Supporting information for

Thorough understanding the nonlinear optical properties of dipyrromethene/c*loso*-dodecaborane/diketopyrrolopyrrole hybrid chromophores: module contribution, linear combination, one-/two-dimensional difference and carborane's arrangement

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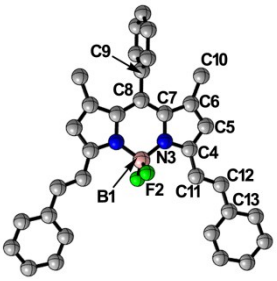
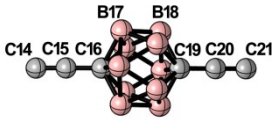
Table S1. Primary bond lengths (Å) of calculated values for **BOD-Cp-DPP** and experimental values for a series of available crystallographic structures containing distyrylborodipyrromethene unit.



compound	**BOD-Cp-DPP**[a]	**BOD-1**[b]	**BOD-2**[c]	**BOD-3**[d]	**BOD-4**[e]
B1-F2	1.400	1.408	1.372	1.413	1.389
B1-N3	1.561	1.542	1.569	1.523	1.517
N3-C4	1.360	1.357	1.360	1.354	1.369
C4-C5	1.421	1.423	1.386	1.408	1.449
C5-C6	1.382	1.375	1.348	1.368	1.355
C6-C7	1.440	1.432	1.425	1.425	1.462
C7-C8	1.406	1.383	1.384	1.395	1.356
C8-C9	1.495	1.474	1.519	1.490	1.499
N3-C7	1.394	1.420	1.385	1.401	1.412
C6-C10	1.501	1.508	1.510	1.497	1.517
C4-C11	1.440	1.429	1.435	1.454	1.422
C11-C12	1.356	1.349	1.340	1.334	1.328
C12-C13	1.456	1.442	1.439	1.462	1.442

[a] The values computed at the B3LYP/6-31G(d) level.
[b-e] Experimental values from crystallographic data in ref. 1-4, corresponding to CCDC numbers: **BOD-1** 934637, **BOD-2** 651605, **BOD-3** 721226, and **BOD-4** 832817, respectively.

Table S2. Primary bond lengths (Å) of calculated values for **BOD-Cp-DPP** and experimental values for a series of available crystallographic structures containing 1,12-bis-ethynyl-*p*-carborane unit.



compound	**BOD-Cp-DPP**[a]	**Cp-1**[b]	**Cp-2**[c]	**Cp-3**[d]	**Cp-4**[e]
C14-C15	1.213	1.154	1.200	1.194	1.206
C15-C16	1.437	1.441	1.450	1.447	1.437
C16-B17	1.730	1.731	1.723	1.725	1.731
B17-B18	1.762	1.766	1.763	1.765	1.781
B18-C19	1.729				
C19-C20	1.437				
C20-C21	1.213				

[a] The values computed at the B3LYP/6-31G(d) level.
[b-e] Experimental values from crystallographic data in ref. 5-7, corresponding to CCDC numbers: **Cp-1** 292701, **Cp-2** 262362, **Cp-3** 284838, and **Cp-4** 284839, respectively.

Table S3. The simulated maximal wavelengths (λ_{max}, nm) and corresponding oscillator strength of dye **BOD-Cp-DPP** with various functionals and basis sets in tetrahydrofuran solvent and vacuum phase

functionals	λ_{max}[a]	f_{os}
vacuum[b]	585.5	1.0303
B3LYP[c]	622.3	1.1379
B3LYP/6-31+G(d)	629.9	1.1248
PBE1PBE	609.6	1.1671
M062X	576.9	1.1854
CAM- B3LYP	574.5	1.2031

[a.] The λ_{max} and f_{os} represent the wavelength and oscillator strength of the low-energy absorption peak.

[b] Calculated in vacuum phase at the B3LYP/6-31G(d) level of theory.

[b] Unless stated otherwise, all of the TD-DFT calculations were carried out using 6-31G(d) basis set in tetrahydrofuran solvent.

Table S4. Simulated wavelengths (λ, nm), excited state transition energies (ΔE_{ge} , eV), oscillator strengths (f_{os}), and major molecular orbital contributions of chromophores **BOD** and **DPP** calculated by TD-B3LYP method in tetrahydrofuran solution

chromophore	crucial state	λ	ΔE_{ge}	f_{os}	Major contribution
BOD	S1	627.0	1.98	1.134	H→L (100%)
	S4	373.8	3.32	1.608	H→L+1 (86%), H-1→L (13%)
DPP	S1	491.1	2.52	0.632	H→L (100%)
	S3	364.5	3.40	0.194	H-1→L (87%), H->L+1 (7%)

[a] Assignment: H = HOMO, L = LUMO, H-1 = HOMO−1, L+1 = LUMO+1, *etc*.

Table S5. Tensorial components of the polarizabilities α (a.u.) of the studied chromophores computed at the ωB97XD/6-31+G(d,p) level of theory

ωB97XD	α_{xx}	α_{yy}	α_{zz}
BOD-Cp-DPP	3039.4	1612.7	961.5
BOD	921.4	989.5	371.9
Cp	118.3	126.0	126.2
DPP	676.2	347.2	412.4
Cp-DPP	1773.8	630.9	616.7
BOD-DPP	3040.7	1490.8	869.3
BOD-Cp	1987.0	1200.7	645.3
BOD-Cm-DPP	2672.4	1888.7	983.4
BOD-Co(L)-DPP	2039.7	2474.2	975.4
BOD-Co-DPP	1903.4	2555.2	983.0
BOD-Co(R)-DPP	1945.0	2527.2	982.8

Table S6. Tensorial components of the polarizabilities α (a.u.) of the studied chromophores computed at the CAM-B3LYP/6-31+G(d,p) level of theory

CAM-B3LYP	α_{xx}	α_{yy}	α_{zz}	α_{ave}
BOD-Cp-DPP	3078.6	1622.4	962.6	1887.9
BOD	930.8	998.6	372.7	767.4
Cp	118.2	125.7	125.7	123.2
DPP	681.9	347.9	413.1	481.0
Cp-DPP	1795.6	631.4	617.6	1014.9
BOD-DPP	3103.4	1500.5	871.3	1825.1
BOD-Cp	2003.8	1210.0	646.0	1286.6
BOD-Cm-DPP	2706.4	1904.0	984.8	1865.1
BOD-Co(L)-DPP	2061.0	2507.8	977.4	1848.7
BOD-Co-DPP	1920.4	2586.8	984.5	1830.5
BOD-Co(R)-DPP	1962.8	2555.8	983.8	1834.1

Table S7. Tensorial components of the first hyperpolarizabilities β (a.u.) of chromophores **BOD**, **DPP**, **Cp-DPP**`**BOD-DPP** and **BOD-Cp** computed by ωB97XD and CAM-B3LYP functionals with 6-31+G(d,p) basis set

method	tensorial component	**BOD**	**DPP**	**Cp-DPP**	**BOD-DPP**	**BOD-Cp**
ωB97XD	β_{xxx}	-6629.1	1426.2	750.0	-12223.2	-10809.8
	β_{xxy}	13.5	-152.8	-266.5	-216.1	-905.5
	β_{xyy}	-11838.3	23.0	42.8	-14268.5	-13926.4
	β_{yyy}	-263.2	21.4	-29.0	226.2	2181.5
	β_{xxz}	0.9	48.9	-65.0	80.2	567.3
	β_{xyz}	-301.6	17.2	30.6	-1207.2	374.6
	β_{yyz}	26.8	10.0	2.8	9.4	697.9
	β_{xzz}	-91.8	32.3	30.5	-145.7	-96.5
	β_{yzz}	-19.8	4.3	-3.8	16.8	-16.5
	β_{zzz}	-5.1	-14.3	34.9	45.0	25.6
CAM-B3LYP	β_{xxx}	-7445.1	1546.8	607.9	-15284.7	-12326.1
	β_{xxy}	20.5	-185.0	-238.3	-199.1	-896.4
	β_{xyy}	-12494.6	27.9	73.6	-15064.4	-14668.1
	β_{yyy}	-282.0	19.1	7.7	232.9	2312.0
	β_{xxz}	5.1	70.6	-58.9	166.9	634.8
	β_{xyz}	-323.8	14.4	34.9	-1281.5	385.0
	β_{yyz}	24.9	11.2	5.9	13.3	739.3
	β_{xzz}	-90.5	26.1	29.7	-154.3	-95.4
	β_{yzz}	-18.4	-0.7	-3.4	15.4	-20.5
	β_{zzz}	-4.9	-0.7	35.1	44.1	23.5

Table S8. Tensorial components of the first hyperpolarizabilities β (a.u.) of triad chromophores computed by ωB97XD and CAM-B3LYP functionals with 6-31+G(d,p) basis set

method	tensorial component	**BOD-Cp-DPP**	**BOD-Cm-DPP**	**BOD-Co-DPP**	**BOD-Co(L)-DPP**	**BOD-Co(R)-DPP**
ωB97XD	β_{xxx}	-10461.1	-14793.7	-17535.3	-16671.6	-18255.4
	β_{xxy}	934.3	-3832.0	6483.5	7252.7	7355.5
	β_{xyy}	-14078.6	-5014.9	4717.1	6737.4	4183.0
	β_{yyy}	-1690.2	17086.0	19323.0	16296.6	22629.0
	β_{xxz}	-28.9	2806.2	2647.4	1938.1	-1588.9
	β_{xyz}	-72.1	1090.4	-1053.8	-1060.4	223.1
	β_{yyz}	-73.9	-313.3	-1925.9	-1302.6	142.1
	β_{xzz}	-39.7	-563.4	-370.9	-235.6	-118.8
	β_{yzz}	-26.5	-112.0	435.6	230.2	93.1
	β_{zzz}	-45.9	159.8	-17.6	56.9	55.6
	β_{x}	-24579.4	-20371.9	-13189.1	-10169.8	-14191.2
	β_{y}	-782.4	13142.0	26242.0	23779.5	30077.7
	β_{z}	-148.8	2652.7	703.8	692.4	-1391.2
	β_{tot}	24592.3	24387.8	29378.4	25872.2	33286.5
CAM-B3LYP	β_{xxx}	-12256.4	-16452.1	-18780.9	-17619.6	-19517.3
	β_{xxy}	910.1	-3817.5	7106.9	7839.6	8303.5
	β_{xyy}	-14806.2	-5513.3	4728.4	6956.4	3887.6
	β_{yyy}	-1799.4	18023.8	21221.1	17619.3	24995.2
	β_{xxz}	-36.6	3034.0	2799.8	2046.6	-1690.2
	β_{xyz}	-79.7	1110.7	-1099.6	-1124.1	231.3
	β_{yyz}	-79.3	-296.7	-2003.4	-1349.1	99.0
	β_{xzz}	-38.2	-599.5	-386.5	-251.9	-127.6
	β_{yzz}	-24.5	-119.9	457.0	228.3	98.6
	β_{zzz}	-45.0	163.8	-16.5	59.3	58.0
	β_{x}	-27100.8	-22564.9	-14438.9	-10915.1	-15757.3
	β_{y}	-913.8	14086.4	28785.0	25687.2	33397.3
	β_{z}	-161.0	2901.2	779.9	756.7	-1533.2
	β_{tot}	27116.7	26758.5	32212.9	27920.3	36959.8

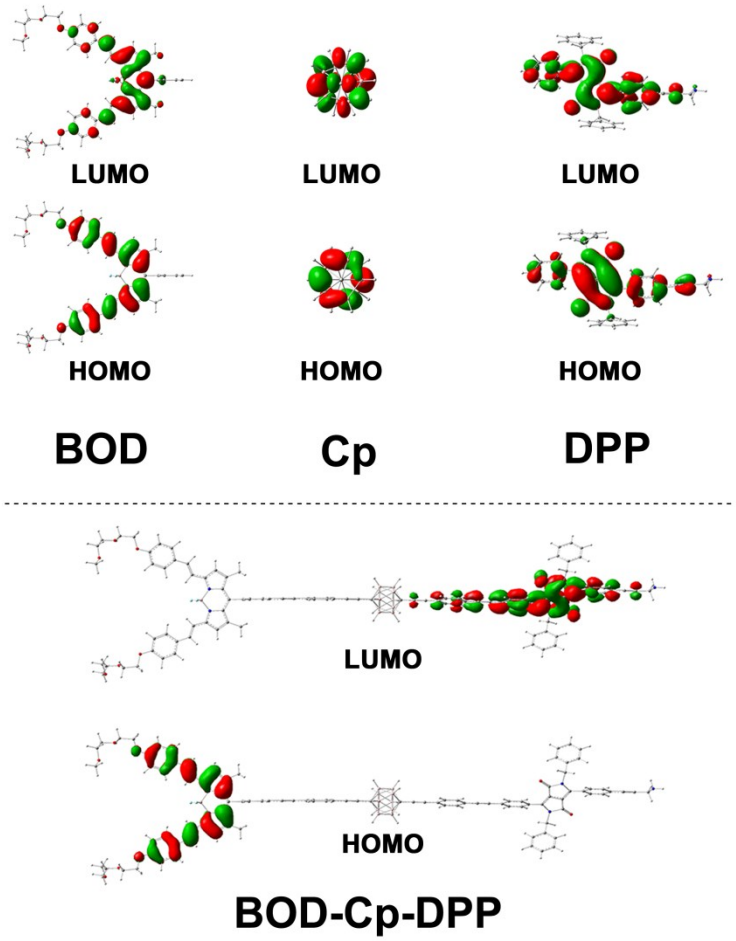


Figure S1. Spatial plots (isovalue = 0.02 a.u.) of frontier molecular orbitals for **BOD**, **Cp**, **DPP** and **BOD-Cp-DPP** chromophores.

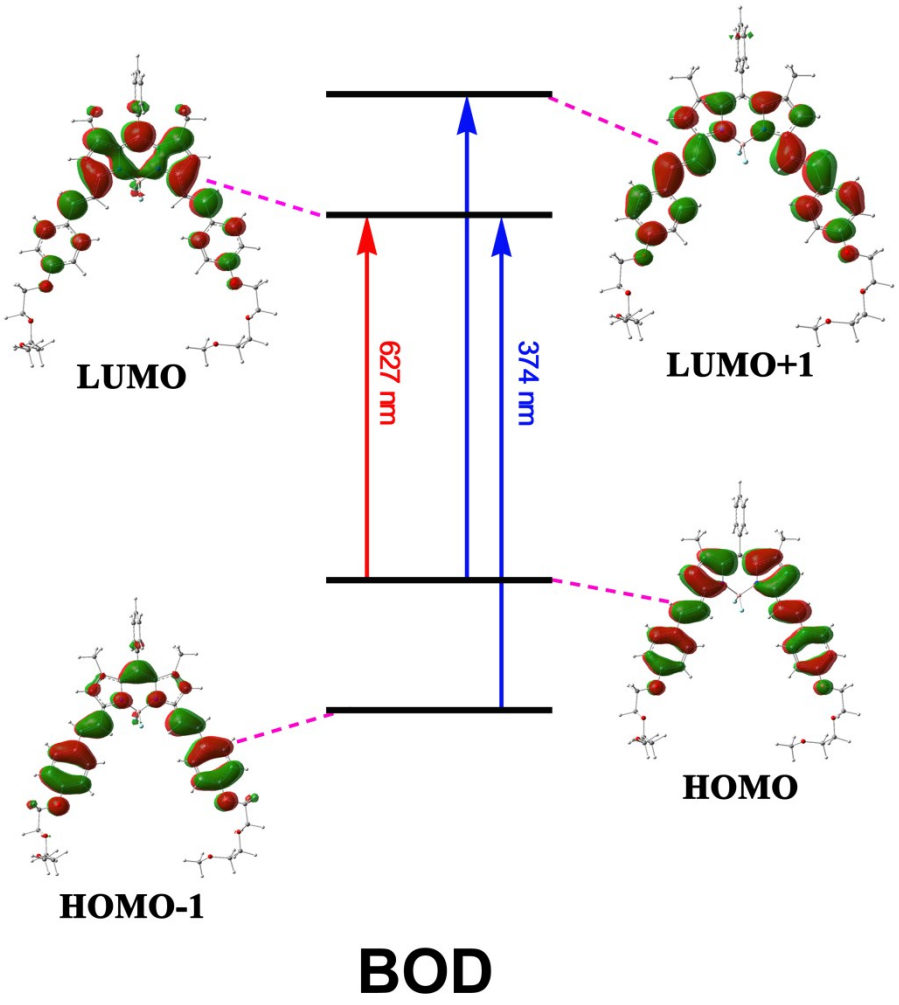


Figure S2. The molecular orbitals involved in the crucial electronic transitions of chromophore **BOD**.

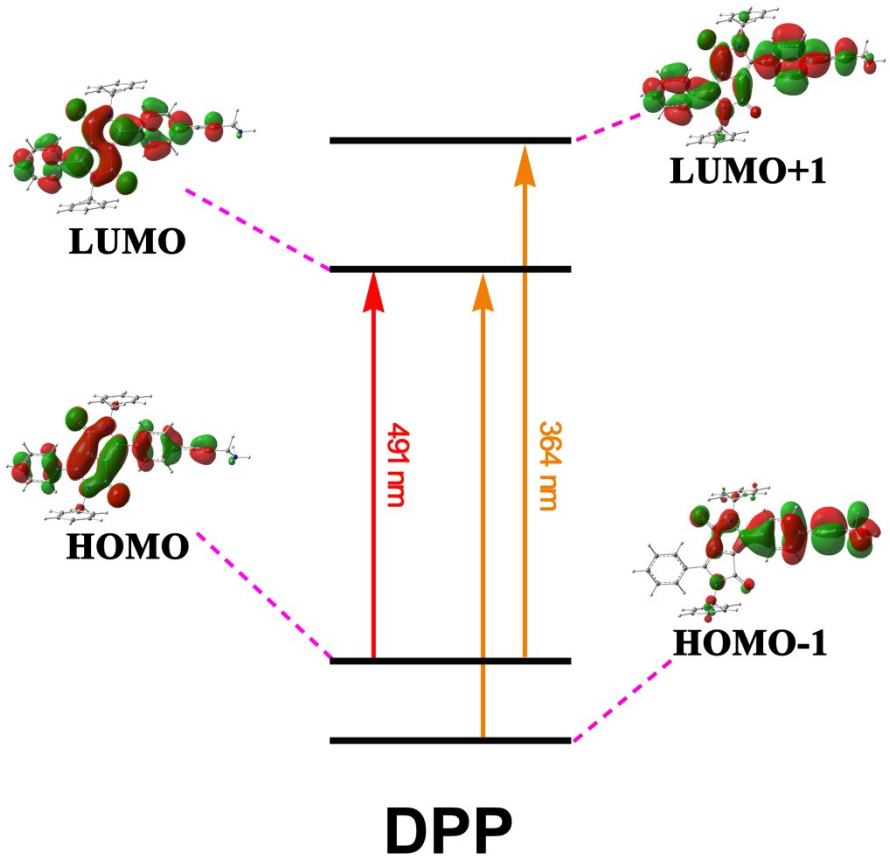


Figure S3. The molecular orbitals involved in the crucial electronic transitions of chromophore **DPP**.

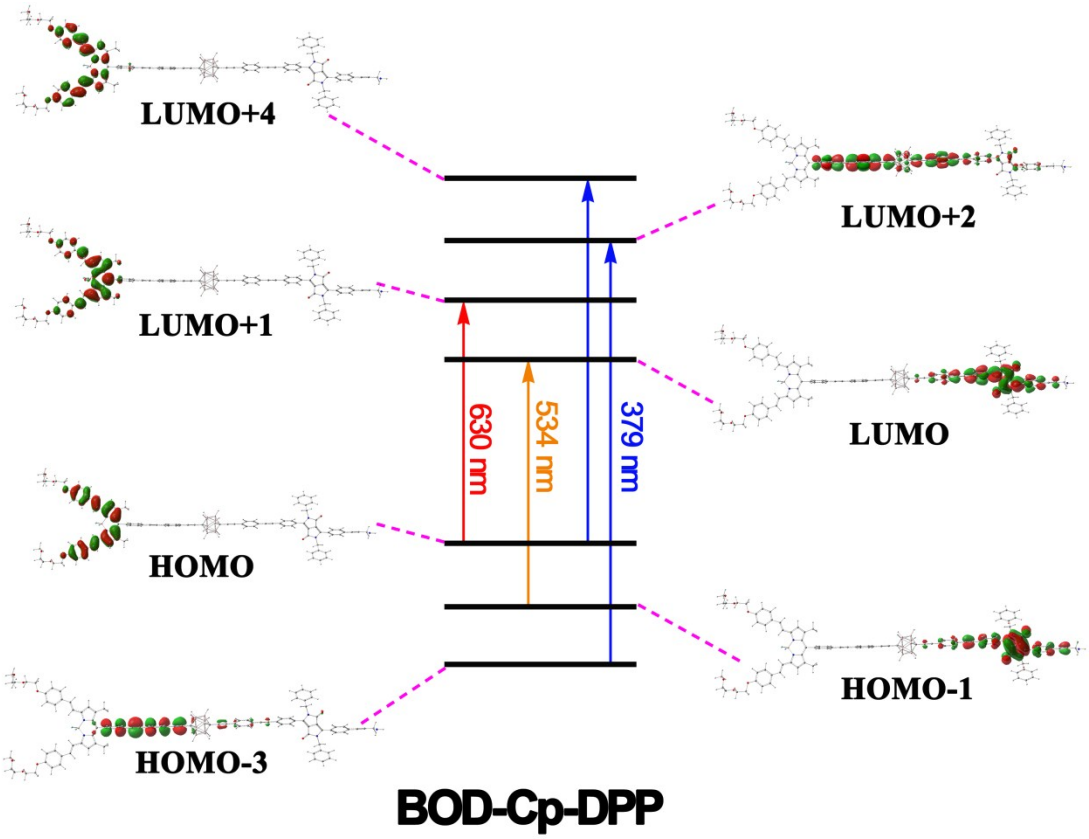


Figure S4. The molecular orbitals involved in the crucial electronic transitions of chromophore **BOD-Cp-DPP**.

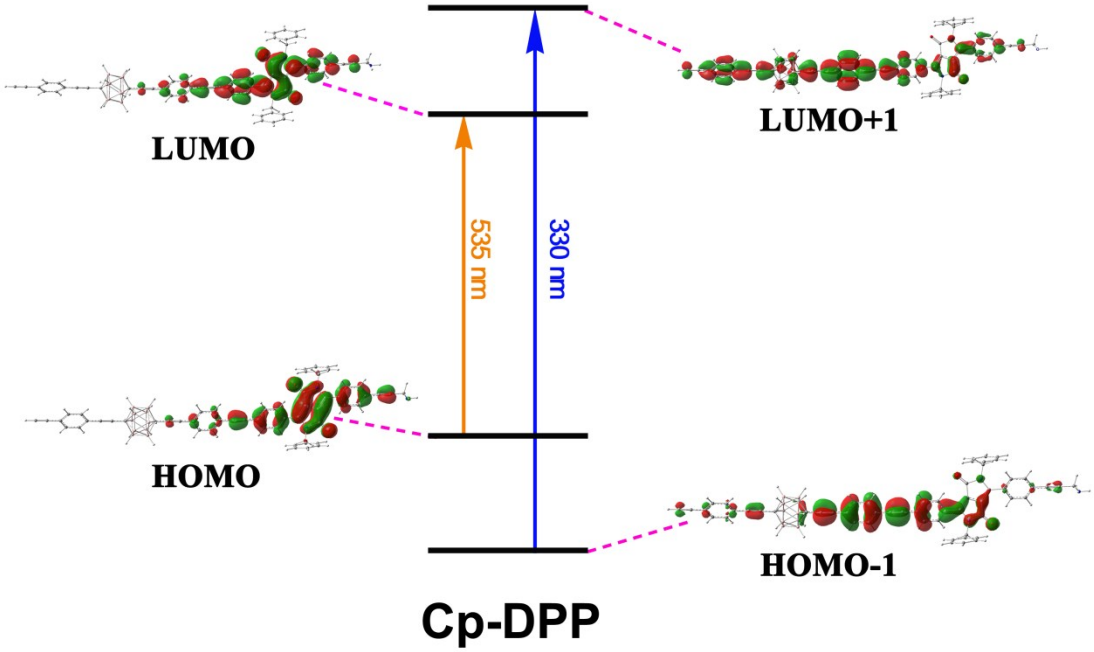


Figure S5. The molecular orbitals involved in the crucial electronic transitions of chromophore **Cp-DPP**.

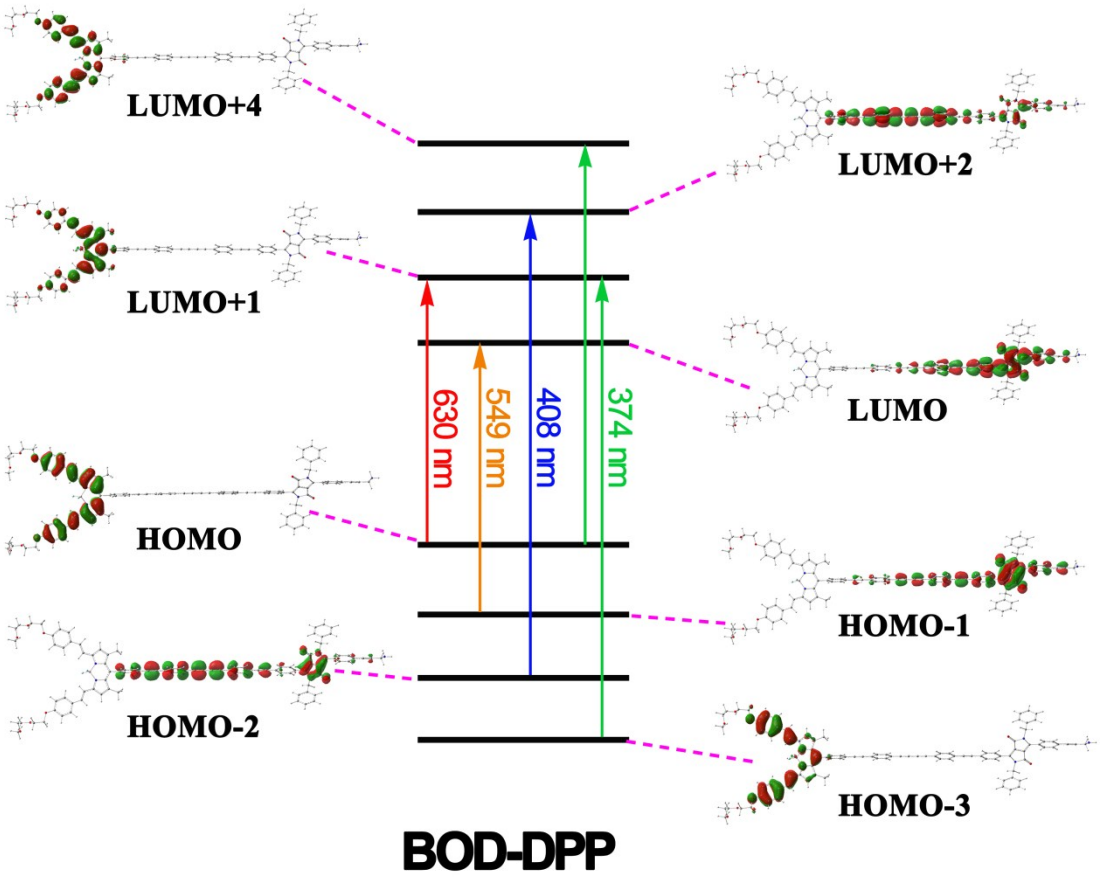


Figure S6. The molecular orbitals involved in the crucial electronic transitions of chromophore **BOD-DPP**.

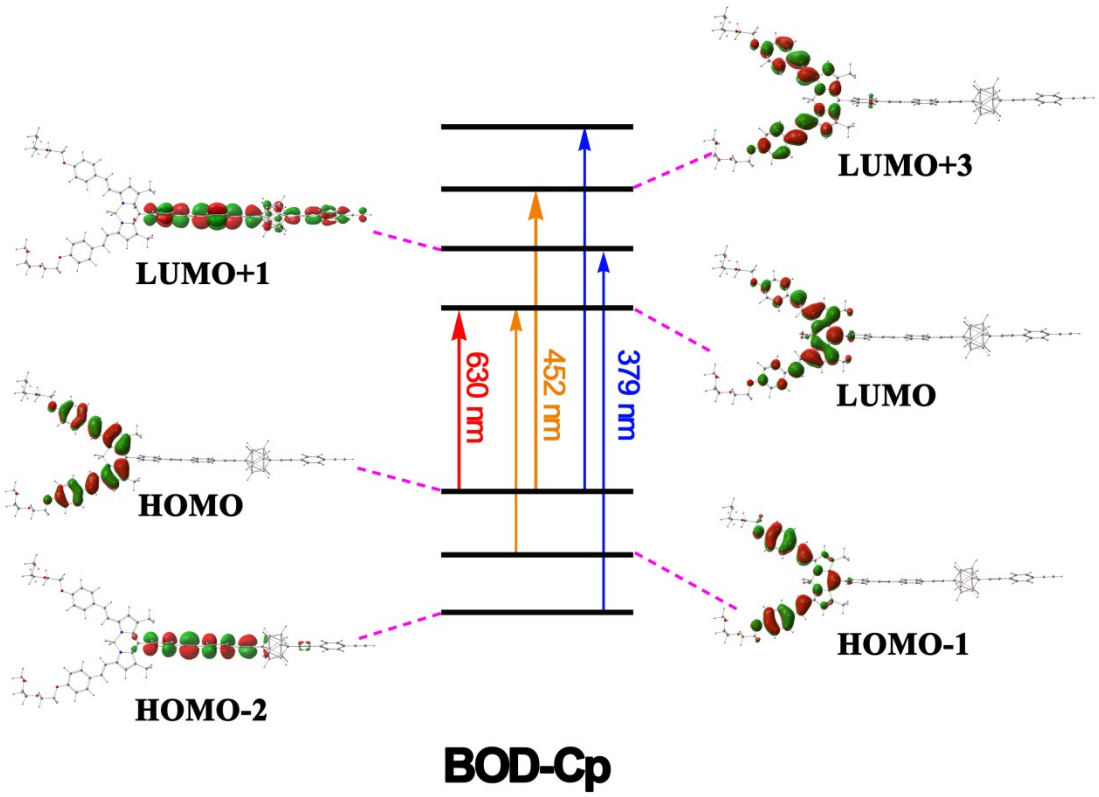


Figure S7. The molecular orbitals involved in the crucial electronic transitions of chromophore **BOD-Cp**.

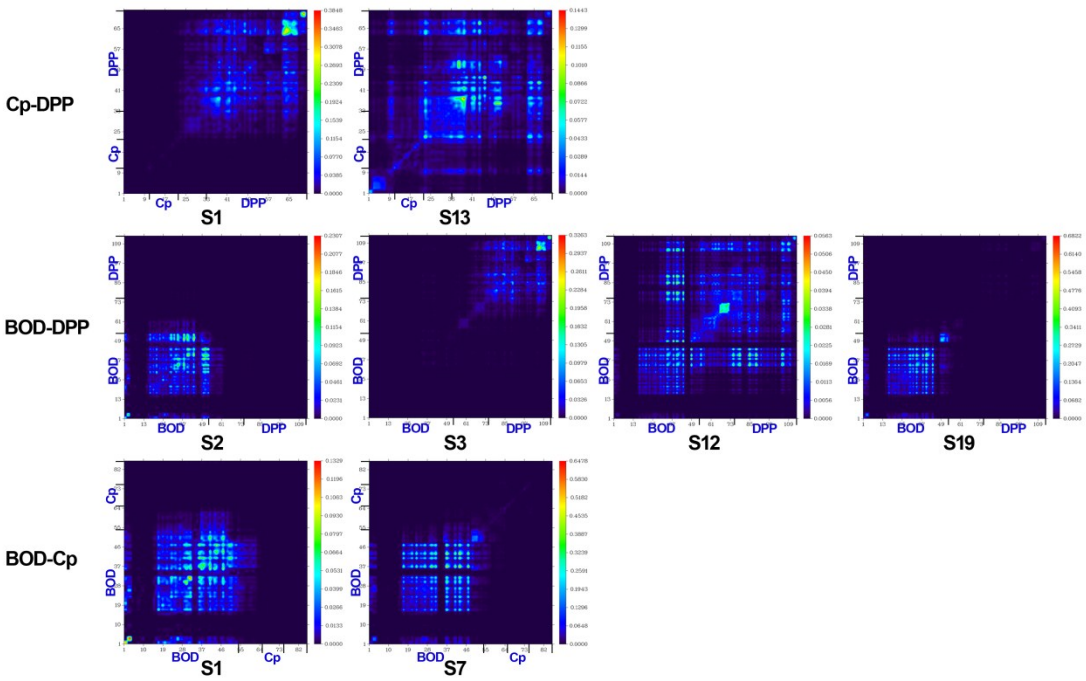


Figure S8. The TDM corresponding to the crucial electronic transitions of **Cp-DPP**, **BOD-DPP** and **BOD-Cp** dyad chromophores.

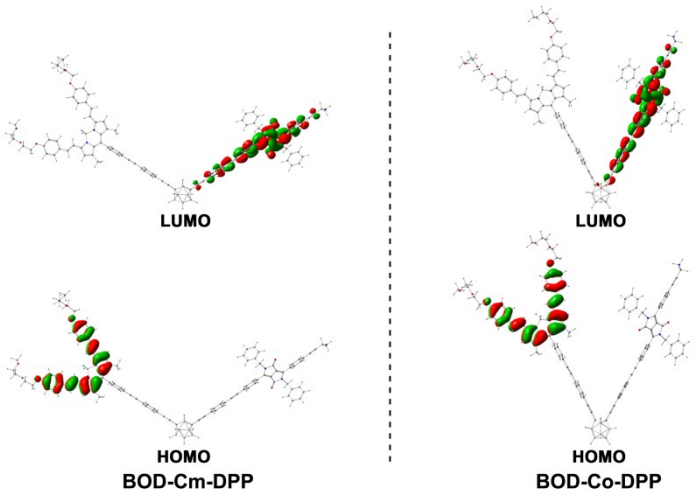


Figure S9. Spatial plots (isovalue = 0.02 a.u.) of frontier molecular orbitals for chromophores **BOD-Cm-DPP** and **BOD-Co-DPP**.

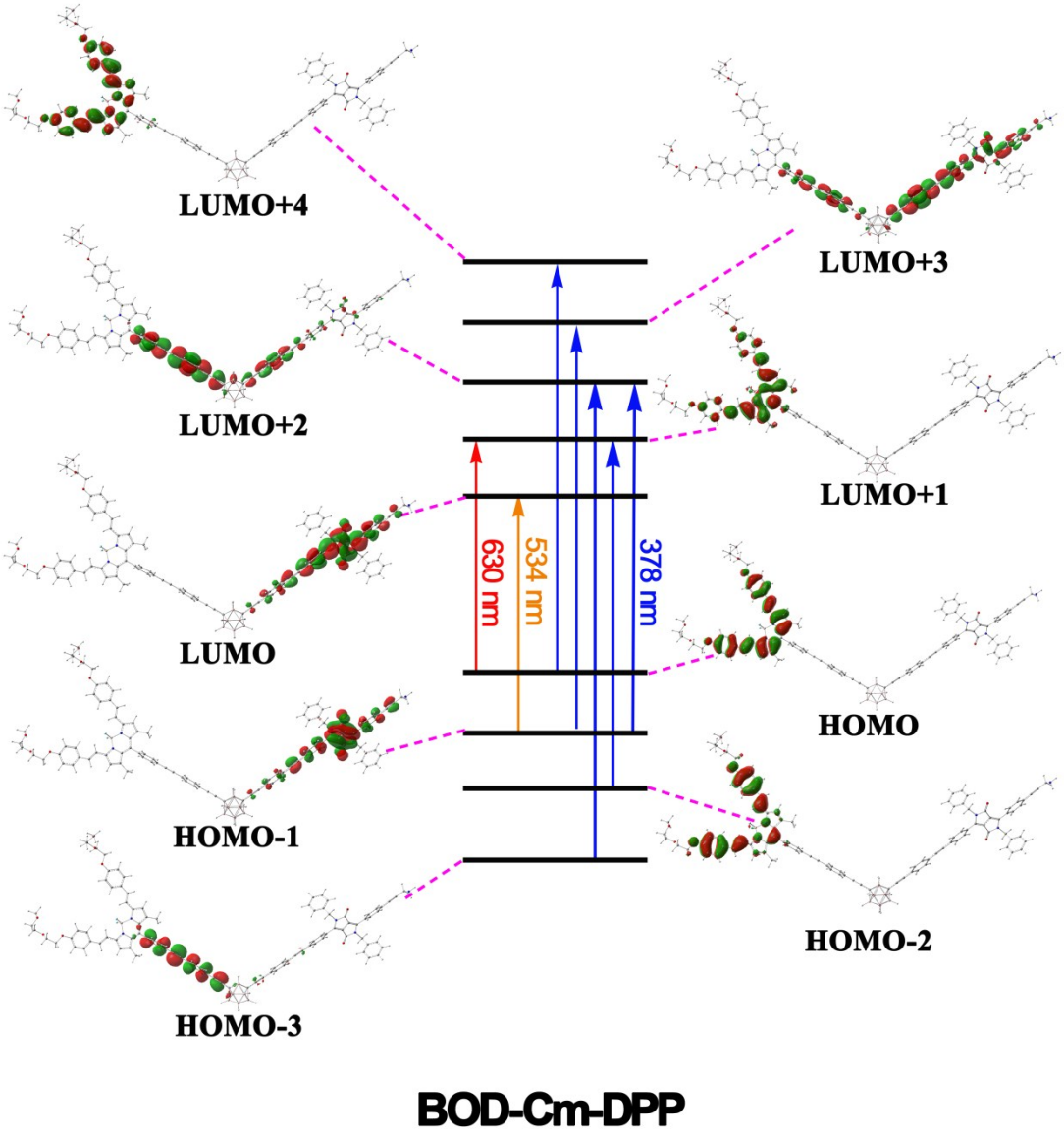


Figure S10. The molecular orbitals involved in the crucial electronic transitions of chromophore **BOD-Cm-DPP**.

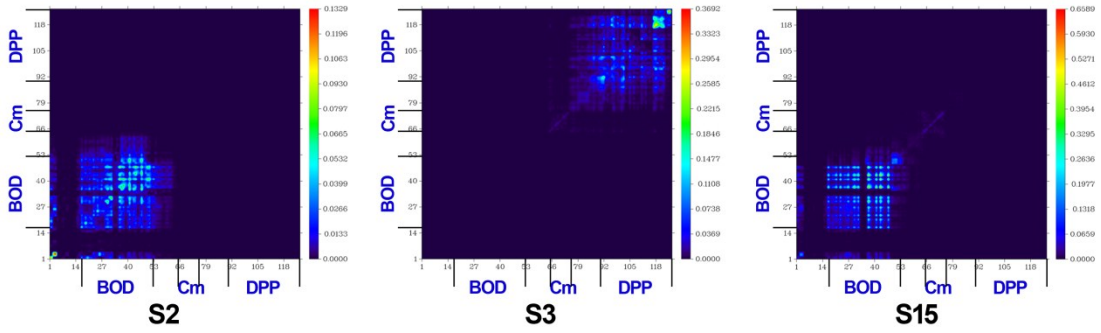


Figure S11. The TDM corresponding to the crucial electronic transitions of **BOD-Cm-DPP**.

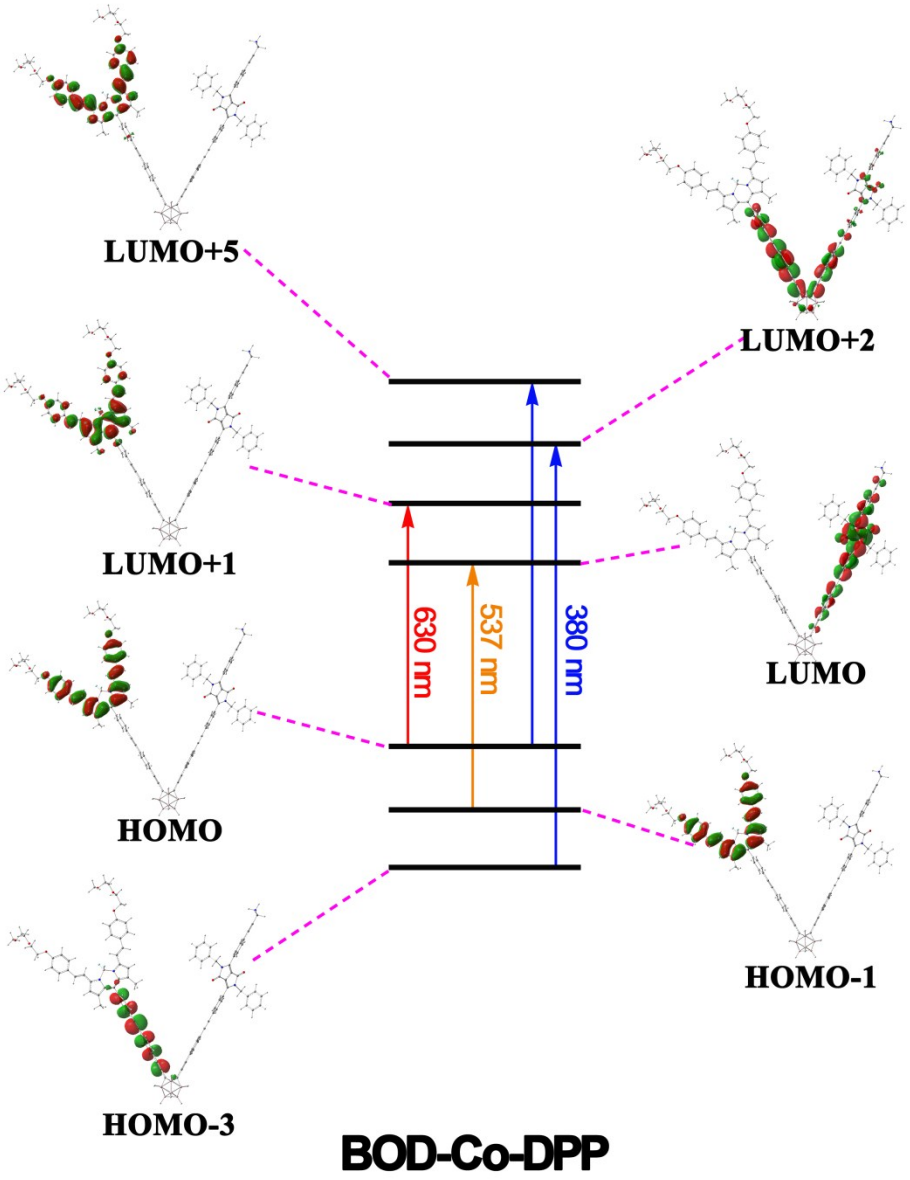


Figure S12. The molecular orbitals involved in the crucial electronic transitions of chromophore **BOD-Co-DPP**.

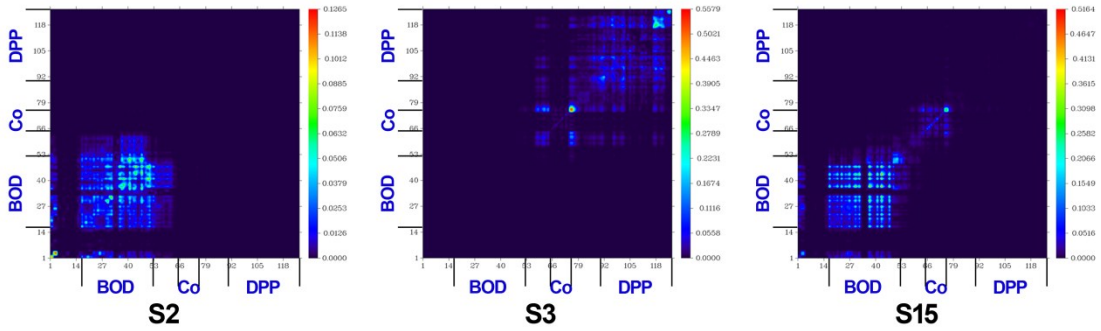


Figure S13. The TDM corresponding to the crucial electronic transitions of **BOD-Co-DPP**.

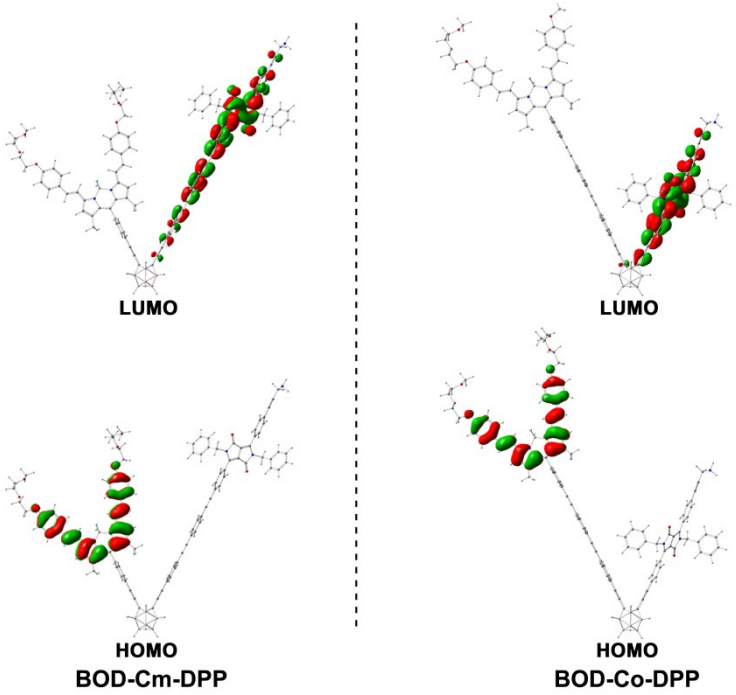


Figure S14. Spatial plots (isovalue = 0.02 a.u.) of frontier molecular orbitals for chromophores **BOD-Co(L)-DPP** and **BOD-Co(R)-DPP**.

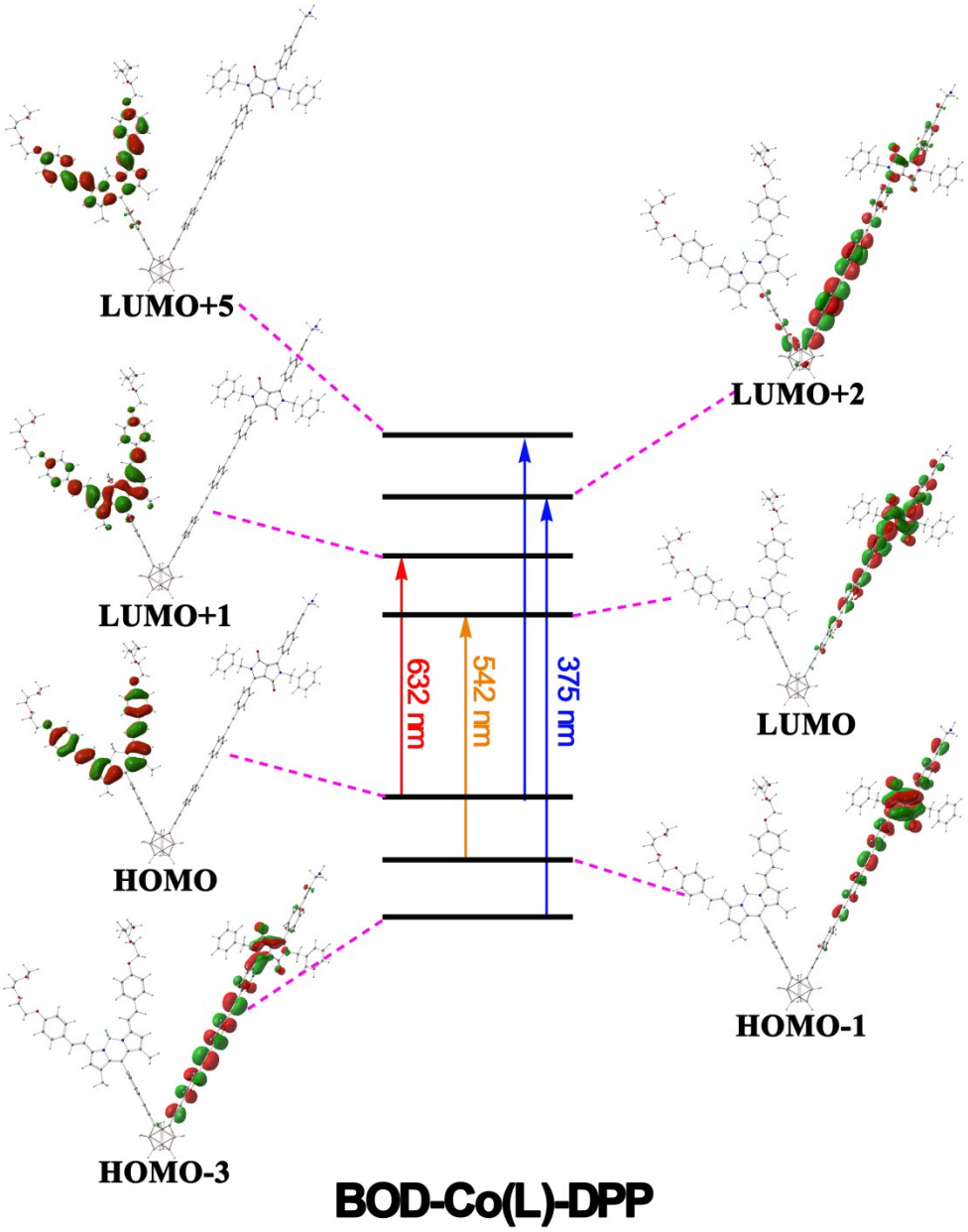


Figure S15. The molecular orbitals involved in the crucial electronic transitions of chromophore **BOD-Co(L)-DPP**.

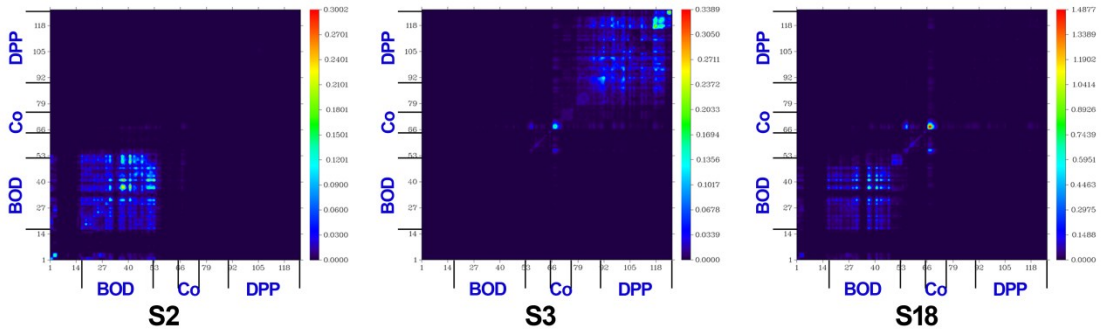


Figure S16. The TDM corresponding to the crucial electronic transitions of **BOD-Co(L)-DPP**.

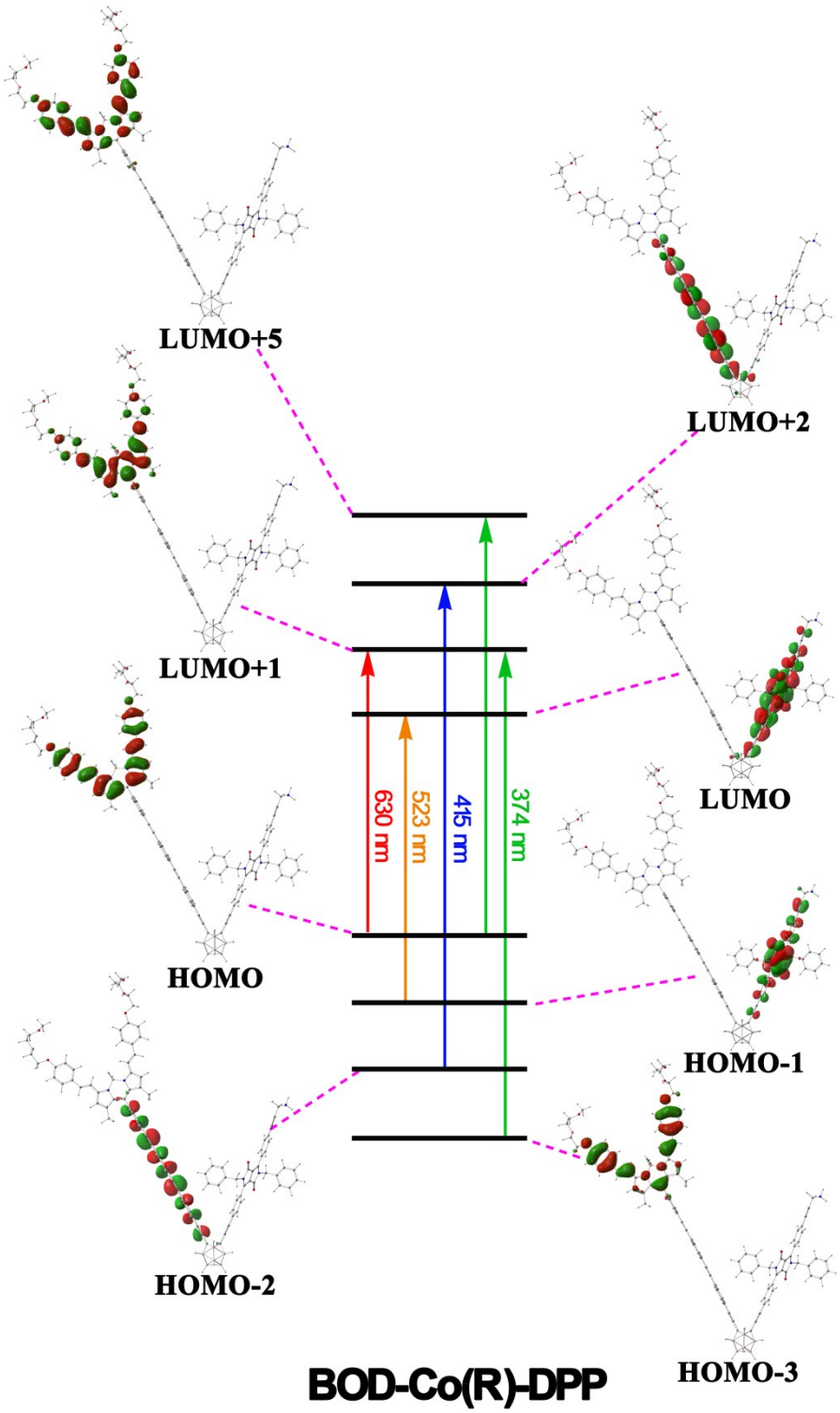


Figure S17. The molecular orbitals involved in the crucial electronic transitions of chromophore **BOD-Co(R)-DPP**.

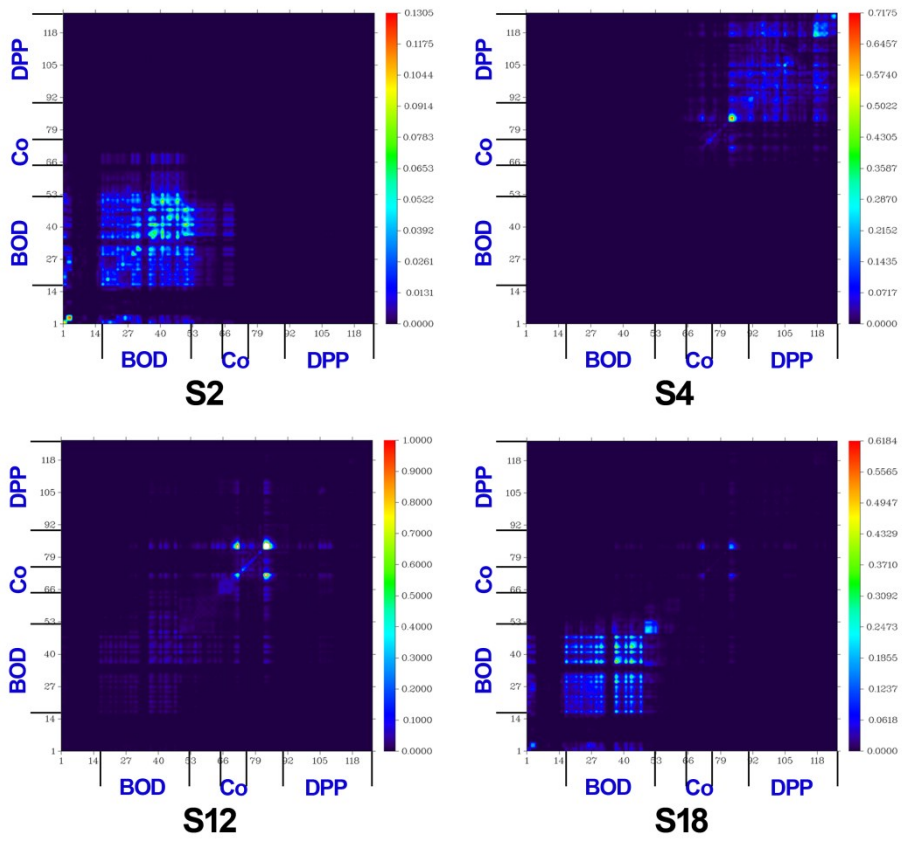


Figure S18. The TDM corresponding to the crucial electronic transitions of **BOD-Co(R)-DPP**.

References

1. A. Nano, P. Retailleau, J. P. Hagon, A. Harriman and R. Ziessel, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10187-10198.
2. R. Ziessel, G. Ulrich, A. Harriman, M. A. H. Alamiry, B. Stewart and P. Retailleau, *Chem. Eur. J.*, 2009, **15**, 1359-1369.
3. J.-Y. Liu, H.-S. Yeung, W. Xu, X. Li and D. K. P. Ng, *Org. Lett.*, 2008, **10**, 5421-5424.
4. J.-s. Lu, H. Fu, Y. Zhang, Z. J. Jakubek, Y. Tao and S. Wang, *Angew. Chem. Int. Ed.*, 2011, **50**, 11658-11662.
5. M. A. Fox, A. M. Cameron, P. J. Low, M. A. J. Paterson, A. S. Batsanov, A. E. Goeta, D. W. H. Rankin, H. E. Robertson and J. T. Schirlin, *Dalton Trans.*, 2006, **29**, 3544-3560.
6. A. Herzog, S. S. Jalisatgi, C. B. Knobler, T. J. Wedge and M. F. Hawthorne, *Chem. Eur. J.*, 2005, **11**, 7155-7174.
7. B. Moore and J. Autschbach, *J. Chem. Theory Comput.*, 2013, **9**, 4991-5003.