

Supporting Information:

Molecular mechanism of the triplet states
formation in bodipy-phenoxazine
photosensitizer dyads and confirmation by ab
initio prediction of the spin polarization

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1 The optimized structures and molecular orbitals at each state of BDP-PXZ

1.1 Ground state/ S_0

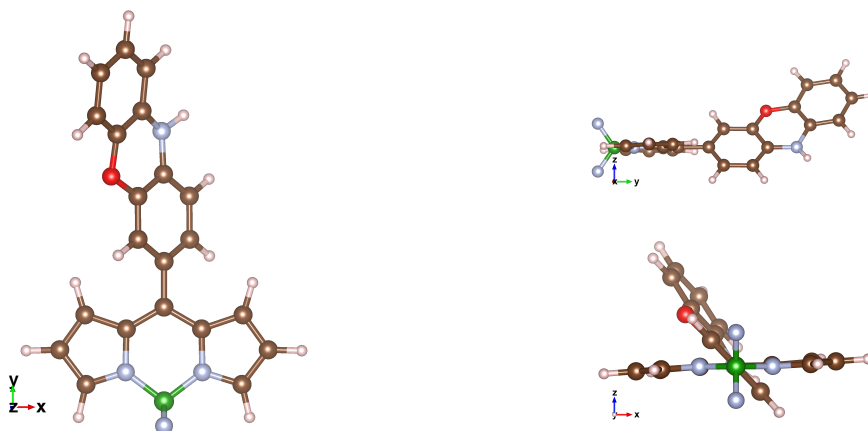
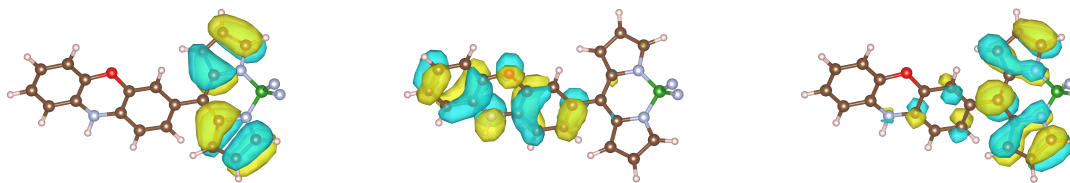


Figure S1: The optimized structure of BDP-PXZ ground state, viewing from each axes. The dihedral angle $\theta = 47^\circ$.



(a) HOMO-1 (BDP's HOMO) (b) HOMO (PXZ's HOMO) (c) LUMO (BDP's LUMO)
Figure S2: Surface plots of canonical MOs at ground state stabilized structure (isovalue=0.03).

1.2 ^1CT state/ S_1

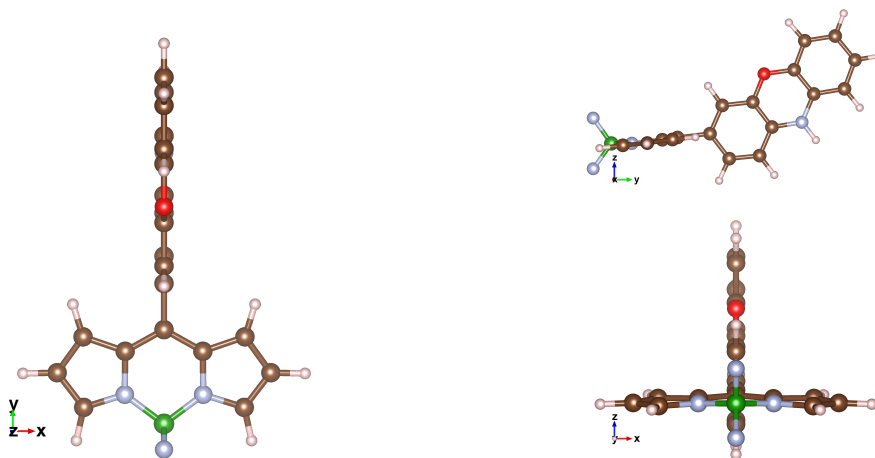
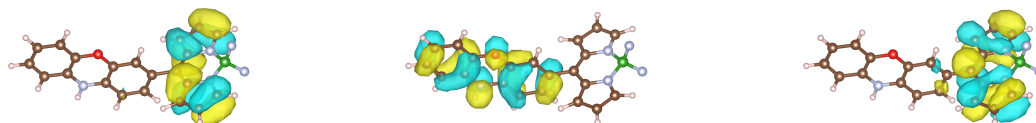


Figure S3: The optimized structure of BDP-PXZ ^1CT state, viewing from each axes. The dihedral angle $\theta = 90^\circ$.



(a) HOMO-1 (BDP's HOMO) (b) HOMO (PXZ's HOMO) (c) LUMO (BDP's LUMO)

Figure S4: Surface plots of canonical MOs at ^1CT state stabilized structure (isovalue=0.03).

1.3 ^3BDP state/ $\text{T}_{1,2}$

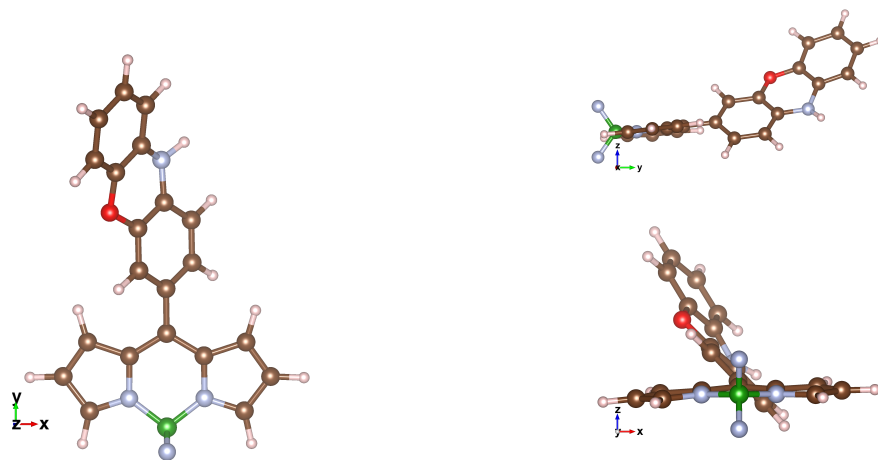
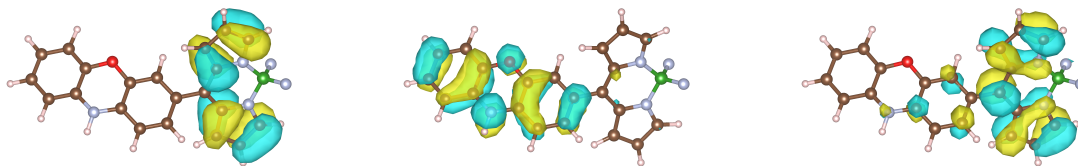


Figure S5: The optimized structure of BDP-PXZ ^3BDP state, viewing from each axes. The dihedral angle $\theta = 46^\circ$.



(a) HOMO-1 (BDP's HOMO) (b) HOMO (PXZ's HOMO) (c) LUMO (BDP's LUMO)

Figure S6: Surface plots of canonical MOs at ^3BDP state stabilized structure (isovalue=0.03).

1.4 ^3CT state/ $\text{T}_{2,1}$

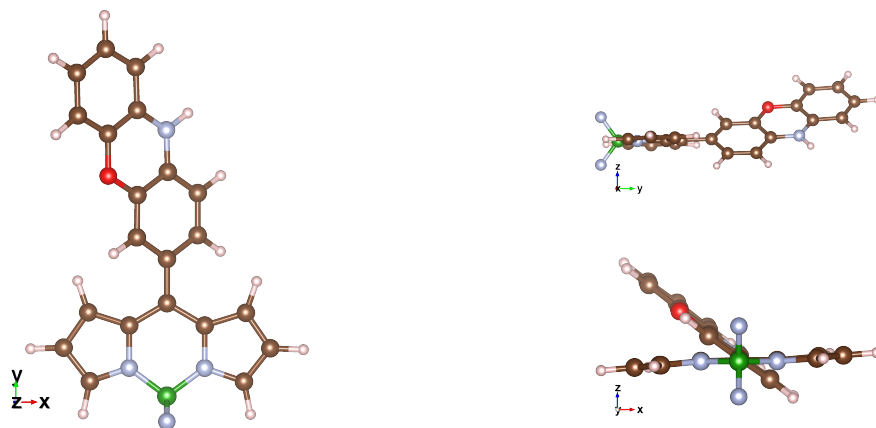
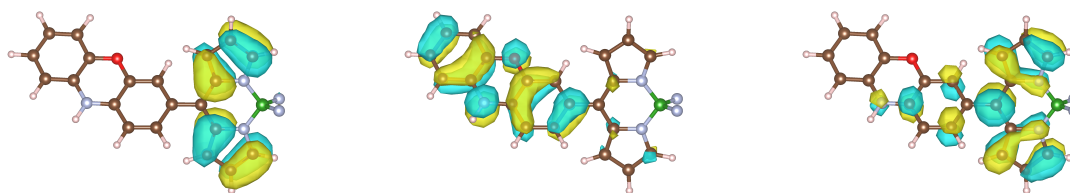


Figure S7: The optimized structure of BDP-PXZ ^3CT state, viewing from each axes. The dihedral angle $\theta = 36^\circ$.



(a) HOMO-1 (BDP's HOMO) (b) HOMO (PXZ's HOMO) (c) LUMO (BDP's LUMO)
Figure S8: Surface plots of canonical MOs at ^3CT state stabilized structure (isovalue=0.03).

2 The optimized structures and molecular orbitals at each state of TMBDP-PXZ

2.1 Ground state/ S_0

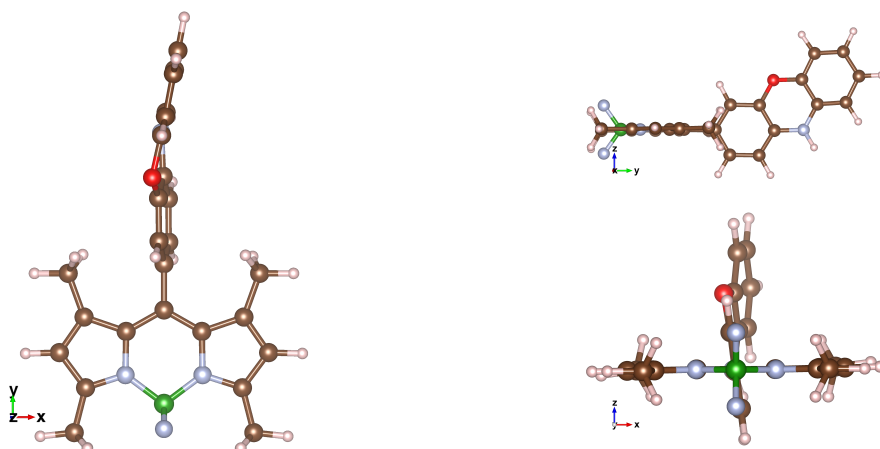
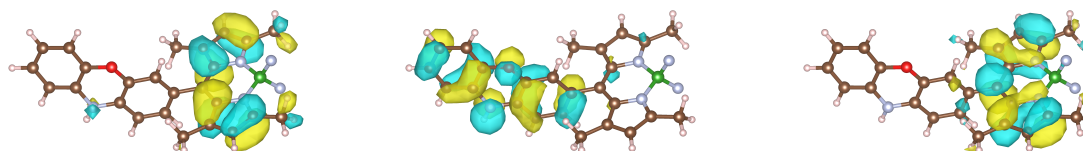


Figure S9: The optimized structure of TMBDP-PXZ ground state, viewing from each axes. The dihedral angle $\theta = 83^\circ$.



(a) HOMO-1 (BDP's HOMO) (b) HOMO (PXZ's HOMO) (c) LUMO (BDP's LUMO)

Figure S10: Surface plots of canonical MOs at ground state stabilized structure (isovalue=0.03).

2.2 ^1CT state/ S_1

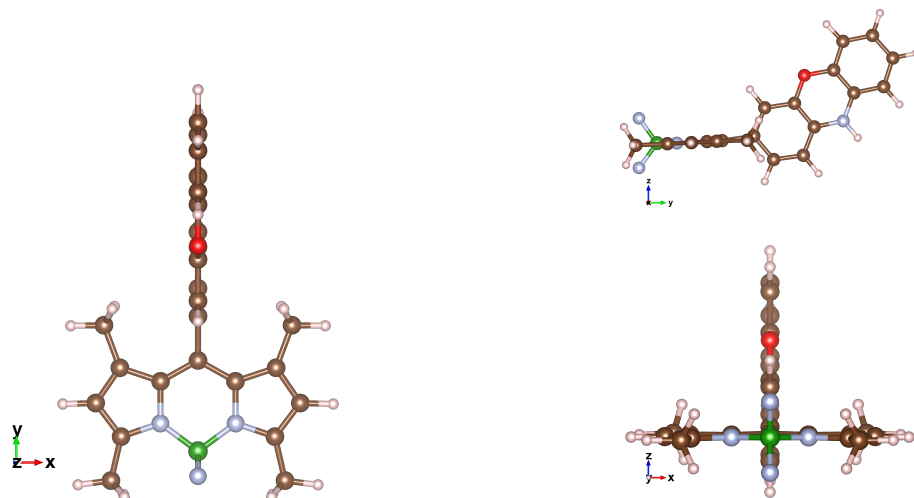
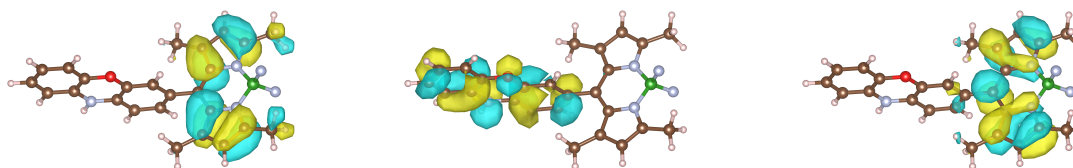


Figure S11: The optimized structure of TMBDP-PXZ ^1CT state, viewing from each axes. The dihedral angle $\theta = 87^\circ$.



(a) HOMO-1 (BDP's HOMO) (b) HOMO (PXZ's HOMO) (c) LUMO (BDP's LUMO)

Figure S12: Surface plots of canonical MOs at ^1CT state stabilized structure (isovalue=0.03).

The optimized geometry at ¹CT structure in toluene solvent effect:

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1CT Total Energy = -1427.964379304 Eh
C      1.440985   -0.357407   2.581850
C      2.570345   -0.062038   3.381012
C      3.633609    0.243928   2.543418
N      3.206664    0.147470   1.242974
C      1.864154   -0.218934   1.239094
H      2.606989   -0.074831   4.467323
C      1.181573   -0.380237   0.006819
C      1.851736   -0.199718  -1.229586
C      1.416826   -0.322403  -2.570152
C      2.539537   -0.018730  -3.375481
C      3.610512    0.276085  -2.543655
H      2.566644   -0.018621  -4.462154
N      3.195042    0.164221  -1.240894
B      4.054648    0.441051  -0.000938
F      4.489093    1.795446    0.005651
F      5.217654   -0.372026  -0.011124
C     -0.264695   -0.659488    0.011685
C     -1.167719    0.398865  -0.014453
C     -0.763337   -1.990581    0.039390
C     -2.524929    0.147830  -0.009312
H     -0.814317    1.428567  -0.037760
C     -2.111661   -2.256930    0.045921
H     -0.044233   -2.807841    0.056374
C     -3.021360   -1.188002    0.021710
O     -3.376384    1.207315  -0.034594
H     -2.493150   -3.277645    0.068461
N     -4.365127   -1.373595    0.025520
C     -4.731695    0.988958  -0.029684
C     -5.253734   -0.311113    0.000602
H     -4.735257   -2.324409    0.047913
C     -5.569454    2.096412  -0.055458
C     -6.639076   -0.498564    0.004942
C     -6.941644    1.899517  -0.050740
H     -5.126636    3.090700  -0.078550
C     -7.474828    0.604090  -0.020597
H     -7.039316   -1.512252    0.028548
H     -7.607251    2.760160  -0.070527
H     -8.553578    0.461261  -0.017176
C      5.005243    0.659379  -2.895846
H      5.269648    1.635746  -2.464677
H      5.729980   -0.065559  -2.498764
H      5.115477    0.711316  -3.985666
C      5.031141    0.624166    2.887733
H      5.752971   -0.094943    2.475090
H      5.290745    1.606130    2.466450
H      5.151259    0.662507    3.977068
C      0.066457   -0.708077  -3.087763
H     -0.265738   -1.692389  -2.722658
H     -0.719777    0.014012  -2.815931
H      0.093776   -0.761826  -4.184255
C      0.095906   -0.752740    3.104910
H     -0.700955   -0.048729    2.817167
H     -0.220446   -1.749303    2.758492
H      0.121782   -0.785001    4.202279

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2.3 ^3BDP state/ T_1

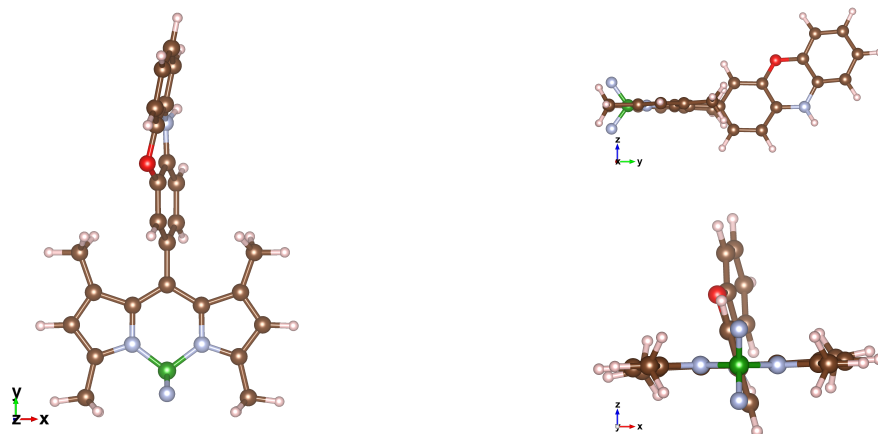
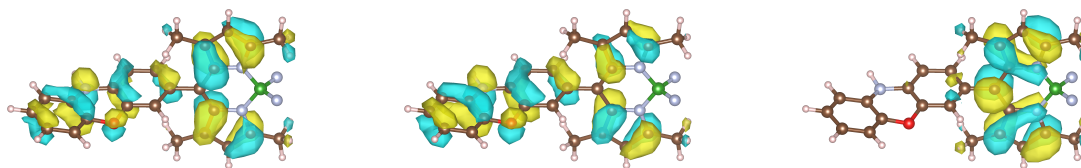


Figure S13: The optimized structure of TMBDP-PXZ ^3BDP state, viewing from each axes. The dihedral angle $\theta = 76^\circ$.



(a) HOMO-1 (BDP's HOMO) (b) HOMO (PXZ's HOMO) (c) LUMO (BDP's LUMO)

Figure S14: Surface plots of canonical MOs at ^3BDP state stabilized structure (iso-value=0.03).

2.4 ^3CT state/ T_2

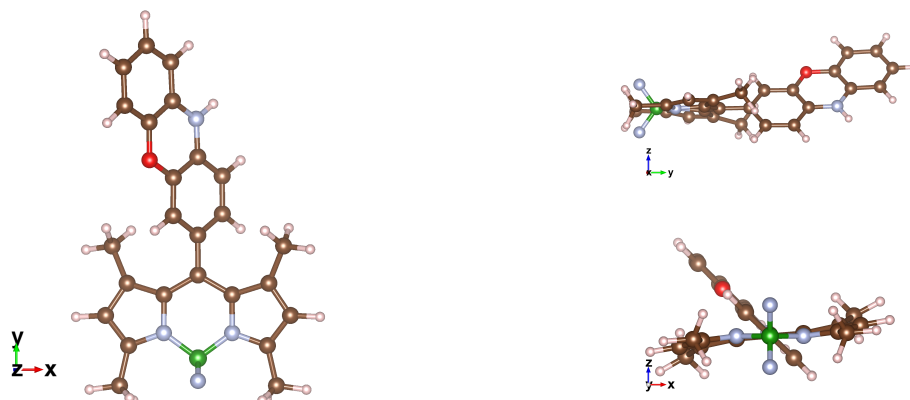
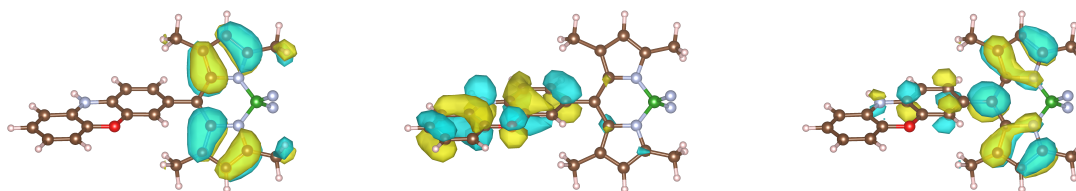


Figure S15: The optimized structure of TMBDP-PXZ ^3CT state, viewing from each axes. The dihedral angle $\theta = 47^\circ$.



(a) HOMO-1 (BDP's HOMO) (b) HOMO (PXZ's HOMO) (c) LUMO (BDP's LUMO)

Figure S16: Surface plots of canonical MOs at ^3CT state stabilized structure (isovalue=0.03).

The geometry of ¹CT - ³BDP near MECP structure in toluene solvent effect:

1CT	Total Energy = -1427.952834002 Eh		
3BDP	Total Energy = -1427.952877002 Eh		
C	1.402802093006	-0.350978154621	2.574308743694
C	2.564988297470	-0.070288716717	3.388857757548
C	3.603714535154	0.237218428816	2.550357143393
N	3.166385533755	0.157440033889	1.261235549867
C	1.808845680028	-0.200512602125	1.266301792880
H	2.604771068886	-0.084524468421	4.477859188778
C	1.189632836293	-0.375240534590	0.006741268438
C	1.801788502323	-0.197936982645	-1.256378557454
C	1.385763730390	-0.339367226120	-2.563356145398
C	2.539642574883	-0.040411886443	-3.384506206067
C	3.584152135135	0.259616995636	-2.550820212945
H	2.570765437233	-0.038048311224	-4.472466286576
N	3.158900551244	0.159820192984	-1.259049902427
B	4.003751414548	0.445617905767	-0.001582152654
F	4.435572845289	1.805592537483	-0.004370268833
F	5.174293532294	-0.363519731257	-0.003219285795
C	-0.255185910728	-0.625609180089	0.009104194245
C	-1.128478632856	0.427511950259	-0.003364887548
C	-0.775844596412	-1.983928666046	0.025346526071
C	-2.490191491333	0.162886538915	-0.000495883050
H	-0.759809433042	1.448626137539	-0.014301335916
C	-2.097719649300	-2.274105315170	0.035770439896
H	-0.029862584289	-2.771223204290	0.026084824705
C	-2.990994734100	-1.186079163261	0.022369640199
O	-3.351782736359	1.189575783206	-0.021008066002
H	-2.483276664937	-3.290587311285	0.054718718777
N	-4.330059423777	-1.351420366937	0.026754294508
C	-4.681526545739	0.991768099028	-0.022737116171
C	-5.212617808402	-0.311311622722	0.004462840774
H	-4.694187312798	-2.307779400040	0.045566236013
C	-5.523072605790	2.111546512696	-0.052375594104
C	-6.608179848654	-0.512964078839	0.006439559763
C	-6.875130391652	1.895881768248	-0.049873436289
H	-5.081727543739	3.103355476134	-0.076614595720
C	-7.419807034872	0.585602350368	-0.019613539322
H	-7.008555093937	-1.525005531665	0.028842734815
H	-7.552150574098	2.746206330918	-0.070327943775
H	-8.500184036500	0.459768123649	-0.017180326430
C	4.991539341571	0.664019633694	-2.885107326958
H	5.244524895113	1.642994045825	-2.453327359492
H	5.721584950024	-0.055215340249	-2.487681000752
H	5.113529226082	0.721978405628	-3.976858500816
C	5.015661837328	0.628452049269	2.877539310927
H	5.737777290287	-0.088337767075	2.461394010667
H	5.269481600709	1.612138574391	2.457656425914
H	5.148108418121	0.670059419543	3.969039831028
C	0.040895944344	-0.723953184181	-3.135622400875
H	-0.322851305391	-1.722277081400	-2.836943679010
H	-0.770012312333	0.003366546704	-2.937014772309
H	0.119825647319	-0.769695979990	-4.230954447778
C	0.069717737913	-0.763052438369	3.152157177462
H	-0.760627893142	-0.065212626988	2.937794316569
H	-0.265467145419	-1.776220391296	2.871604788021
H	0.144984652912	-0.785036576509	4.248844915516

3 The potential energy curves for BDP-PXZ derivatives with different substituent groups

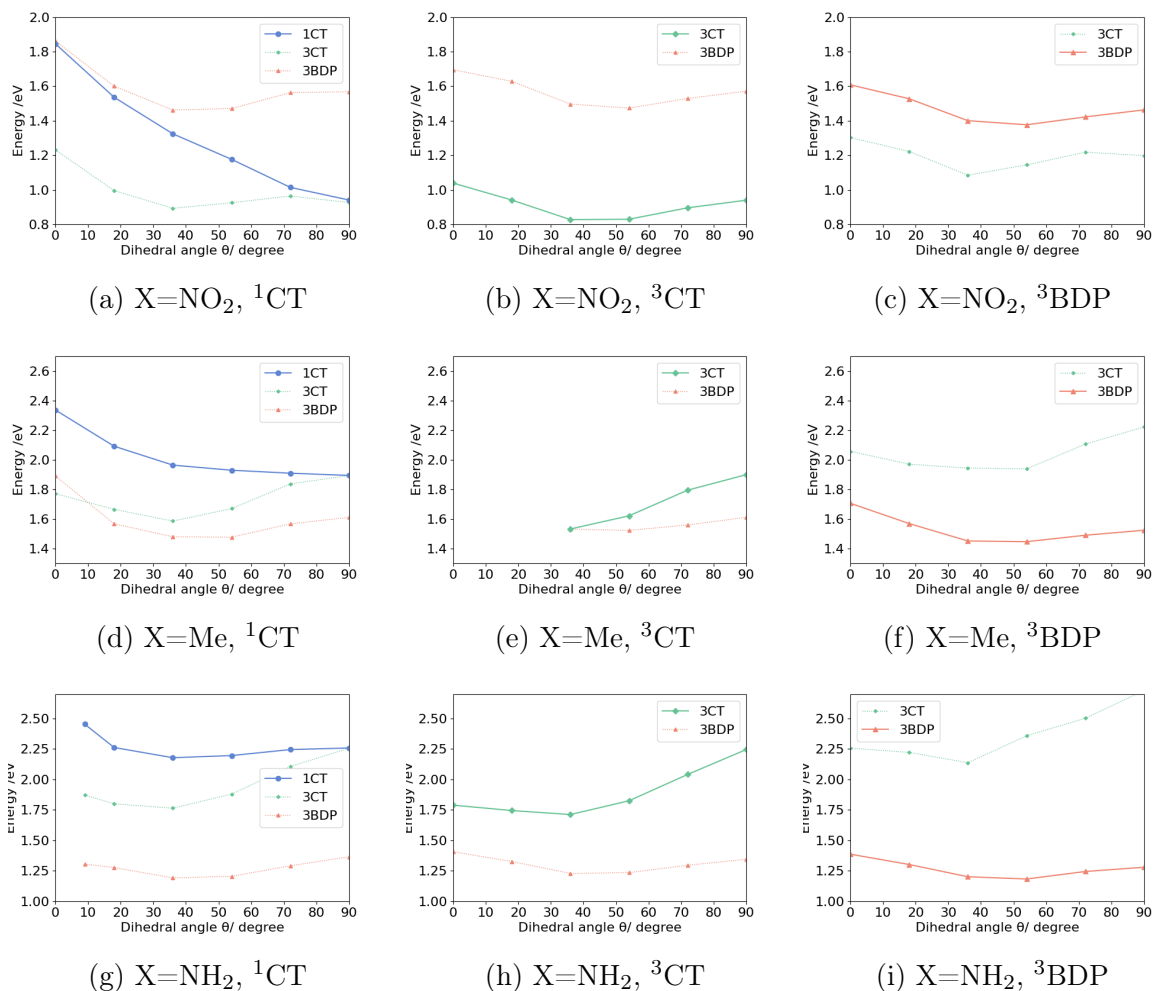


Figure S17: Potential energy curves of ^1CT , ^3CT , and ^3BDP states along the dihedral angle between BDP and PXZ moieties for BDP-PXZ derivatives with substituent groups X at C3,5 atoms on BDP moiety. The geometries were optimized with ^1CT , ^3CT , and ^3BDP states for each derivative under constraints for the dihedral angle θ between BDP and PXZ moieties. The target state is depicted with solid lines, while others with dotted lines.

Table S1: The excitation energies for the BDP monomer and TMBDP-PXZ dyad systems.

	¹ CT	³ CT	³ BDP	(¹ BDP)	
BDP monomer					
LC-BLYP($\mu = 0.15$)/def2-TZVP	–	-	1.71	(3.32)	
LC-BLYP($\mu = 0.33$)/def2-TZVP	-	-	1.59	(3.30)	
EOM-CCSD ^a /def2-SVP	-	-	1.77	(2.31)	a
EOM-CCSD ^a /def2-TZVP	-	-	1.72	(2.33)	
TMBDP-PXZ dyad					
LC-BLYP($\mu = 0.15$)/def2-TZVP	2.29	2.27	1.59	(3.10)	
LC-BLYP($\mu = 0.33$)/def2-TZVP	3.13	2.86	1.51	(3.33)	
EOM-CCSD ^a /def2-SV(P)	2.28	n.a.	1.63	(2.75)	
bt-PNO-STEOM-CCSD implemented in ORCA6. ^{S1–S8}					

4 Comparison of the excitation energies of LC-BLYP and EOM-CCSD

To assess the reliability of the excitation energies obtained with the LC-BLYP functional, we performed the EOM-CCSD calculations for TMBDP-PXZ and TMBDP molecules for comparison exploiting the various acceleration techniques, back-transformation PNO, similarity transformed EOM implemented in ORCA6.^{S9,S10} It has been reported that TD-DFT fails to reproduce the energy levels of low-lying singlet and triplet states of heterocyclic aromatic compounds containing B and N atoms, such as BODIPY and DABNA derivatives,^{S11–S13} and the coupled cluster approach gives a better description though the conventional EOM-CCSD is often too expensive and its approximated methods such as ADC(2), CC2, and SCS-CC2 can be enough for practical purpose. TD-DFT sometimes fails to reproduce the excitation energies of charge transfer states even with the long-range corrected functionals, in fact, LC-BLYP with the original range separation parameter ($\mu = 0.33$) overestimates the excitation energy of ¹CT by 0.85 eV as shown in Table S1. In contrast, LC-BLYP calculations with $\mu = 0.15$, which was adopted in this study, well reproduce the excitation energies of ¹CT, ³CT, and BDP-PXZ 3 states. That of BDP-PXZ 1 is significantly overestimated with both $\mu = 0.15$ and 0.33 , but the state is irrelevant to the mechanism analyzed in this study.

References

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