Supporting Information

Title: **Dimerization Effects on Electronic Properties of OLED Candidate Materials for Optimized Performance: A quantum DFT study**

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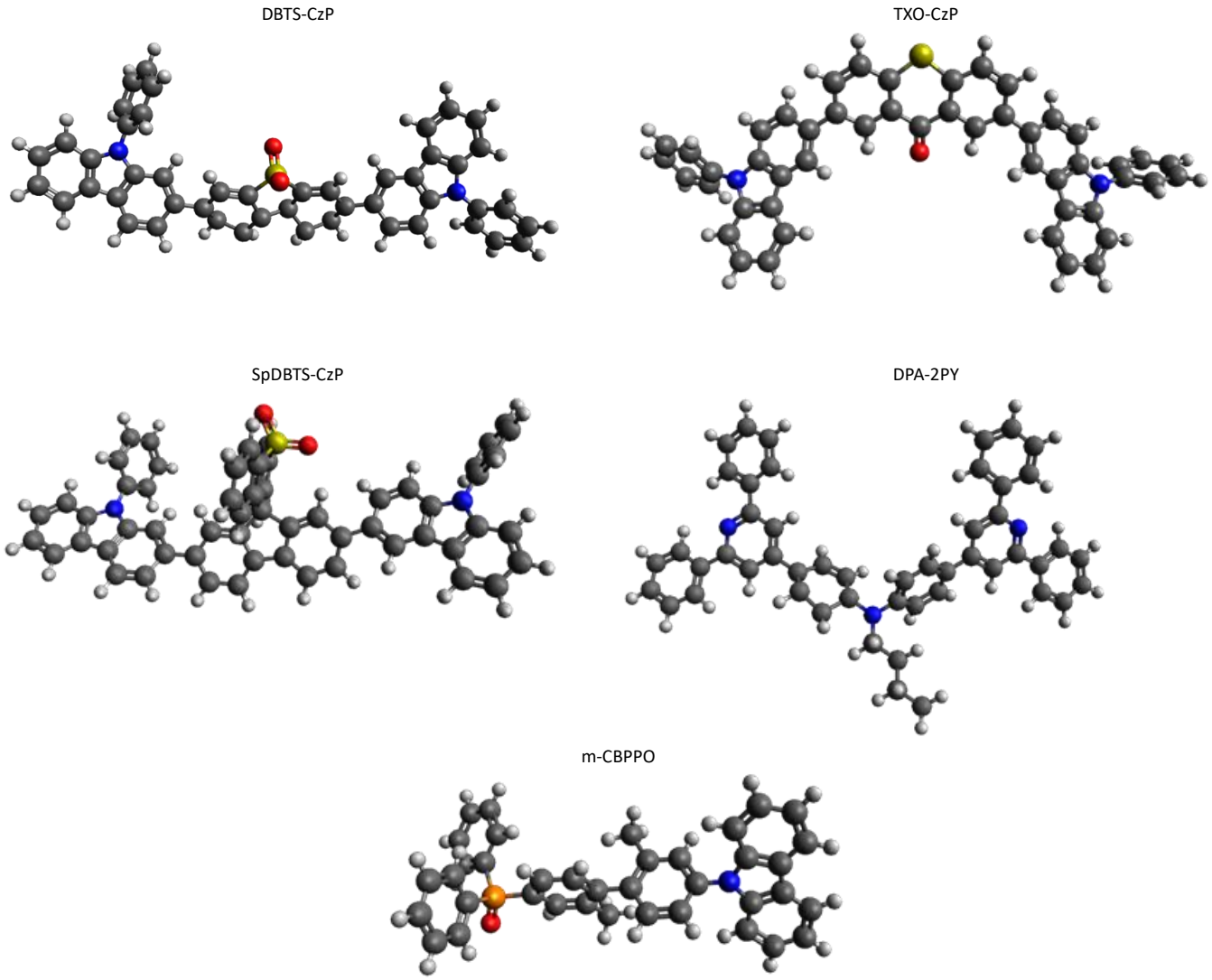


Figure S1. We utilized the advanced B3LYP/6-311++g(dp) method, a technique within the density functional theory (DFT) family, to meticulously optimize the molecular structures of each individual compound. This method is widely acclaimed for its exceptional balance between computational efficiency and accuracy, enabling us to delve deeply into the three-dimensional shapes of the compounds. The resulting optimized structures, depicted in Figure 1, grant us a comprehensive insight into the intricate ways in which the geometric properties of each molecule influence its behavior within diverse chemical environments.

Frontier molecule orbital density distribution

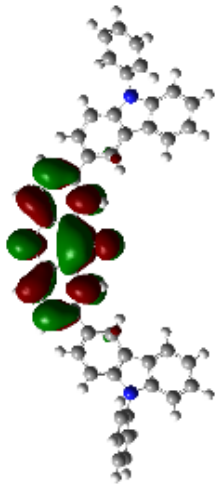
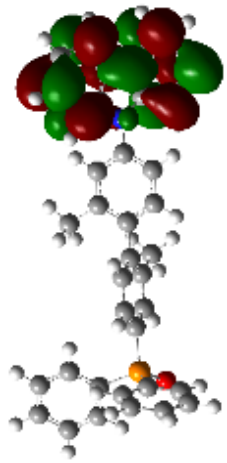
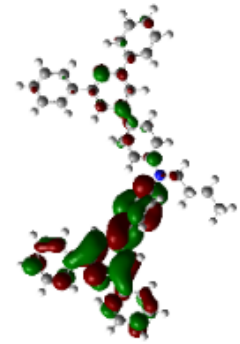
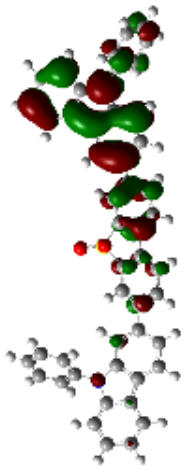
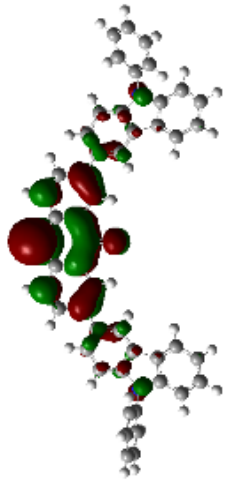
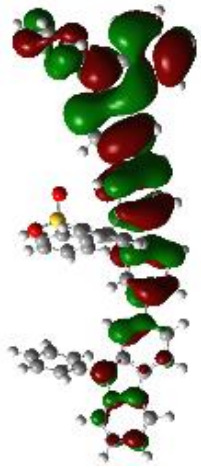
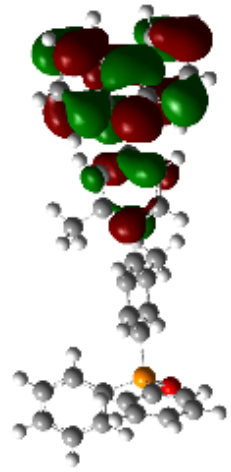
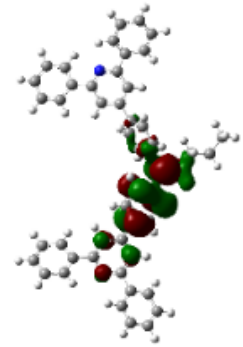
compound	DBTS-CzP	TXO-CzP	SpDBTS-CzP	m-CBPPO	DPA
LUMO (S1) eV					
HOMO (S0) eV					

Figure S2. In understanding how a molecule might behave, an important factor to consider is the behavior of its frontier orbitals, namely the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These orbitals are key players in determining the reactivity and properties of the molecule. To gain insights into these orbitals, we employed Density Functional Theory (DFT) to calculate them, and the detailed results are presented in Table 1. Furthermore, in Figure 2, we have provided a visual representation of the orbital density distributions, which vividly illustrates the probable locations of electrons within the molecule. This visualization plays a crucial role in deepening our understanding of the electronic properties of each compound and predicting their potential chemical reactions.

The fragmentation of the single compounds for DOS analysis

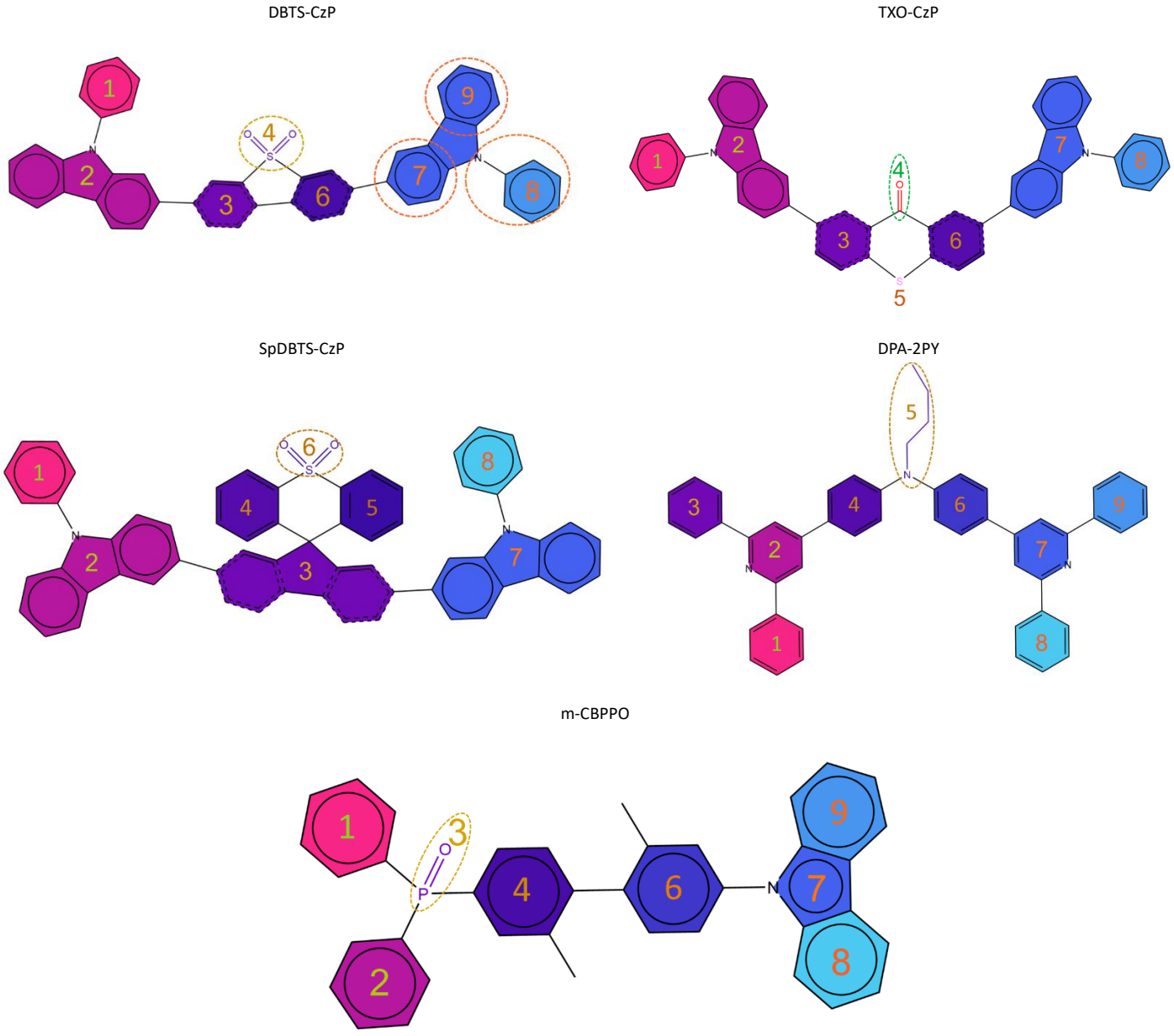
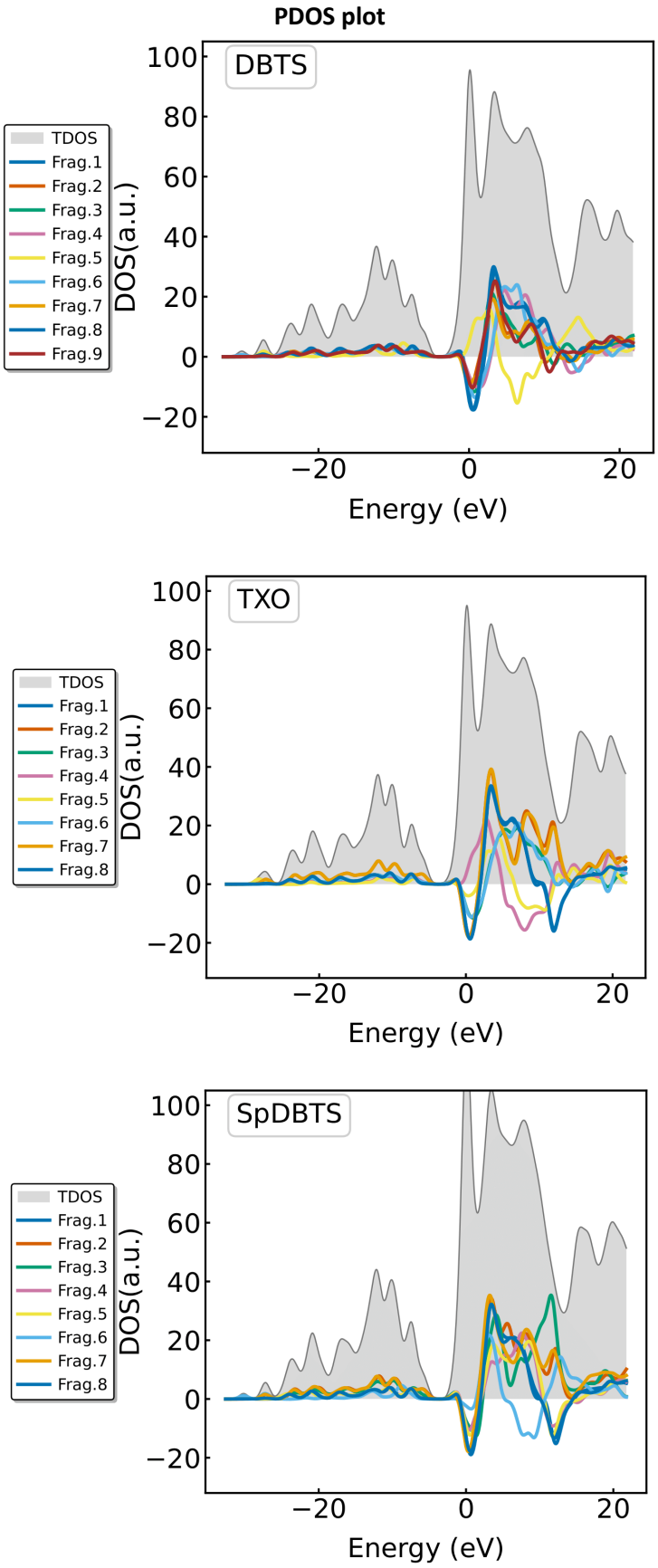


Figure S3. In our research, we sought to enhance our comprehension of the distribution of electronic states within these compounds through a comprehensive density of states (DOS) analysis. This involved deconstructing each compound into key fragments in order to discern the individual contributions to the overall electronic structure. In Figure 4, the DOS profiles for these fragments are depicted, providing valuable insights into the electronic behavior of each molecular component. This analysis offers a detailed examination of their respective roles in influencing the HOMO-LUMO gap, which is crucial for understanding their electronic properties.

Partial density of states of the monomer compounds. The fragmentations have been explained in the last section.



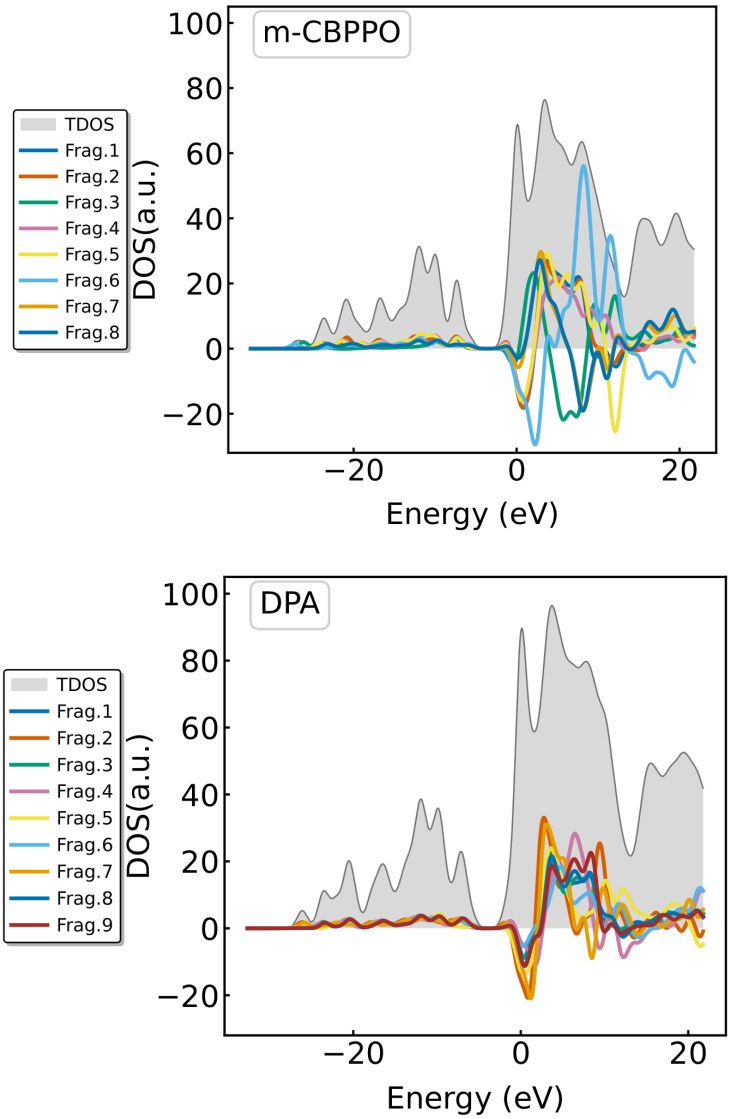
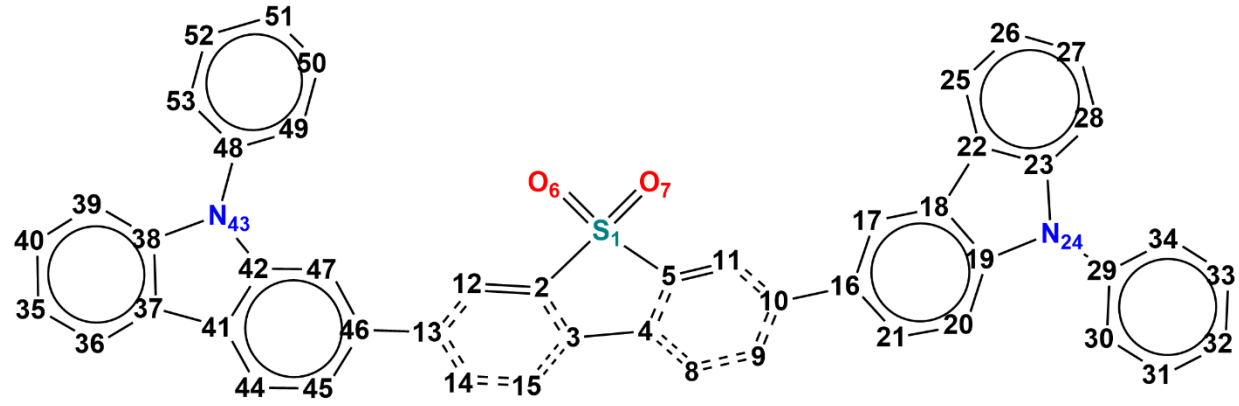


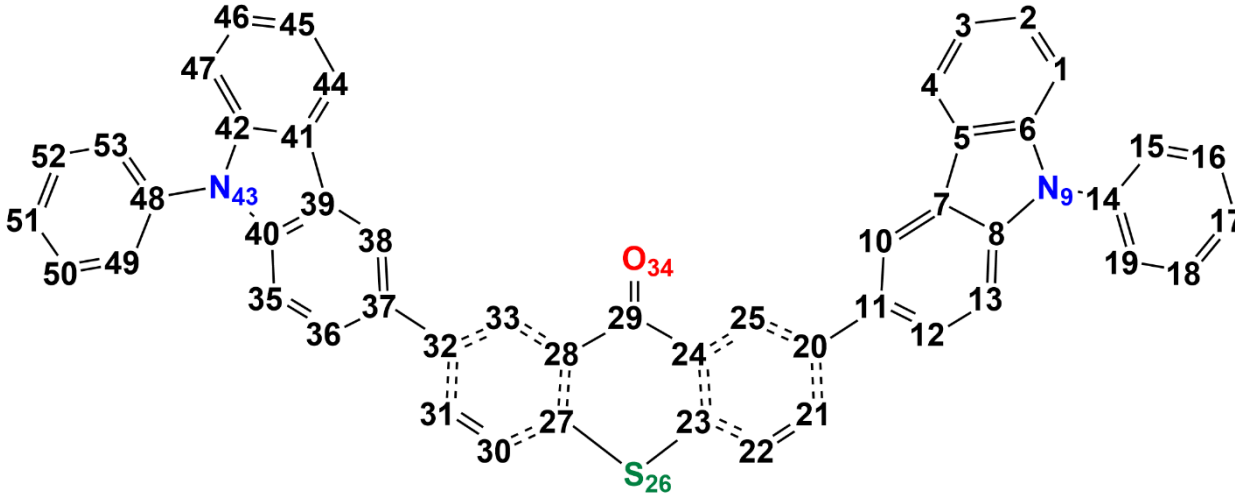
Figure S4. Partial density of states (PDOS) of monomer compounds.

Atom numbers of each monomer structure.

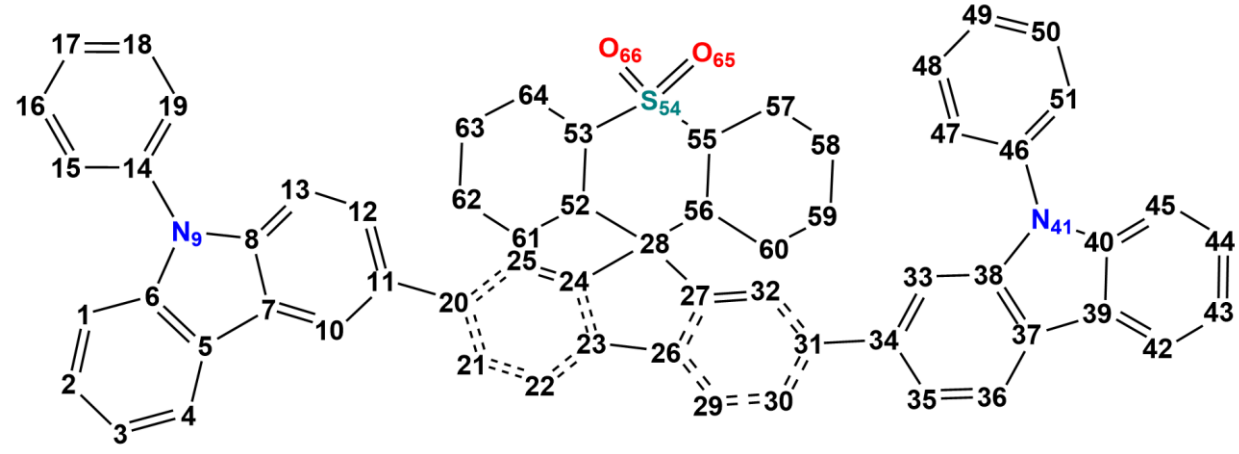
DBTS-CzP



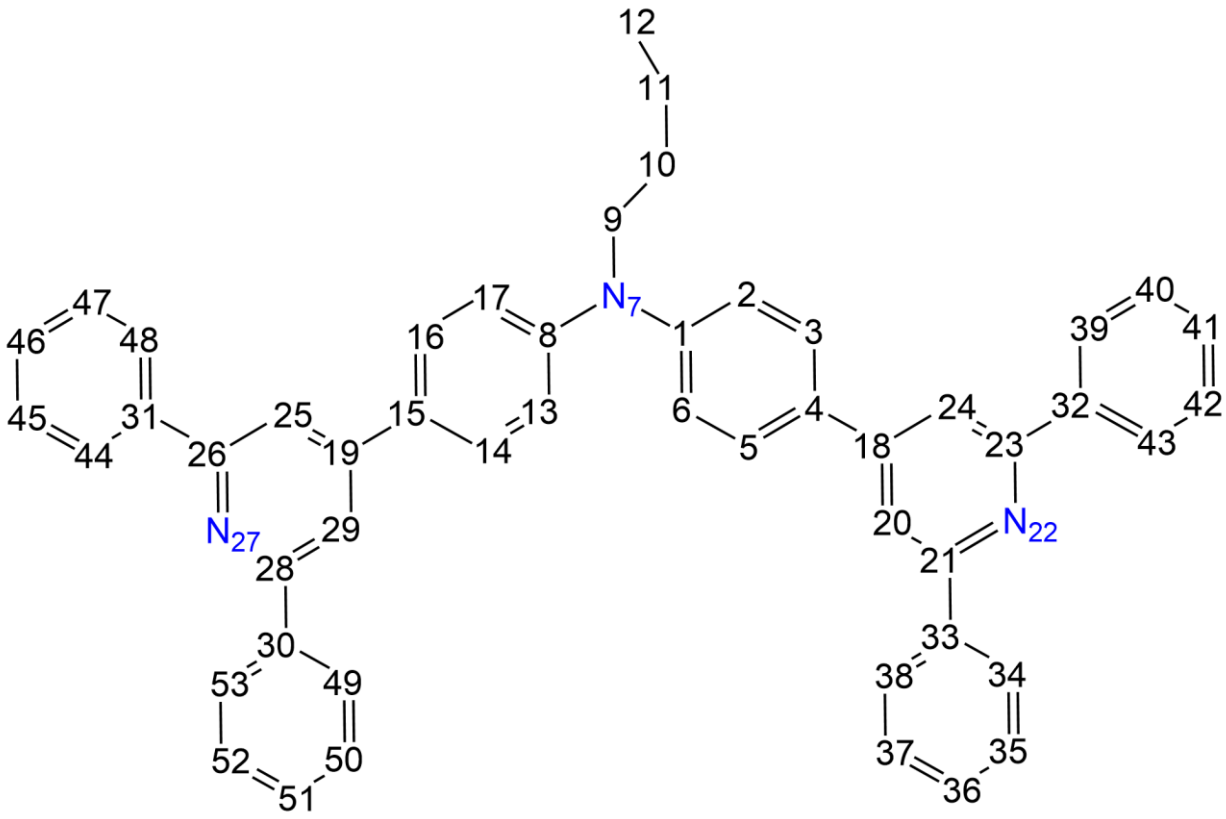
TXO-CzP



SpDBTS



DPA-2PY



m-CBPPO

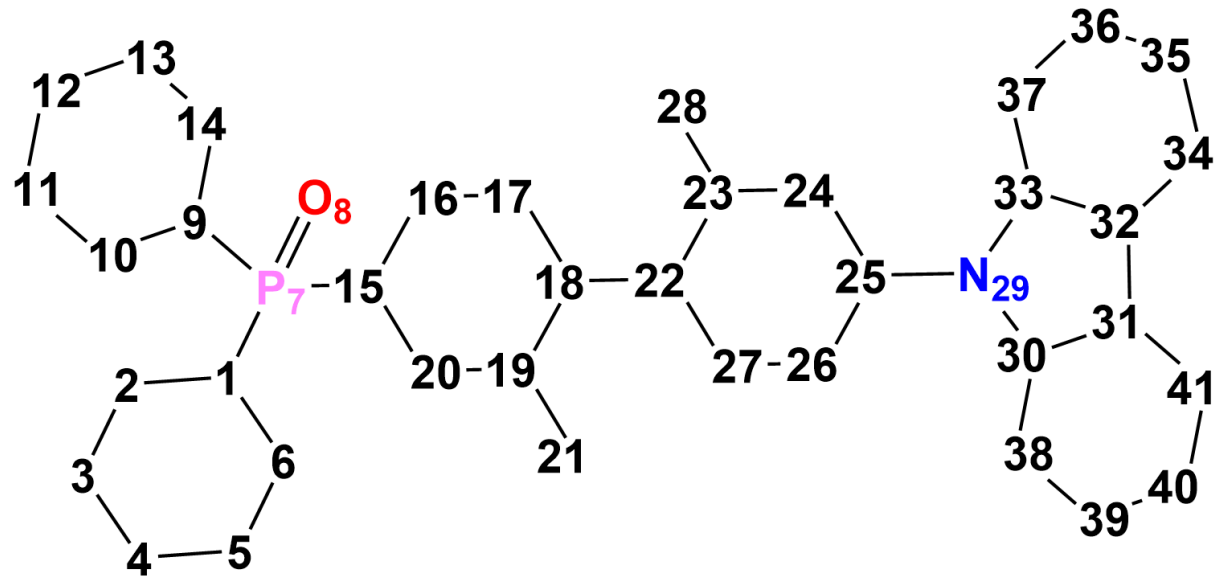
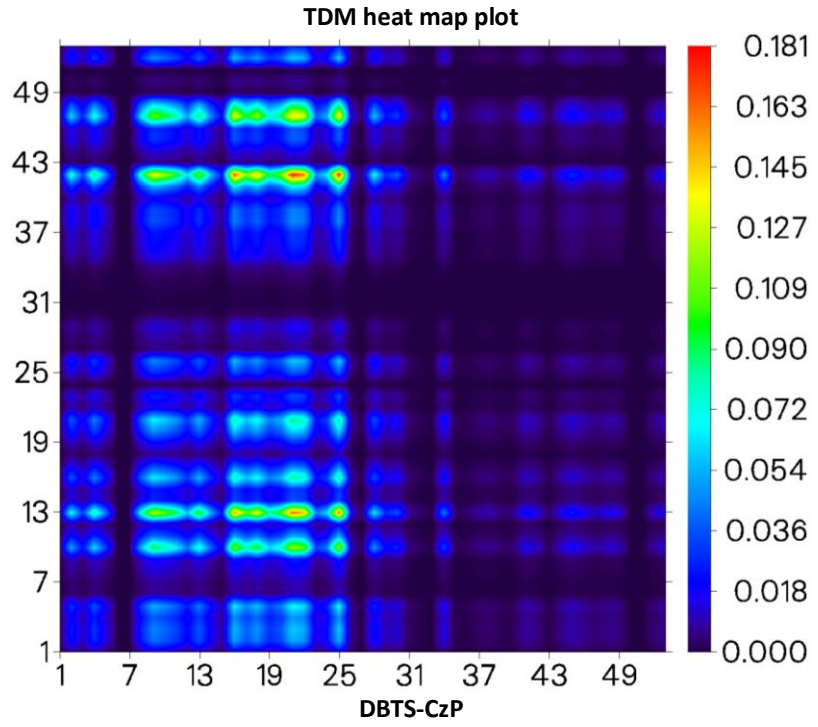
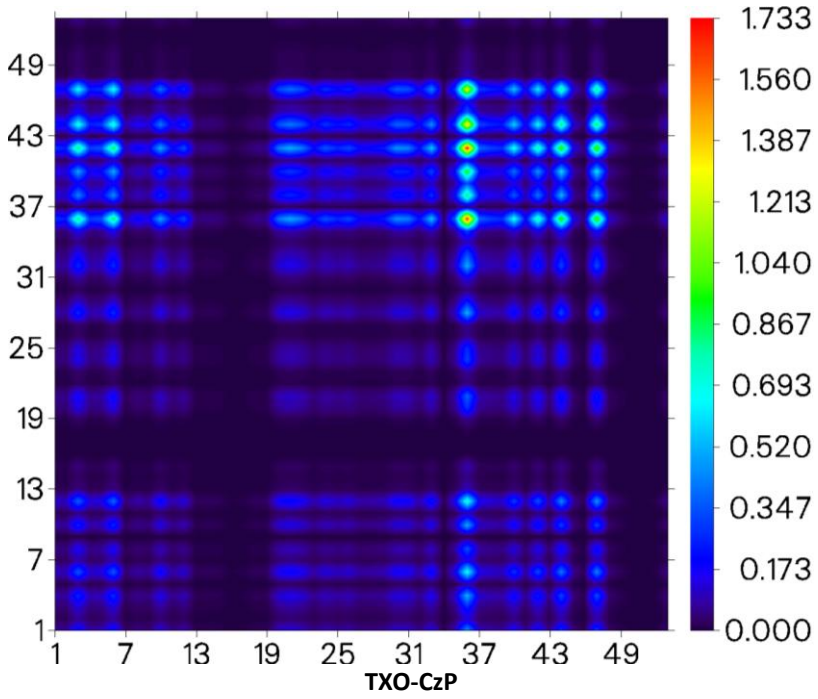
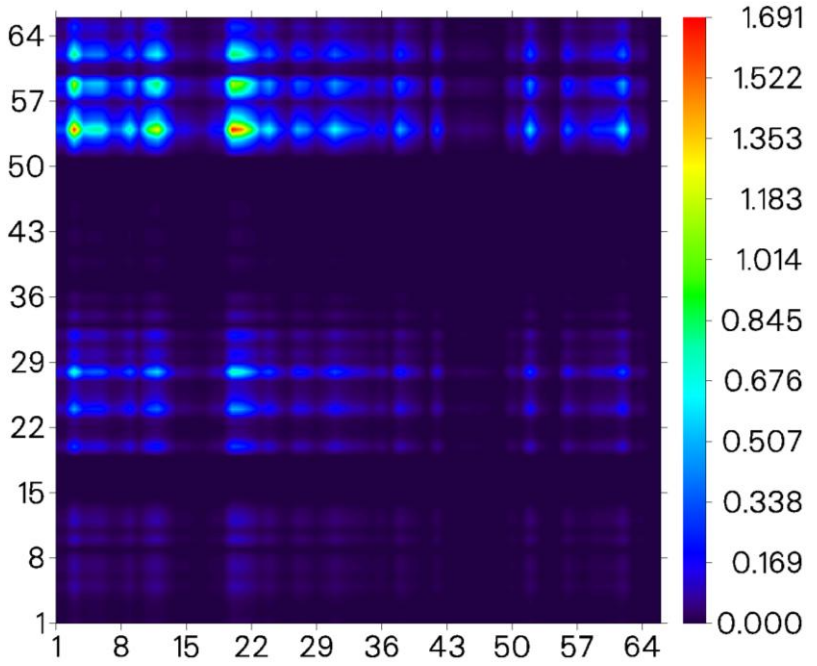


Figure S°. To clarify the atom numbering used in the Transition Density Matrix (TDM) analyses (Figures 4, 8, and S5), a labeled 2D sketch of the molecular structures is included in this section. Each atom in the structures is explicitly numbered, allowing for easy cross-referencing with the TDM maps and other analyses discussed in the main text.

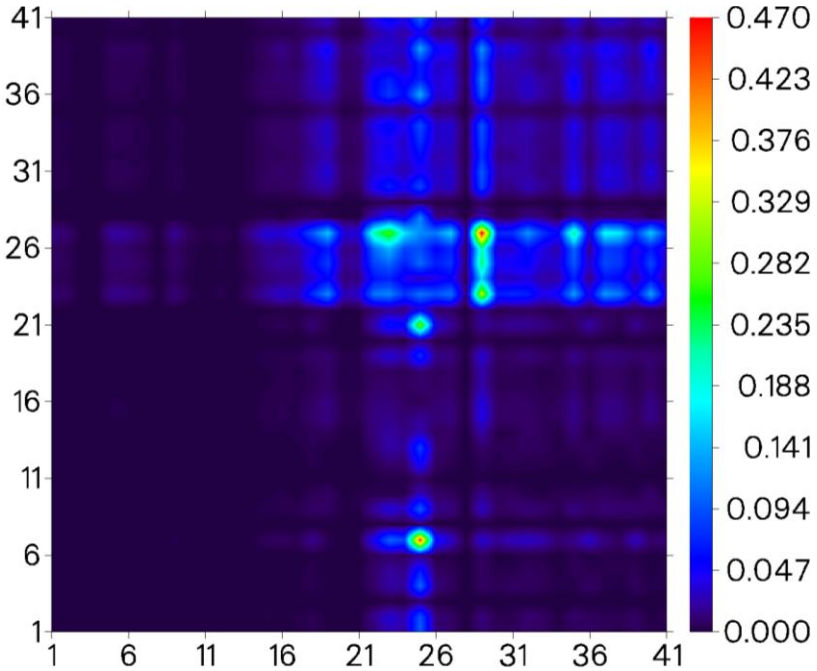
Transition density matrix heat maps for all monomer compounds.







SpDBTS-CzP



m-CBPPO

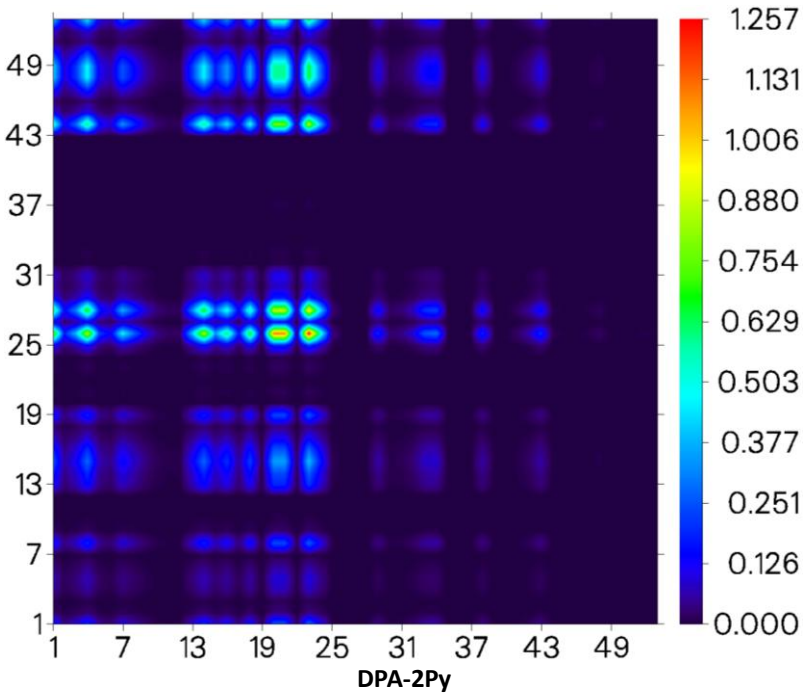


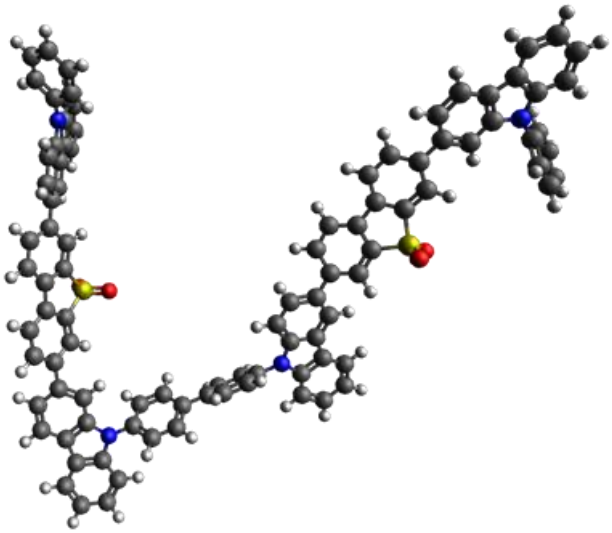
Figure S٦. Transition density matrix (TDM) heat maps of monomer compounds.

Table S1. Calculated dipole moments (μ), total dipole moment (μ_{tot}) in Debye, polarizability (α) in atomic unit (a.u.), total polarizability (α_{tot}) in A3, hyperpolarizability (β) in atomic unit (a.u.), and total hyperpolarizability (β_{tot}) in cm^5/esu for the monomeric compounds.

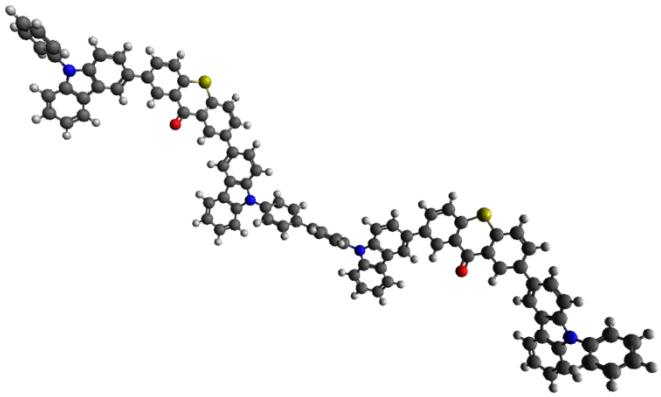
NLO parameters	DBTS-CzP	TXO-CzP	SpDBTS-CzP	m-CBPPO	DPA-2PY
μ_x	1.188	0.003	-0.835	-0.216	-1.083
μ_y	-1.44	0.769	-0.368	1.315	-1.272
μ_z	-1.404	0.436	-0.865	1.006	-0.331
α_{xx}	1115.62	980.845	1180.5	604.73	886.293
α_{yy}	626.883	682.379	772.452	431.571	738.89
α_{zz}	348.131	381.28	522.21	396.78	374.583
α_{xy}	29.199	5.711	18.995	-9.805	4.289
α_{xz}	9.458	8.167	-4.285	-1.222	-9.575
α_{yz}	17.947	37.549	-14.165	44.577	-12.169
β_{xxx}	4602.36	10.084	9588.51	987.226	-3103.99
β_{yyy}	-330.053	-396.264	-294.291	-81.684	643.953
β_{zzz}	97.351	45.023	-110.214	-121.864	99.68
β_{xyy}	-41.437	22.745	-794.393	-286.482	-719.125
β_{xxy}	3592.74	-1591.28	1027.84	41.688	-3120.35
β_{xxz}	480.549	-651.161	146.054	9.332	-195.702
β_{xzz}	13.813	-4.576	47.145	-195.729	-75.04
β_{yzz}	17.883	93.05	22.496	-66.486	68.359
β_{yyz}	67.057	376.58	131.398	-66.372	-157.633
μ	2.336297	0.884	1.258	1.67	1.703
α	103.266	100.988	122.26	70.786	98.778
β	4.89524E-29	1.64886E-29	7.6675E-29	4.71919E-30	3.96454E-29

Optimized structures of the dimer compounds with B3LYP/6-311++g(d,p) DFT method

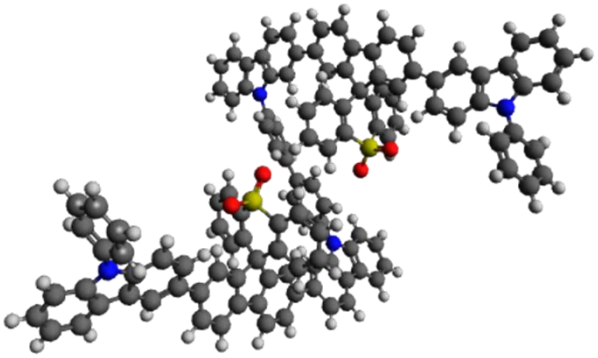
D-DBTS-CzP



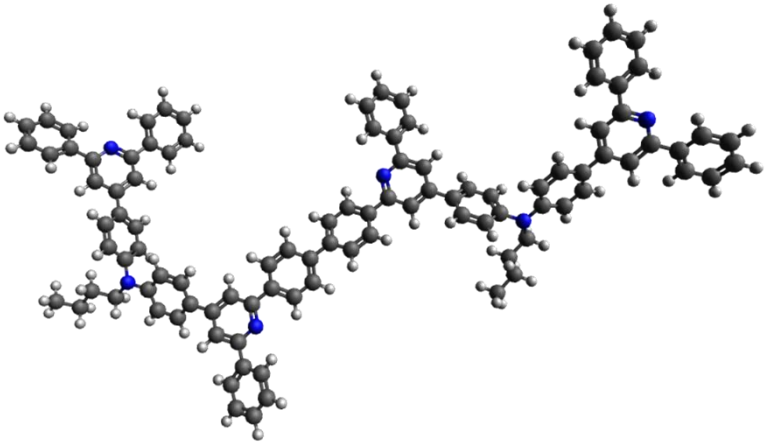
D-TXO-CzP



D-SpDBTS-CzP



D-DPA-2PY



D-m-CBPPO

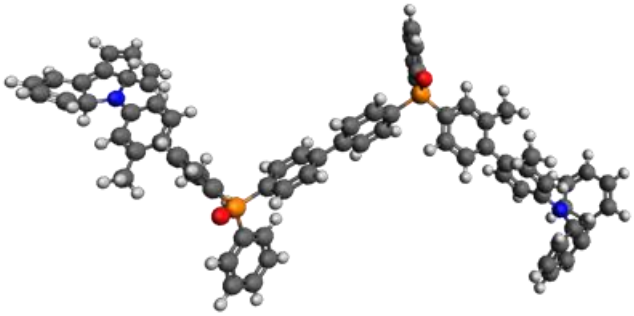


Figure S^{V}. In our research, we delved beyond single compounds and proceeded to analyze the dimer forms, which are essentially pairs of molecules interacting with each other. To do this, we used the DFT method to optimize the structures of these dimers, and their optimized configurations are illustrated in Figure 5. Our focus on dimers is crucial as it provides us with a deeper understanding of how these molecules interact with each other. This detailed exploration sheds light on complex phenomena such as π-π stacking and hydrogen bonding, which ultimately impact the overall properties of the compounds.

Frontier molecule orbital density distribution for dimer compounds

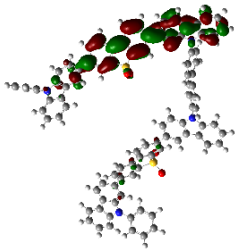
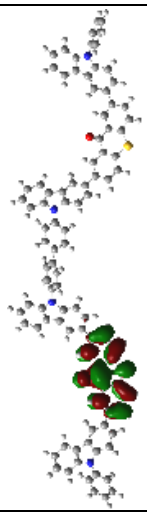
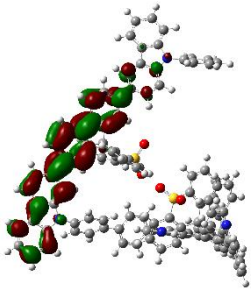
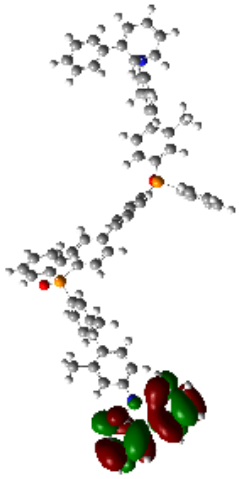
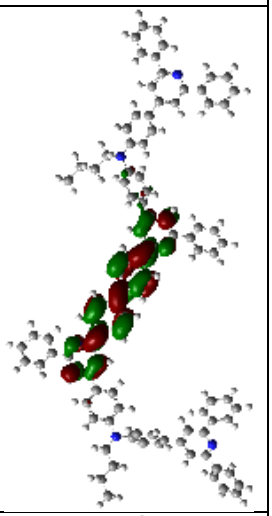
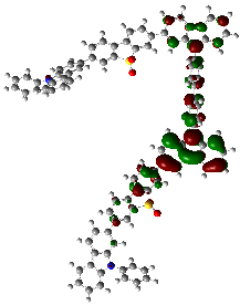
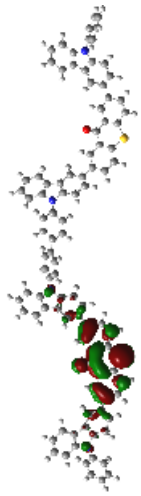
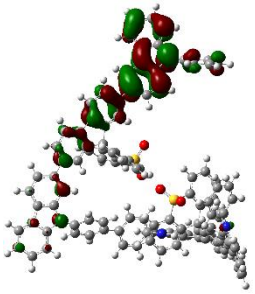
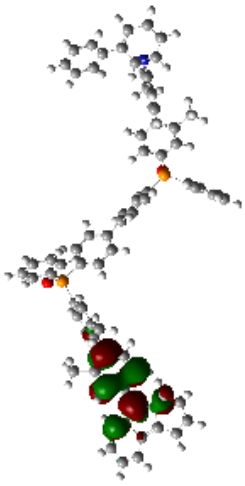
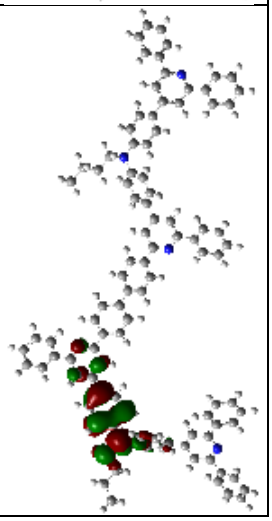
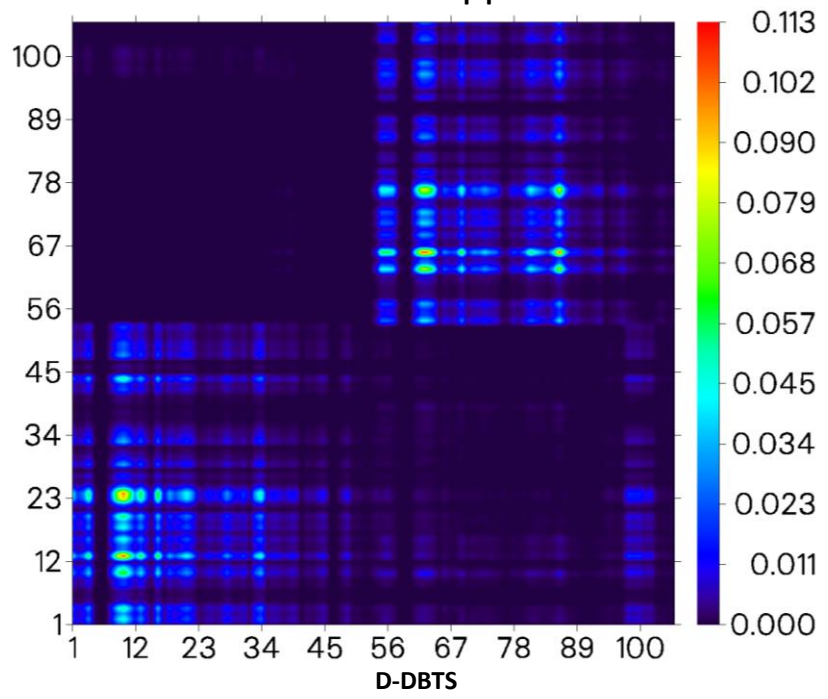
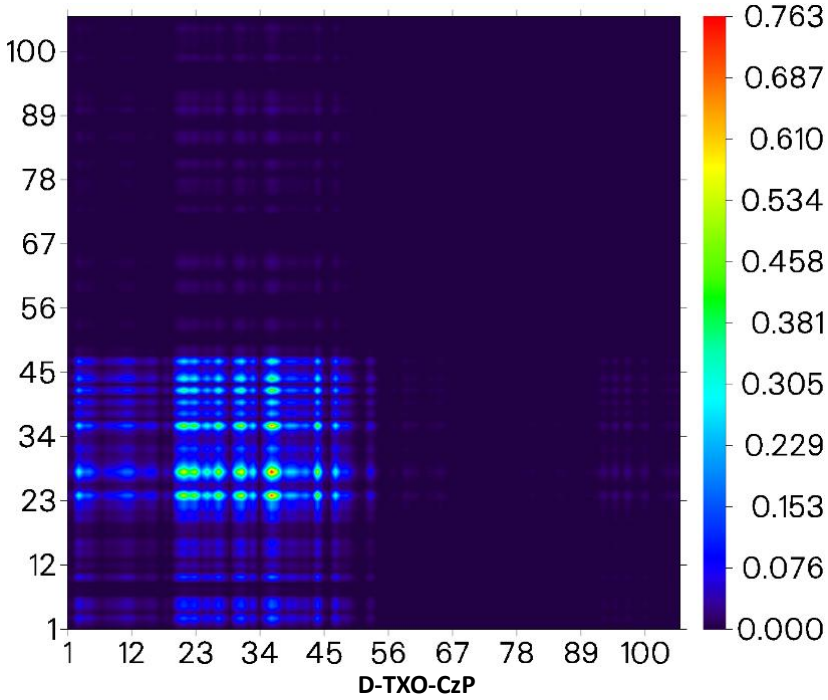
compound	D-DBTS-CzP	D-TXO-CzP	D-SpDBTS-CzP	D-m-CBPPO	D-DPA
LUMO (S1) eV					
HOMO (S0) eV					

Figure S^. In our analysis, we carried out calculations of the frontier orbitals for the dimers in order to assess and compare their electronic properties with those of the single compounds. Our findings are summarized in Table 2, which presents the HOMO and LUMO levels for each dimer. Additionally, the accompanying orbital density plots in Figure 6 visually illustrate how the electron clouds are distributed within the molecular structures. This detailed information is particularly crucial for gaining insights into the absorption properties of the dimers and understanding the potential movement of charge between the two molecular units.

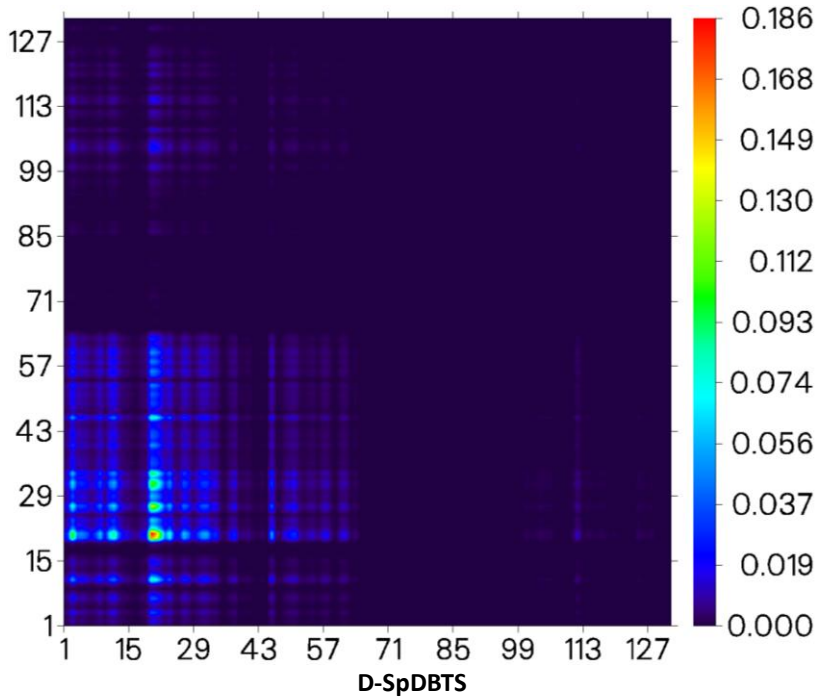
TDM heat map plot



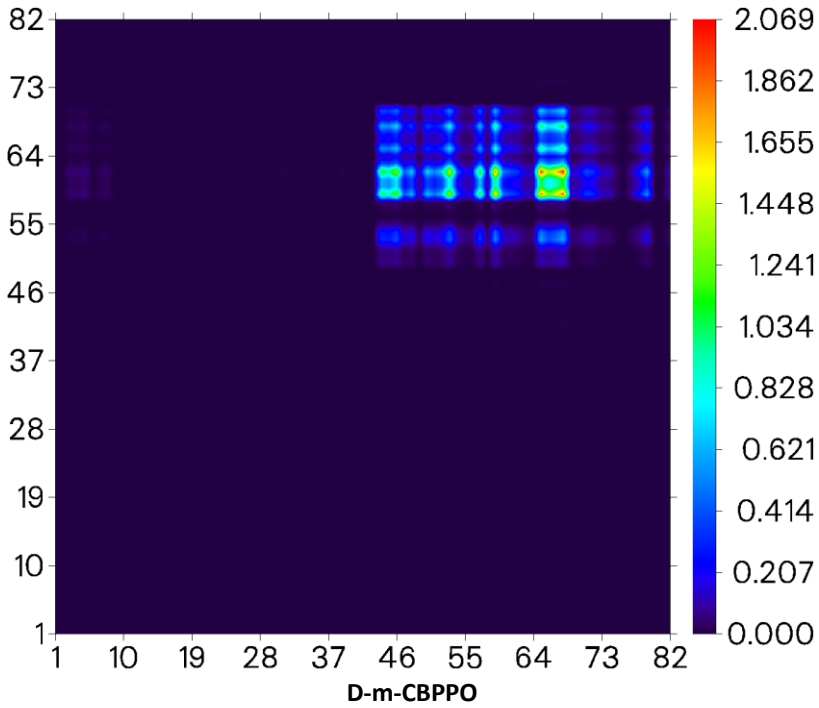
D-DBTS



D-TXO-CzP



D-SpDBTS



D-m-CBPPO

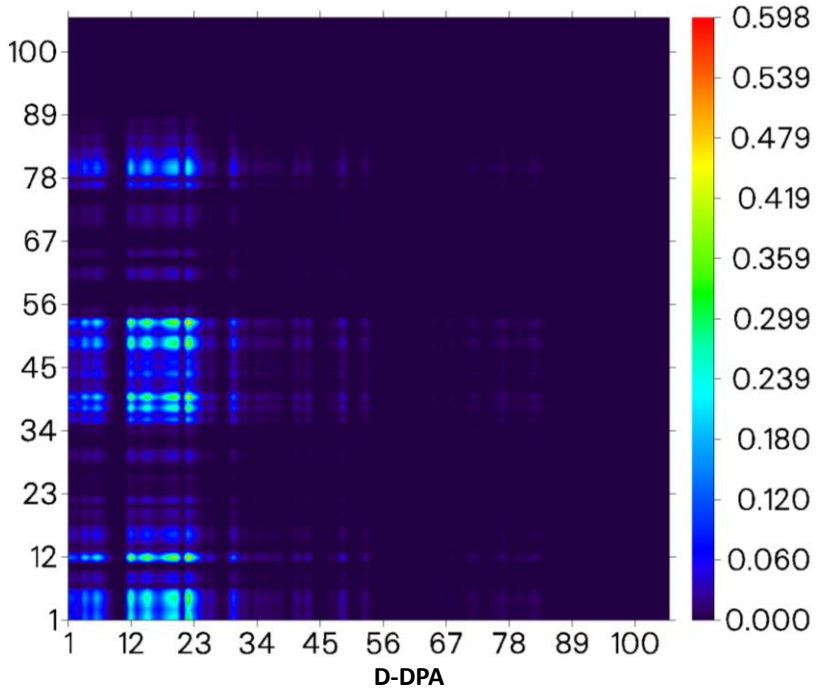


Figure S9. Transition density matrix heat maps for all dimer compounds.

Table S2. Calculated dipole moments (μ), total dipole moment (μ_{tot}) in Debye, polarizability (α) in atomic unit (a.u.), total polarizability (α_{tot}) in A3, hyperpolarizability (β) in atomic unit (a.u.), and total hyperpolarizability (β_{tot}) in cm^5/esu for the dimer compounds.

NLO parameters	D-DBTS-CzP	D-TXO-CzP	D-SpDBTS-CzP	D-m-CBPPO	D-DPA-2PY
μ_x	2.107	-0.043	-0.046	-0.762	-2.712
μ_y	2.696	-1.471	-0.478	0.015	1.025
μ_z	-0.956	0.768	0.05	4.491	1.107
α_{xx}	1691.85	1985.93	1678.04	1201.53	1833.03
α_{yy}	1720.99	1188.85	1705.85	1027.31	1556.19
α_{zz}	866.264	1085.6	1627.9	809.595	793.577
α_{xy}	-386.235	36.662	40.603	21.301	-18.946
α_{xz}	-57.984	-16.856	69.346	62.686	78.399
α_{yz}	-76.05	-219.062	79.907	-71.999	42.203
β_{xxx}	-772.244	390.485	-2523.22	-35.37	-7943.94
β_{yyy}	590.128	701.863	7463.01	567.138	855.278
β_{zzz}	-187.519	-1101.81	-1831.79	-340.007	-47.498
β_{xyy}	261.767	-259.082	2118.45	81.374	-1879.77
β_{xxy}	-1879.84	1412.13	1530.17	-129.544	459.709
β_{xxz}	1152.24	-1838.42	-2654.5	708.725	1678.91
β_{xzz}	-11.835	131.838	-1871.69	-78.318	-467.602
β_{yzz}	259.153	157.451	1149.53	41.032	36.621
β_{yyz}	2576.9	47.386	2360.88	-15.679	-56.116
μ	3.553	1.66	0.483445	4.556	3.104
α	211.365	210.441	247.556	150.083	206.608
β	3.21841E-29	3.1857E-29	9.1664E-29	5.14574E-30	9.07001E-29