Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ultrafast Optical-Limiting in *trans*-Stilbene Enhanced and Broadened by Donor-π-Acceptor Structure (Supplementary Information)*

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Mayer bond order and multicenter bond order (MCBO)

For restricted closed-shell systems, the expression of Mayer bond order[1] between two selected atoms A and B is defined as

$$I_{AB} = \sum_{a\in A}\sum_{b\in B}(PS)_{ab}(PS)_{ba} \tag{1}$$

where P and S are the density matrix and the overlap matrix, respectively. Then, a and b indicate the indices of basis functions centered at atoms A and B, respectively. In physical essence, the Mayer bond order reflects the average number of electron pairs shared between two atoms[2]. If the density matrix of π electrons is used to calculate the Mayer bond order, it means that the π Mayer bond order, which can be used to characterize the average number of π electron pairs shared between two atoms.

Multicenter bond order (MCBO)[3], which is also known as multicenter index, is defined as

$$I_{ABCDEF\ldots K} = \sum_{a\in A}\sum_{b\in B}\sum_{c\in C}\cdots\sum_{k\in K}(PS)_{ab}(PS)_{bc}(PS)_{cd}\ldots(PS)_{ka} \tag{2}$$

where P is the density matrix, S is the overlap matrix, the A,B,C... represent the indices of the atoms in the ring, the a,b,c... represent the indices of the basis functions at corresponding atoms. And these atoms are adjacent to each other according to the way they are connected in the ring. MCBO may be regarded as an extension of Mayer bond order to multicenter cases. Accordingly, the MCBO calculated based on the density matrix of π electrons, MCBO-π, can describe the degree of conjugation in multicenter systems.

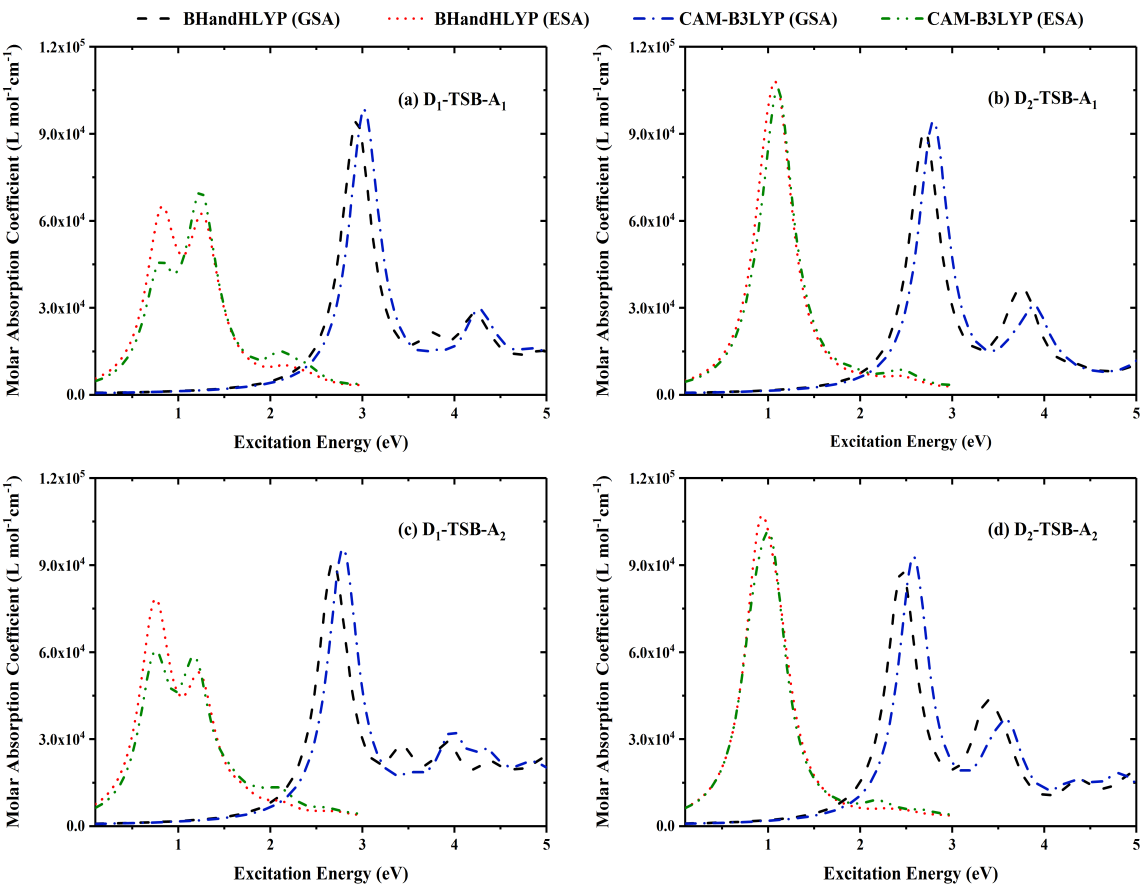

FIG. S1: Comparisons of simulated absorption spectra of TSB derivative(D-TSB-A) in the ground state S_0 (GSA) and first singlet excited state S_1 (ESA) by using BHandHLYP and CAM-B3LYP functionals respectively.

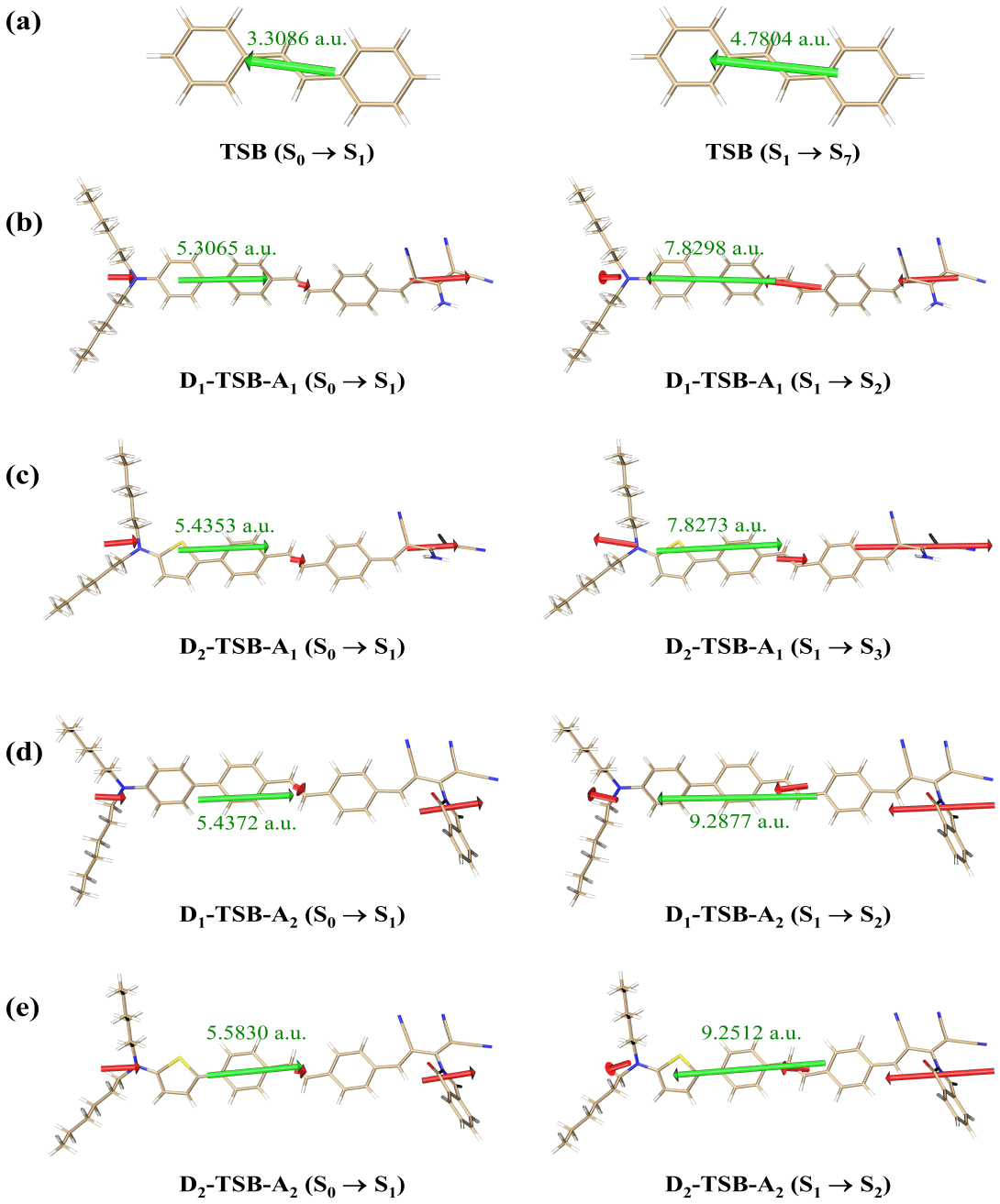

FIG. S2: Transition dipole moment vector contributed by different molecular fragments of D-TSB-A derivatives. The total transition dipole moments of all four D-TSB-A derivatives were decomposed into the contributions of three fragments, donor (D), TSB and acceptor (A). The red arrows represent the contribution of each fragment, and the green arrows represent the total transition dipole moment vector of the entire molecule. The length of the cylindrical part of the arrow corresponds to the value of the transition dipole moment contributed by the fragment, and the direction of the arrow shows the direction of the transition dipole moment vector.

References

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