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Second-order nonlinear optical properties of two chalcone derivatives: insights from sum-over-states†

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In the following study, a combined experimental and theoretical study of the nonlinear optical properties (NLO) of two chalcone derivatives, (*E*)-3-(2-methoxyphenyl)-1-(2-(phenylsulfonylamine)phenyl)prop-2-en-1-one (MPSP) and (*E*)-3-(3-nitrophenyl)-1-(2-(phenylsulfonylamine)phenyl)prop-2-en-1-one (NPSP) in DMSO is reported. Single crystal structures of the compounds, which differ only by the type and position of one substituent, were grown from slow evaporation technique, and the main structural differences are discussed. The two-photon absorption and first-order hyperpolarizability measurements were performed via the Z-scan technique and Hyper-Rayleigh Scattering experiment in DMSO. The theoretical calculations were performed using the Functional Density Theory (DFT) at the CAM-B3LYP/6-311++G(d,p) level, and the Sum-over-states (SOS) approach in both, static and dynamic cases. Besides the electron conjugation achieved by the aromatic rings, olefin, and carbonyl groups, both compounds have a nearly flat chalcone backbone, which is believed to contribute to the nonlinear optical properties. MPSP and NPSP have different positions, even though they have roughly the same conformation and form C-H…O interactions. For several studied frequencies, the HRS first hyperpolarizabilities values for MPSP are greater than for NPSP, indicating that in most cases the NLO properties of MPSP are better. The comparison among the theoretical and experimental results for the HRS first hyperpolarizability showed a good agreement. In addition, the two-dimensional second order nonlinear optics spectra obtained from the Sum-over-states model indicate good second-order NLO responses of the two chalcone derivatives under external fields. Our findings are important not only to show the potential nonlinear optical application of two new compounds but also to bring insight into how different chemical compositions might affect crystal structures and physico-chemical properties.

Table S1: Optimized coordinates in DMSO for NPSP

16	3.909774000	0.039066000	-0.767049000
8	0.270680000	-0.186566000	0.750096000
8	-8.050856000	-1.860787000	-0.069543000
8	3.323333000	0.047910000	-2.114747000
8	5.151885000	0.794348000	-0.565805000
8	-6.299794000	-2.921310000	0.633339000
7	2.787595000	0.562935000	0.397983000
1	2.032609000	-0.124257000	0.520866000
7	-6.852007000	-1.921697000	0.184459000
6	-6.029097000	-0.724594000	-0.063973000
6	-4.668860000	-0.779615000	0.215425000
1	-4.237461000	-1.690828000	0.606558000
6	-3.871124000	0.349724000	-0.013750000
6	-2.443120000	0.259445000	0.289972000
1	-2.102905000	-0.700213000	0.668663000
6	-1.519622000	1.228544000	0.153037000
1	-1.787504000	2.205463000	-0.222566000
6	-0.102039000	0.965556000	0.484766000
6	0.863630000	2.097975000	0.464380000
6	2.268041000	1.880410000	0.383343000
6	4.130033000	-1.657972000	-0.237810000
6	3.514461000	-2.676608000	-0.962271000
1	2.910226000	-2.442508000	-1.828938000
6	3.701330000	-3.994813000	-0.549586000
1	3.232958000	-4.800115000	-1.102304000
6	4.488765000	-4.273583000	0.566912000
1	4.630201000	-5.300490000	0.882932000
6	3.138162000	2.977005000	0.341826000
1	4.203046000	2.801121000	0.285482000
6	2.644234000	4.273596000	0.398997000
1	3.337257000	5.106559000	0.373191000
6	1.273120000	4.504996000	0.516629000
1	0.888759000	5.514790000	0.589159000
6	0.403461000	3.426148000	0.546614000
1	-0.655057000	3.617658000	0.656400000
6	-4.484679000	1.510123000	-0.524511000
1	-3.894357000	2.398162000	0.711944000
6	-5.846913000	1.541080000	-0.797098000
1	-6.298540000	2.443252000	-1.190014000
6	-6.640139000	0.418649000	-0.568997000
1	-7.700881000	0.425258000	-0.775099000
6	4.924476000	-1.917843000	0.879302000
1	5.398837000	-1.108222000	1.419119000
6	5.099452000	-3.239426000	1.279147000
1	5.713905000	-3.460901000	2.143336000

Table S2: Optimized coordinates in DMSO for MPSP

16	3.751086	-0.58614	-1.03097
8	-0.01209	-0.04501	-2.06711
8	-3.96139	0.899894	1.189164
8	4.944137	0.205816	-0.72449
8	3.79542	-1.58826	-2.09906
7	2.527341	0.468291	-1.51533
1	1.769144	-0.03671	-1.99066
6	0.613742	1.649003	-0.52058
6	3.212384	-1.38002	0.488947
6	2.017245	1.513317	-0.70479
6	-0.35503	0.679438	-1.11735
6	-1.70343	0.588061	-0.53731
1	-1.92793	1.139704	0.359103
6	-4.67449	0.05799	0.403424
6	-4.00796	-0.48403	-0.73163
6	-2.63491	-0.20718	-1.11451
1	-2.31684	-0.72878	-2.01416
6	0.149571	2.74995	0.220883
1	-0.91506	2.899124	0.339103
6	-6.00429	-0.28513	0.665553
1	-6.51436	0.123643	1.526294
6	3.67187	-0.89435	1.71243
1	4.369931	-0.06861	1.746134
6	2.327621	-2.45654	0.410407
1	1.992214	-2.82547	-0.55068
6	2.88861	2.442077	-0.12508
1	3.952817	2.332138	-0.28058
6	-4.73746	-1.36322	-1.55751
1	-4.23655	-1.78041	-2.42426
6	3.228313	-1.5046	2.884839
1	3.580665	-1.14135	3.842783
6	-6.05711	-1.70373	-1.29701
1	-6.58761	-2.38254	-1.95325
6	-6.68691	-1.15843	-0.17909
1	-7.71745	-1.40996	0.044356
6	2.342391	-2.57941	2.82388
1	2.002848	-3.05108	3.738594
6	1.894541	-3.0553	1.59009
1	1.212827	-3.89607	1.544545
6	1.019651	3.669706	0.788908
1	0.630122	4.511326	1.34839
6	2.39435	3.503493	0.623262
1	3.086827	4.21475	1.05842
6	-4.57865	1.474508	2.348008
1	-5.43943	2.087404	2.069682

1	-3.81508	2.101604	2.802711
1	-4.88474	0.698365	3.053658

Table S3: Electric dipole moment (input orientation) for MPSP

(Debye = 1.00E-17 statcoulomb cm, SI units = Cm)				
		(au)	(Debye)	(10**-30 SI)
	Tot	0.602260D+01	0.153079D+02	0.510617D+02
	x	0.577535D+01	0.146795D+02	0.489655D+02
	y	0.838442D+00	0.213111D+01	0.710860D+01
	z	0.148796D+01	0.378202D+01	0.126154D+02

Table S4: Electric dipole moment (input orientation) for NPSP

(Debye = 1.00E-17 statcoulomb cm, SI units = Cm)				
		(au)	(Debye)	(10**-30 SI)
	Tot	0.192336D+01	0.488869D+01	0.163069D+02
	x	-0.676360D+00	-0.171913D+01	-0.573442D+01
	y	-0.577218D+00	-0.146714D+01	-0.489386D+01
	z	0.170548D+01	0.433490D+01	0.144597D+02

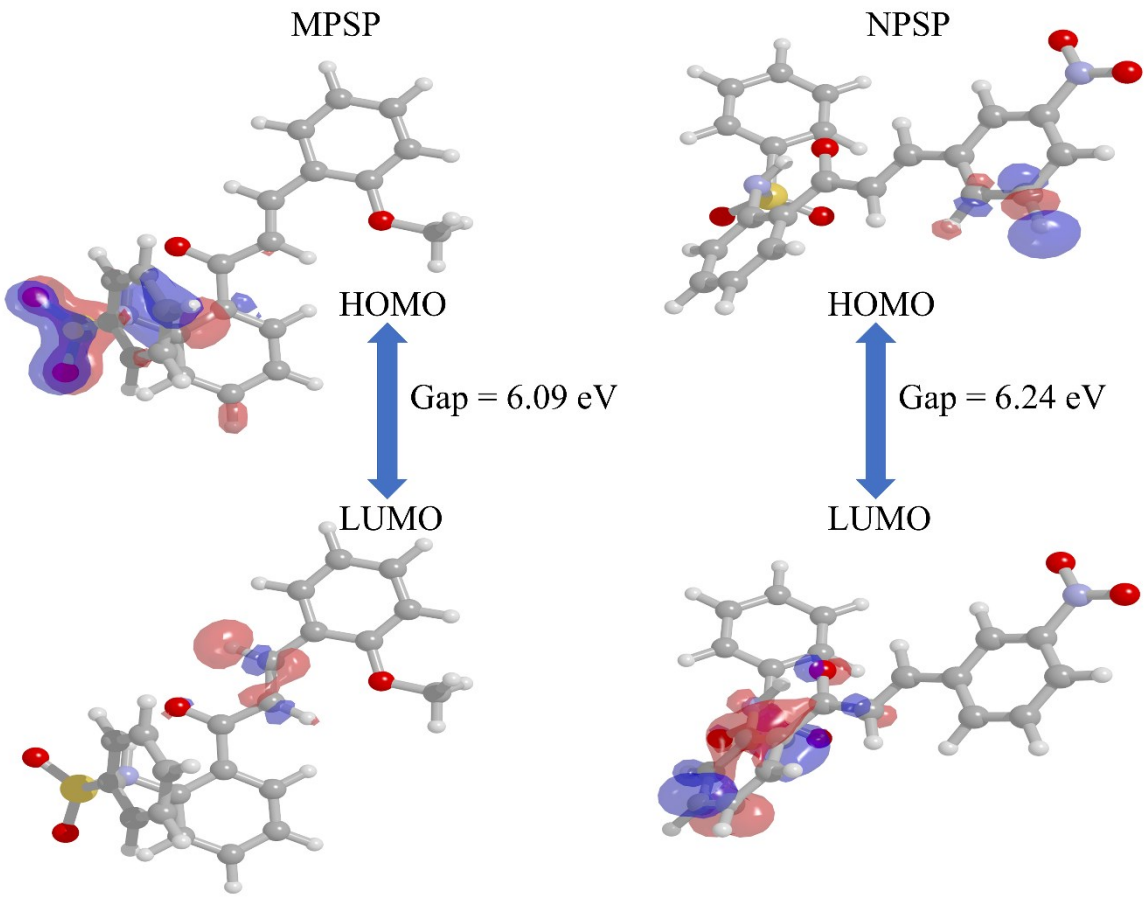

Figure S1: HOMO-LUMO of MPSP and NPSP structures