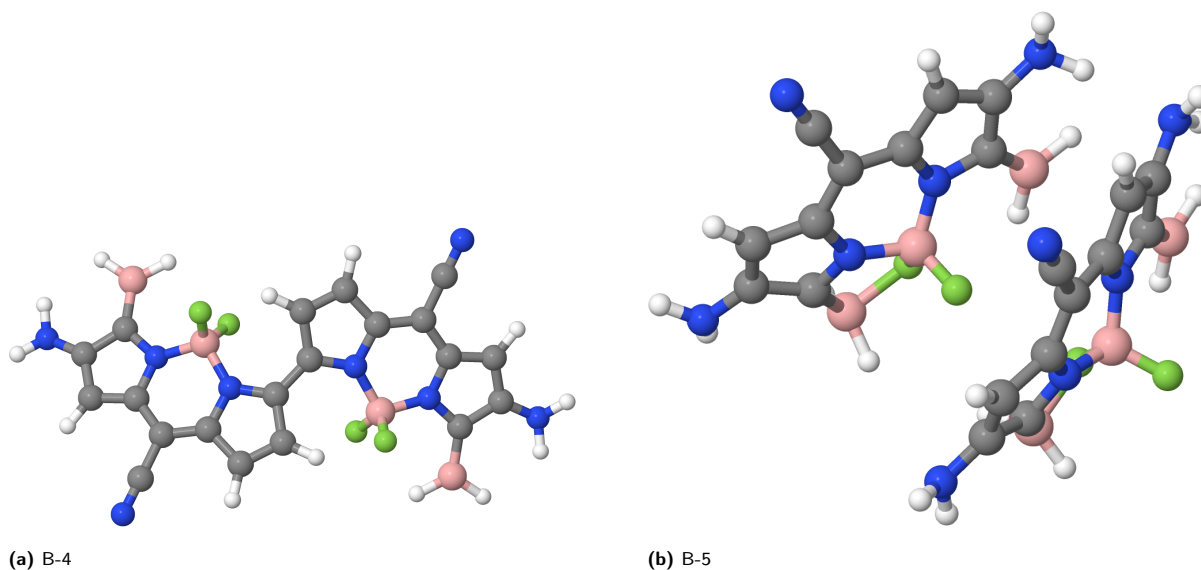
System	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	RICC2 <sup>a</sup>			XMCQDPT <sup>b</sup>			Diradical indexes <sup>c</sup>		
				$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$D$ (%)	$y_0$	$y_1$
A	H	H	H	2.90	2.00	1.10	2.62	1.81	1.00	2.56	0.12	0.05
A-24	OH	H	H	3.15	2.50	1.85	2.94	2.33	1.73	1.52	0.11	0.05
A-25	C≡CH	H	H	2.71	1.84	0.97	2.38	1.68	0.97	2.12	0.11	0.06
A-26	CN	H	H	2.69	1.71	0.73	2.38	1.53	0.68	3.00	0.14	0.05
A-27	Ph	H	H	2.83	2.02	1.21	2.53	1.82	1.11	1.80	0.10	0.06
A-28	C=CH <sub>2</sub>	H	H	2.76	1.98	1.72	2.49	1.88	1.27	1.60	0.10	0.08

<sup>a</sup> Calculated using RICC2/def2-TZVP level of theory <sup>b</sup> Calculated using SA5-XMCQDPT/cc-pVDZ level of theory. <sup>c</sup> Calculated using natural orbitals from SA5-CASSCF/cc-pVDZ level of theory

**Table S22** The energies of  $S_1$ ,  $T_1$  states (eVs), SF thermodynamic condition  $\Delta_{SF}$  (eVs), diradical indexes % $D$ ,  $y_0$  and  $y_1$  (dimensionless quantities) for simultaneous substitutions at  $\alpha$ ,  $\beta$  and meso positions of BODIPY. The ball stick representation of the optimized geometries are shown in Fig. S14. The active space used are (8,7), (8,9), (10,10), (10,9), (8,8), (8,9), (8,7) from top to bottom.

System	$R_1$	$R_2$	$R_3$	RICC2 <sup>a</sup>			XMCQDPT <sup>b</sup>			Diradical indexes <sup>c</sup>		
				$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$E(S_1)$	$E(T_1)$	$\Delta_{SF}$	$D$ (%)	$y_0$	$y_1$
A-29	CN	NH <sub>2</sub>	BH <sub>2</sub>	1.45	0.82	0.19	1.38	0.84	0.30	4.56	0.33	0.05
A-30	C≡CH	NH <sub>2</sub>	BH <sub>2</sub>	1.52	0.97	0.42	1.48	0.95	0.42	5.20	0.22	0.05
A-31	Ph	BH <sub>2</sub>	H	2.80	2.11	1.42	2.54	1.84	1.14	2.20	0.10	0.06
A-32	C=CH <sub>2</sub>	NH <sub>2</sub>	BH <sub>2</sub>	1.61	1.11	0.61	1.29	0.94	0.59	4.42	0.18	0.08
A-33	CN	OH	BH <sub>2</sub>	1.86	1.12	0.38	1.74	1.16	0.58	4.32	0.25	0.05
A-34	C≡CH	OH	BH <sub>2</sub>	1.90	1.25	0.60	1.76	1.19	0.62	4.42	0.19	0.05
A-35	CN	NH <sub>2</sub>	NH <sub>2</sub>	2.60	1.49	0.38	2.27	1.47	0.66	3.72	0.13	0.05

<sup>a</sup> Calculated using RICC2/def2-TZVP level of theory <sup>b</sup> Calculated using SA5-XMCQDPT/cc-pVDZ level of theory. <sup>c</sup> Calculated using natural orbitals from SA5-CASSCF/cc-pVDZ level of theory



**Figure S22** Two dimers prepared from A-29 molecule by (a) covalently bonding (b)  $\pi$  stacking the two monomer units.

**Table S23** The energies of single exciton ( $S_1$ ), multiexciton ( $^1TT$ ) and quintet state ( $^5TT$ ) for covalently bonded and  $\pi$  stacked dimers of A-29 by using SA8-XMCQDPT(8,8)/cc-pVDZ level of theory.

System	$E(S_1)$	$E(^1TT)$	$E(^5TT)$
B-4	1.30	2.04	2.57
B-5	1.78	2.56	2.64

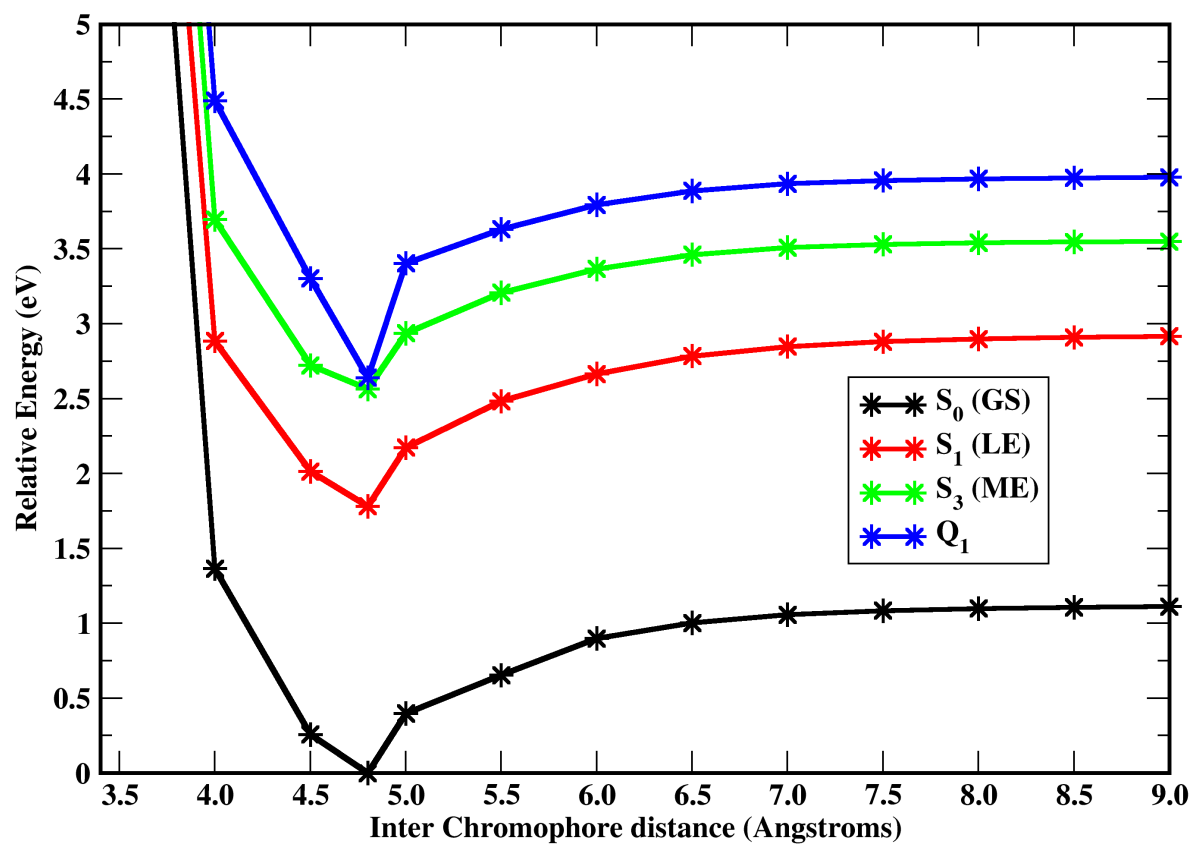


Figure S23 Rigid scan of energies of the electronic states  $S_0$  (GS),  $S_1$  (LE),  $S_3$  (ME) and  $Q_1$  along the interchromophoric distances 4.0 - 9.0 Å.