Supporting information for: Second-order Nonlinear Optical Properties of Stenhouse Photoswitches: Insights from Density Functional Theory

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Relative energies

Table S1: Relative Gibbs free energies (ΔG°, kcal/mol) between closed and open forms, calculated at the PCM:M06/6-311G(d) level in various solvents, using standard temperature (T = 298.15 K) and pressure (p = 1 atm) conditions. Positive values indicate that the open form is more stable.

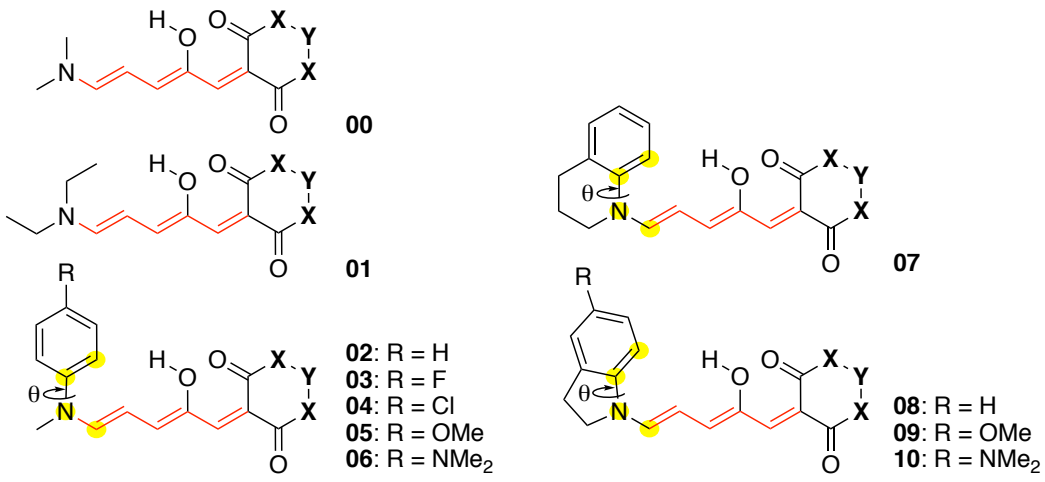
Compound	Toluene	Dichloromethane	Water
BA00	15.74	9.53	6.55
BA01	17.52	11.17	8.71
BA02	17.72	12.00	9.89
BA03	19.00	13.38	10.86
BA04	18.76	13.33	11.21
BA05	17.87	10.70	9.08
BA06	17.17	10.79	8.87
BA07	-5.20	-6.81	-7.20
BA08	-3.41	-3.55	-3.96
BA09	-2.28	-4.48	-3.36
BA10	-1.50	-0.80	-0.22
MA00	17.12	9.74	6.52
MA01	17.41	10.15	7.09
MA02	20.35	13.65	10.47
MA03	20.65	14.46	11.38
MA04	21.71	14.45	11.24
MA05	18.88	13.12	9.74
MA06	18.73	12.14	8.83
MA07	-3.30	-4.47	-4.60
MA08	-2.87	-3.18	-3.12
MA09	-0.85	-1.00	-0.71
MA10	1.39	1.15	1.71

Molecular geometries

The geometrical parameters characterizing the strength of electron conjugation in open form DASAs, namely the bond length alternation (BLA) along the conjugated path and the torsional angle within the acyclic- and cyclic-substituted N-methylaniline moieties, are defined in Scheme S1. For a conjugated chain containing N carbon atoms, the BLA is calculated as:

$$BLA = \frac{1}{N-2} \sum_{i=1}^{N-2} (d_{i+1,i+2} - d_{i,i+1}) \times (-1)^{i+1} \tag{1}$$

where $d_{i,j}$ is the interatomic distance between carbons i and j.



Scheme S1: Open form DASAs, with (in red) the conjugated segment considered for the calculation of the bond length alternation, and the torsional angle (θ, defined by the highlighted atoms) between the donor moiety and the conjugated chain.

Table S2: Bond Length Alternation (BLA, Å) along the conjugated path and torsional angle (θ, degrees) between the donor moiety and the conjugated chain, calculated at the PCM:M06/6-311G(d) level for open form DASAs in various solvents. See Scheme S1 for the definition of the geometrical parameters.

	Toluene		Dichloromethane		Water	
Comp.	BLA	θ	BLA	θ	BLA	θ
BA00	0.016	-	0.002	-	-0.005	-
BA01	0.014	-	0.000	-	-0.007	-
BA02	0.025	41.5	0.015	42.1	0.010	42.2
BA03	0.026	42.9	0.016	43.8	0.011	44.1
BA04	0.029	40.4	0.019	41.1	0.014	41.7
BA05	0.021	46.2	0.010	46.6	0.006	46.7
BA06	0.017	45.0	0.006	44.8	0.001	44.7
BA07	0.026	29.0	0.016	29.1	0.012	28.9
BA08	0.023	-0.2	0.013	0.0	0.008	0.0
BA09	0.019	0.9	0.007	1.1	0.002	1.1
BA10	0.012	1.2	-0.001	1.3	-0.007	1.3
MA00	0.017	-	0.001	-	-0.006	-
MA01	0.012	-	-0.003	-	-0.011	-
MA02	0.026	42.2	0.015	43.0	0.009	43.2
MA03	0.027	43.1	0.016	44.0	0.010	44.3
MA04	0.030	40.6	0.019	41.3	0.013	41.5
MA05	0.023	43.3	0.011	43.6	0.005	43.8
MA06	0.018	45.4	0.006	43.6	0.000	43.5
MA07	0.027	29.4	0.016	29.7	0.010	29.8
MA08	0.024	0.5	0.012	0.6	0.006	0.6
MA09	0.020	-0.8	0.007	-0.1	0.001	1.2
MA10	0.013	-1.2	-0.001	-0.5	-0.008	0.9

Ground state dipole moments

Table S3: Ground state dipole moment μ_{S_0} (D) calculated for open and closed DASAs at the PCM:M06-2X/6-311+G(d) level.

	Toluene		Dichloromethane		Water	
Comp.	Open	Closed	Open	Closed	Open	Closed
BA00	12.448	17.649	15.626	19.719	17.099	20.632
BA01	13.033	18.542	16.167	20.550	17.613	21.425
BA02	10.331	18.956	12.729	20.796	13.824	21.602
BA03	8.582	17.178	10.943	18.952	12.064	19.719
BA04	7.886	17.172	10.086	18.876	11.164	19.601
BA05	11.434	19.471	13.834	21.058	14.928	21.767
BA06	14.874	22.247	17.676	24.125	18.920	24.885
BA07	10.261	3.551	12.579	4.035	13.628	4.271
BA08	10.429	3.370	13.033	3.886	14.269	4.123
BA09	11.680	3.129	14.452	3.549	15.735	3.789
BA10	15.934	3.434	19.509	4.076	21.124	4.316
MA00	11.134	17.103	14.267	19.403	15.773	20.489
MA01	12.088	17.958	15.320	20.233	16.824	21.272
MA02	9.196	18.502	11.683	20.588	12.881	21.548
MA03	7.585	16.648	10.005	18.681	11.206	19.574
MA04	6.952	16.634	9.219	18.593	10.360	19.446
MA05	10.340	19.173	12.788	21.126	13.965	21.978
MA06	13.573	21.832	16.430	23.950	17.762	24.871
MA07	9.084	6.369	11.510	7.688	12.665	8.489
MA08	9.363	5.862	12.037	7.148	13.350	7.804
MA09	10.480	7.221	13.328	8.577	14.711	9.292
MA10	14.518	5.928	18.189	7.110	19.893	7.722

Electronic absorption properties

The variation of the total electron density from the ground (S_0) to the excited state (S_n) can be defined as:

$$\Delta\rho = \rho_{S_n} - \rho_{S_0} = \Delta\rho^+ + \Delta\rho^- \tag{2}$$

where $\Delta\rho^+$ and $\Delta\rho^-$ describe the increasing (> 0) and decreasing (< 0) areas of the electron density, respectively. The corresponding total charge displaced upon excitation is calculated as:

$$\Delta q = \int \Delta\rho^+(\mathbf{r})d\mathbf{r} = \int \Delta\rho^-(\mathbf{r})d\mathbf{r} \tag{3}$$

The charge transfer distance ΔR is evaluated as the distance separating the centroids of the $\Delta\rho^+$ and $\Delta\rho^-$ functions, while the $\overrightarrow{\Delta R}$ vector points from the negative to the positive center by convention. The photo-induced variation of the electric dipole moment is then defined as:

$$\overrightarrow{\Delta\mu} = \Delta q \cdot \overrightarrow{\Delta R} \tag{4}$$

Table S4: Transition energy (ΔE_{ge}, eV), transition wavelength (λ_{ge}, nm), and oscillator strength (f_{ge}) for excitations from the ground state towards the low-lying bright ($f \geq 0.1$) excited states of **closed** form DASAs, as well as photoinduced charge displacement (Δq, |e|), charge transfer distance (ΔR, Å), and variation of the permanent dipole moment ($\Delta\mu$, D) calculated at the PCM:M06-2X/6-311+G(d) level in **toluene**.

	state	ΔE_{ge}	λ_{ge}	f_{ge}	Δq	ΔR	$\Delta\mu$
BA00	5	5.289	234	0.108	0.738	1.629	5.774
	7	5.434	228	0.163	0.648	1.624	5.055
BA01	5	5.304	234	0.122	0.732	2.028	7.131
BA02	7	5.325	233	0.176	0.595	1.380	3.945
BA03	7	5.316	233	0.154	0.664	1.567	4.997
BA04	7	5.315	233	0.152	0.672	1.607	5.185
BA05	8	5.322	233	0.178	0.583	1.322	3.699
BA06	7	5.070	245	0.511	0.649	1.094	3.409
BA07	5	5.052	245	0.156	0.675	0.450	1.459
BA08	6	5.219	238	0.230	0.550	0.748	1.978
BA09	7	5.167	240	0.169	0.732	1.152	4.051
BA10	5	4.801	258	0.120	0.803	1.097	4.231
MA00	5	5.299	234	0.273	0.479	0.061	0.139
MA01	5	5.290	234	0.282	0.483	0.125	0.289
MA02	7	5.302	234	0.272	0.481	0.175	0.405
MA03	7	5.301	234	0.269	0.481	0.135	0.312
MA04	7	5.302	234	0.267	0.483	0.121	0.280
MA05	8	5.289	234	0.273	0.483	0.200	0.463
MA06	7	5.072	244	0.514	0.597	0.567	1.628
MA07	5	5.211	238	0.133	0.801	1.551	5.972
MA08	5	5.248	236	0.220	0.585	0.523	1.471
MA09	6	5.261	236	0.267	0.605	0.983	2.857
MA10	4	4.579	271	0.103	0.897	1.342	5.780
	6	5.019	247	0.264	0.670	1.002	3.225

Table S5: Transition energy (ΔE_{ge}, eV), transition wavelength (λ, nm), and oscillator strength (f_{ge}) for excitations from the ground state towards the low-lying bright ($f_{ge} \geq 0.1$) excited states of **open** form DASAs, as well as photoinduced charge displacement (Δq, |e|), charge transfer distance (ΔR, Å), and variation of the permanent dipole moment ($\Delta\mu$, D) calculated at the PCM:M06-2X/6-311+G(d) level in **toluene**.

	state	ΔE_{ge}	λ_{ge}	f_{ge}	Δq	ΔR	$\Delta\mu$
BA00	1	2.588	479	1.457	0.366	0.980	1.724
BA01	1	2.574	482	1.500	0.367	0.875	1.543
BA02	1	2.513	493	1.666	0.406	1.537	2.996
BA03	1	2.523	492	1.652	0.409	1.618	3.182
BA04	1	2.516	493	1.707	0.416	1.691	3.380
BA05	1	2.500	496	1.689	0.403	1.554	3.010
BA06	1	2.446	507	1.777	0.422	1.906	3.860
BA07	1	2.468	502	1.724	0.420	1.728	3.488
BA08	1	2.410	514	1.796	0.413	1.697	3.370
BA09	1	2.370	523	1.847	0.418	1.781	3.575
BA10	1	2.288	542	1.974	0.439	2.203	4.641
MA00	1	2.702	459	1.406	0.358	0.850	1.460
MA01	1	2.696	460	1.444	0.354	0.657	1.117
MA02	1	2.617	474	1.617	0.396	1.390	2.641
MA03	1	2.629	472	1.603	0.400	1.492	2.869
MA04	1	2.619	473	1.663	0.411	1.551	3.060
MA05	1	2.598	477	1.646	0.401	1.479	2.851
MA06	1	2.548	487	1.727	0.420	1.864	3.757
MA07	1	2.568	483	1.675	0.412	1.604	3.174
MA08	1	2.505	495	1.745	0.406	1.581	3.079
MA09	1	2.462	504	1.796	0.410	1.696	3.339
MA10	1	2.375	522	1.921	0.435	2.207	4.607

Table S6: Transition energy (ΔE_{ge}, eV), transition wavelength (λ_{ge}, nm), and oscillator strength (f_{ge}) for excitations from the ground state towards the low-lying bright ($f_{ge} \geq 0.1$) excited states of **closed** form DASAs, as well as photoinduced charge displacement (Δq, |e|), charge transfer distance (ΔR, Å), and variation of the permanent dipole moment ($\Delta \mu$, D) calculated at the PCM:M06-2X/6-311+G(d) level in **dichloromethane**.

	state	ΔE_{ge}	λ_{ge}	f_{ge}	Δq	ΔR	$\Delta \mu$
BA00	4	5.279	235	0.387	0.446	0.331	0.710
BA01	4	5.274	235	0.397	0.444	0.305	0.650
BA02	5	5.254	236	0.173	0.864	3.543	14.692
	6	5.301	234	0.229	0.719	3.120	10.770
BA03	6	5.286	235	0.381	0.443	0.226	0.481
BA04	6	5.286	235	0.380	0.443	0.217	0.462
BA05	6	5.279	235	0.360	0.456	0.350	0.766
BA06	5	5.032	246	0.495	0.616	0.910	2.693
	6	5.060	245	0.253	0.858	0.929	3.827
	8	5.270	235	0.376	0.447	0.315	0.676
BA07	5	5.018	247	0.239	0.652	0.474	1.484
	7	5.369	231	0.105	0.924	1.908	8.469
BA08	3	4.578	271	0.102	0.568	0.717	1.957
	5	5.148	241	0.136	0.636	0.473	1.444
	6	5.168	240	0.196	0.595	0.707	2.019
BA09	3	4.302	288	0.100	0.582	0.714	1.997
	7	5.186	239	0.256	0.700	2.224	7.476
BA10	2	4.090	303	0.104	0.597	0.450	1.292
	5	4.761	260	0.195	0.734	1.018	3.590
	6	4.939	251	0.250	0.816	2.588	10.143
MA00	3	5.173	240	0.407	0.485	0.575	1.338
MA01	3	5.171	240	0.414	0.488	0.594	1.393
MA02	4	5.174	240	0.398	0.486	0.519	1.212
MA03	4	5.173	240	0.378	0.489	0.382	0.898
MA04	5	5.178	239	0.372	0.502	0.483	1.165
MA05	4	5.171	240	0.393	0.490	0.604	1.421
MA06	5	5.041	246	0.702	0.524	2.227	5.602
	6	5.166	240	0.416	0.489	0.602	1.414
MA07	4	4.891	254	0.160	0.808	1.221	4.739
	5	5.196	239	0.185	0.821	2.142	8.451
MA08	3	4.728	262	0.109	0.527	0.840	2.125
	4	5.114	242	0.182	0.751	1.118	4.032
	5	5.219	238	0.180	0.730	2.080	7.291
MA09	3	4.405	281	0.125	0.536	0.308	0.795
	5	5.077	244	0.112	0.883	1.956	8.300
	6	5.203	238	0.288	0.645	1.146	3.547
MA10	4	4.575	271	0.198	0.796	0.297	1.136
	5	4.821	257	0.113	0.940	3.119	14.078
	6	4.987	249	0.233	0.754	1.542	5.580

Table S7: Transition energy (ΔE_{ge}, eV), transition wavelength (λ_{ge}, nm), and oscillator strength (f_{ge}) for excitations from the ground state towards the low-lying bright ($f_{ge} \geq 0.1$) excited states of **open** form DASAs, as well as photoinduced charge displacement (Δq, |e|), charge transfer distance (ΔR, Å), and variation of the permanent dipole moment ($\Delta \mu$, D) calculated at the PCM:M06-2X/6-311+G(d) level in **dichloromethane**.

	state	ΔE_{ge}	λ_{ge}	f_{ge}	Δq	ΔR	$\Delta \mu$
BA00	1	2.396	517	1.537	0.380	0.484	0.884
BA01	1	2.397	517	1.570	0.381	0.523	0.958
BA02	1	2.317	535	1.728	0.413	1.192	2.364
BA03	1	2.324	534	1.714	0.415	1.273	2.537
BA04	1	2.318	535	1.762	0.425	1.427	2.915
BA05	1	2.309	537	1.743	0.411	1.111	2.192
BA06	1	2.255	550	1.832	0.437	1.471	3.090
BA07	1	2.274	545	1.791	0.429	1.439	2.966
BA08	1	2.211	561	1.869	0.422	1.322	2.678
BA09	1	2.179	569	1.912	0.428	1.260	2.589
BA10	1	2.101	590	2.051	0.457	1.626	3.571
MA00	1	2.513	493	1.479	0.370	0.574	1.020
MA01	1	2.529	490	1.507	0.377	0.766	1.387
MA02	1	2.421	512	1.672	0.400	0.986	1.894
MA03	1	2.429	510	1.659	0.403	1.079	2.090
MA04	1	2.420	512	1.712	0.414	1.206	2.399
MA05	1	2.406	515	1.697	0.406	0.997	1.945
MA06	1	2.350	528	1.784	0.435	1.477	3.088
MA07	1	2.373	523	1.737	0.416	1.218	2.436
MA08	1	2.306	538	1.815	0.412	1.144	2.264
MA09	1	2.271	546	1.860	0.416	1.132	2.265
MA10	1	2.187	567	1.998	0.455	1.646	3.598

Table S8: Transition energy (ΔE_{ge}, eV), transition wavelength (λ_{ge}, nm), and oscillator strength (f_{ge}) for excitations from the ground state towards the low-lying bright ($f_{ge} \geq 0.1$) excited states of **closed** form DASAs, as well as photoinduced charge displacement (Δq, |e|), charge transfer distance (ΔR, Å), and variation of the permanent dipole moment ($\Delta \mu$, D) calculated at the PCM:M06-2X/6-311+G(d) level in **water**.

	state	ΔE_{ge}	λ_{ge}	f_{ge}	Δq	ΔR	$\Delta \mu$
BA00	4	5.241	237	0.424	0.475	0.508	1.160
BA01	4	5.233	237	0.457	0.461	0.450	0.996
BA02	4	5.238	237	0.449	0.456	0.359	0.786
BA03	4	5.215	238	0.223	0.800	3.249	12.484
	5	5.260	236	0.234	0.701	2.391	8.052
BA04	5	5.235	237	0.227	0.754	2.804	10.160
	6	5.265	235	0.199	0.786	3.630	13.701
BA05	5	5.235	237	0.431	0.455	0.384	0.838
BA06	5	5.006	248	0.766	0.520	2.021	5.045
	8	5.233	237	0.467	0.458	0.435	0.958
BA07	5	5.001	248	0.274	0.650	0.591	1.846
	7	5.365	231	0.132	0.911	1.750	7.657
BA08	3	4.563	272	0.119	0.572	0.758	2.082
	5	5.130	242	0.338	0.556	1.106	2.951
BA09	3	4.290	289	0.104	0.598	0.886	2.546
	7	5.201	238	0.306	0.684	2.211	7.268
BA10	2	4.073	304	0.126	0.599	0.439	1.264
	5	4.740	262	0.227	0.718	1.009	3.482
	6	4.950	250	0.280	0.800	2.447	9.400
MA00	3	5.110	243	0.475	0.490	0.645	1.517
MA01	3	5.107	243	0.482	0.493	0.662	1.567
MA02	3	5.114	242	0.473	0.492	0.661	1.562
MA03	3	5.114	242	0.472	0.494	0.635	1.505
MA04	3	5.114	242	0.471	0.491	0.635	1.497
MA05	3	5.111	243	0.479	0.493	0.668	1.582
MA06	5	5.008	248	0.767	0.520	2.137	5.332
	6	5.106	243	0.485	0.493	0.682	1.613
MA07	3	4.697	264	0.118	0.546	1.168	3.062
	4	4.889	254	0.210	0.773	0.990	3.672
	5	5.193	239	0.198	0.835	2.261	9.063
MA08	3	4.708	263	0.130	0.534	0.892	2.286
	4	5.104	243	0.300	0.635	0.492	1.499
	5	5.227	237	0.112	0.844	2.381	9.657
MA09	3	4.383	283	0.145	0.543	0.355	0.924
	5	5.086	244	0.161	0.846	2.421	9.838
	6	5.174	240	0.260	0.706	1.304	4.421
MA10	3	4.234	293	0.107	0.588	0.706	1.993
	4	4.561	272	0.234	0.778	0.151	0.564
	5	4.847	256	0.165	0.865	3.054	12.684
	6	4.976	249	0.179	0.851	2.039	8.328

Table S9: Transition energy (ΔE_{ge}, eV), transition wavelength (λ_{ge}, nm), and oscillator strength (f_{ge}) for excitations from the ground state towards the low-lying bright ($f_{ge} \geq 0.1$) excited states of **open** form DASAs, as well as photoinduced charge displacement (Δq, |e|), charge transfer distance (ΔR, Å), and variation of the permanent dipole moment ($\Delta\mu$, D) calculated at the PCM:M06-2X/6-311+G(d) level in **water**.

	state	ΔE_{ge}	λ_{ge}	f_{ge}	Δq	ΔR	$\Delta\mu$
BA00	1	2.335	531	1.556	0.401	0.804	1.548
BA01	1	2.342	529	1.584	0.405	0.922	1.794
BA02	1	2.244	553	1.743	0.416	0.935	1.867
BA03	1	2.249	551	1.729	0.417	0.991	1.982
BA04	1	2.244	553	1.773	0.426	1.174	2.403
BA05	1	2.239	554	1.754	0.415	0.782	1.557
BA06	1	2.187	567	1.843	0.446	1.126	2.410
BA07	1	2.201	563	1.806	0.432	1.202	2.493
BA08	1	2.139	580	1.886	0.425	1.019	2.080
BA09	1	2.112	587	1.927	0.433	0.876	1.823
BA10	1	2.039	608	2.072	0.472	1.201	2.726
MA00	1	2.457	505	1.495	0.396	1.020	1.939
MA01	1	2.483	499	1.519	0.411	1.268	2.505
MA02	1	2.351	527	1.683	0.402	0.703	1.356
MA03	1	2.356	526	1.671	0.404	0.772	1.498
MA04	1	2.346	529	1.720	0.414	0.921	1.832
MA05	1	2.337	531	1.706	0.410	0.663	1.305
MA06	1	2.283	543	1.795	0.446	1.129	2.416
MA07	1	2.301	539	1.751	0.418	0.937	1.881
MA08	1	2.236	555	1.831	0.415	0.812	1.618
MA09	1	2.207	562	1.874	0.423	0.719	1.460
MA10	1	2.128	583	2.019	0.472	1.233	2.794

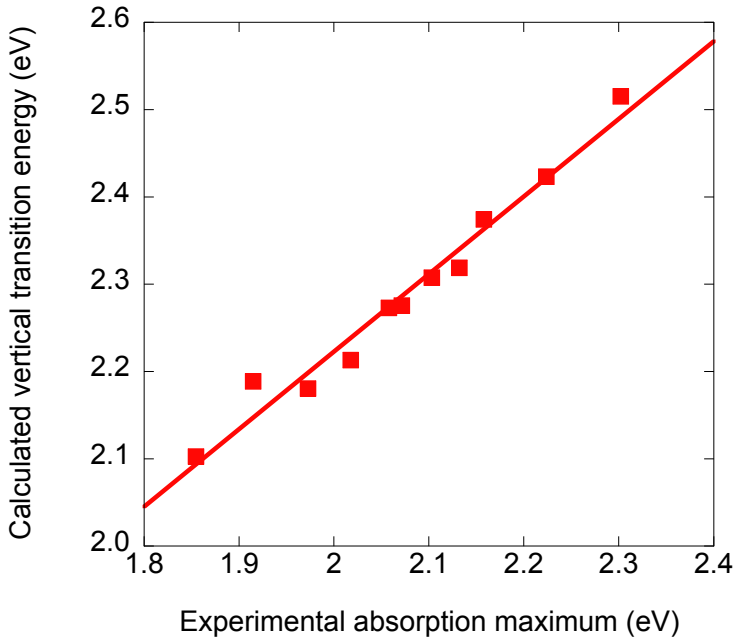


Figure S1: Vertical transition energies of open form DASAs calculated at the PCM:M06-2X/6-311+G(d) level in dichloromethane plotted against the experimental absorption maxima. The line is a linear fit (correlation coefficient $R^2 = 0.97$).

Second-order nonlinear optical properties

Static second-order NLO responses

Table S10: Static β_{HRS} and β_J values (a.u.), as well as ρ and DR, calculated for closed and open form DASAs at the M06-2X/6-311+G(d) level in **toluene**.

	Closed form					Open form					Contrast
Comp.	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	O/C
BA00	310	2.211	358	844	2.360	3098	4.059	5397	5727	1.061	9.99
BA01	298	2.113	324	830	2.560	2971	3.789	5032	5798	1.152	9.97
BA02	403	3.048	611	915	1.497	6158	4.558	11188	10299	0.921	15.27
BA03	347	2.275	414	931	2.249	6669	4.822	12339	10570	0.857	19.20
BA04	366	2.328	448	970	2.168	7233	4.755	13325	11622	0.872	19.75
BA05	338	1.845	288	1003	3.480	6805	5.081	12792	10221	0.799	20.12
BA06	489	2.349	603	1288	2.137	9479	5.420	18143	13244	0.730	19.40
BA07	260	2.935	384	603	1.570	7908	4.715	14528	12810	0.882	30.45
BA08	224	2.591	302	560	1.851	8956	4.677	16410	14620	0.891	39.99
BA09	190	2.072	201	535	2.658	11061	5.022	20720	16817	0.812	58.13
BA10	218	2.431	278	563	2.028	16906	5.141	31887	25074	0.786	77.69
MA00	215	2.211	248	585	2.360	2788	4.197	4920	5015	1.019	12.97
MA01	198	1.986	195	567	2.902	2286	3.772	3863	4475	1.159	11.56
MA02	295	3.220	462	646	1.400	5336	4.503	9655	9023	0.935	18.07
MA03	243	2.173	274	666	2.432	5805	4.784	10714	9271	0.865	23.92
MA04	245	2.083	261	687	2.630	6330	4.704	11621	10278	0.884	25.83
MA05	235	1.729	166	716	4.304	6272	5.072	11784	9439	0.801	26.74
MA06	436	2.686	606	1068	1.762	8427	5.391	16106	11846	0.736	19.32
MA07	263	3.950	454	497	1.096	6817	4.657	12474	11175	0.896	25.90
MA08	219	3.647	365	440	1.206	7807	4.633	14262	12860	0.902	35.59
MA09	97	3.779	164	189	1.156	9794	4.992	18313	14986	0.818	101.31
MA10	181	4.585	329	301	0.914	15118	5.111	28467	22561	0.793	83.57

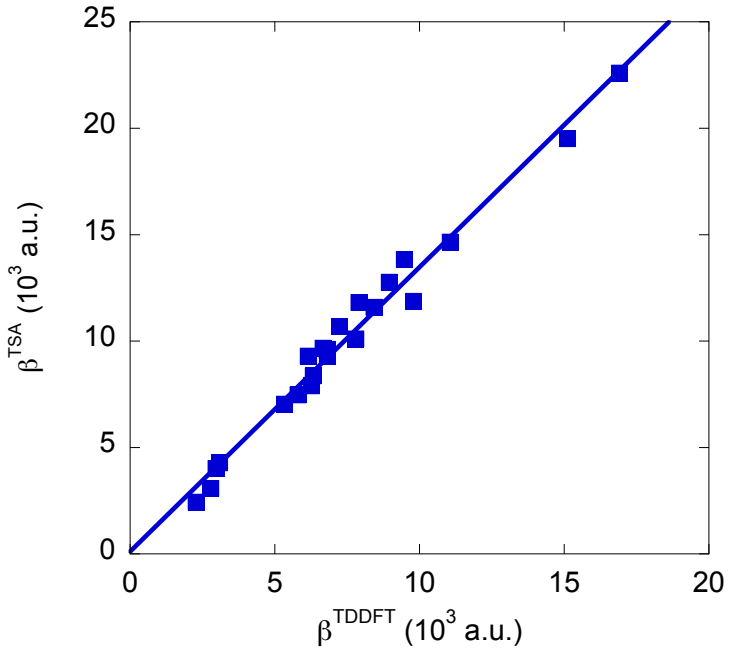


Figure S2: Static β_{HRS} values of open form DASAs evaluated in toluene using the two-state approximation (TSA), plotted against the values calculated using TDDFT. The line is a linear fit (correlation coefficient $R^2 = 0.98$; fit equation: $\beta_{HRS}^{TSA} = 1.336\beta_{HRS}^{TDDFT} + 0.122$).

Table S11: Static β_{HRS} and β_J values (a.u.), as well as ρ and DR, calculated for closed and open form DASAs at the M06-2X/6-311+G(d) level in **dichloromethane**.

	Closed form					Open form					Contrast
Comp.	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	O/C
BA00	350	1.673	218	1084	4.973	3391	2.417	4303	8805	2.046	9.69
BA01	343	1.619	179	1077	6.021	3779	2.559	5049	9510	1.883	11.02
BA02	398	2.080	423	1116	2.638	6660	4.082	11628	12257	1.054	16.73
BA03	387	1.726	273	1182	4.332	7186	4.452	12953	12278	0.948	18.58
BA04	400	1.759	300	1211	4.038	13274	3.498	21671	27464	1.267	33.21
BA05	437	1.841	371	1297	3.500	6596	4.800	12188	10501	0.862	15.10
BA06	712	2.723	1000	1730	1.730	10205	5.676	19769	13473	0.681	14.33
BA07	367	3.025	554	838	1.512	9059	4.442	16315	15510	0.951	24.65
BA08	315	2.515	414	799	1.930	10152	4.297	18070	17897	0.990	32.28
BA09	238	1.957	229	686	2.997	11631	4.914	21645	18086	0.836	48.95
BA10	299	2.902	440	700	1.593	19347	5.253	36713	28021	0.763	64.62
MA00	259	1.584	114	820	7.185	2824	2.421	3590	7326	2.041	10.92
MA01	248	1.513	43	802	18.573	3345	2.738	4715	8098	1.717	13.48
MA02	286	1.939	271	829	3.062	5299	3.930	9112	10054	1.103	18.53
MA03	284	1.611	143	893	6.242	5791	4.368	10369	10063	0.971	20.42
MA04	319	1.723	224	975	4.360	6737	4.392	12086	11652	0.964	21.14
MA05	368	2.111	400	1025	2.565	5859	4.898	10893	9141	0.839	15.91
MA06	688	3.209	1074	1510	1.406	9280	5.664	17968	12284	0.684	13.49
MA07	395	4.324	704	692	0.983	7296	4.358	13052	12704	0.973	18.48
MA08	308	3.784	521	602	1.154	8284	4.200	14622	14891	1.018	26.90
MA09	133	3.113	204	298	1.459	9845	4.911	18319	15317	0.836	73.96
MA10	244	3.969	421	459	1.090	17210	5.242	32639	24983	0.765	70.56

Table S12: Static β_{HRS} and β_J values (a.u.), as well as ρ and DR, calculated for closed and open form DASAs at the M06-2X/6-311+G(d) level in **water**.

	Closed form					Open form					Contrast
Comp.	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	O/C
BA00	380	1.563	146	1212	8.295	5777	3.079	8804	13021	1.479	15.19
BA01	378	1.552	133	1209	9.099	6400	3.237	10039	13963	1.391	16.92
BA02	410	1.794	326	1231	3.780	6210	3.500	10141	12846	1.267	15.15
BA03	422	1.657	251	1312	5.222	6542	3.900	11215	12488	1.114	15.51
BA04	434	1.668	267	1348	5.052	7783	4.175	13708	14059	1.026	17.92
BA05	503	1.920	467	1466	3.137	5545	4.139	9733	10088	1.036	11.02
BA06	825	2.839	1194	1955	1.638	9163	5.872	17902	11566	0.646	11.11
BA07	426	3.060	647	964	1.490	8700	4.098	15213	15960	1.049	20.43
BA08	364	2.519	480	925	1.926	9260	3.772	15652	18131	1.158	25.42
BA09	260	1.923	243	757	3.122	9966	4.631	18204	16425	0.902	38.30
BA10	338	3.046	511	766	1.499	17971	5.353	34281	25475	0.743	53.23
MA00	299	1.540	92	960	10.464	4821	3.063	7323	10903	1.489	16.11
MA01	295	1.546	97	943	9.684	5771	3.404	9295	12170	1.309	19.59
MA02	307	1.620	161	963	5.993	4718	3.206	7360	10359	1.408	15.38
MA03	338	1.676	212	1045	4.925	4990	3.669	8331	9976	1.198	14.77
MA04	364	1.848	312	1079	3.463	6136	3.724	10313	12132	1.176	16.87
MA05	454	2.299	548	1212	2.213	4705	4.266	8353	8346	0.999	10.35
MA06	817	3.319	1298	1752	1.350	8289	5.886	16204	10427	0.643	10.15
MA07	465	4.547	844	779	0.923	6612	3.903	11337	12613	1.112	14.23
MA08	361	3.915	621	688	1.108	7328	3.588	12108	14890	1.230	20.28
MA09	161	3.008	241	368	1.523	8069	4.621	14727	13323	0.905	50.22
MA10	283	3.741	477	558	1.170	16013	5.354	30548	22691	0.743	56.49

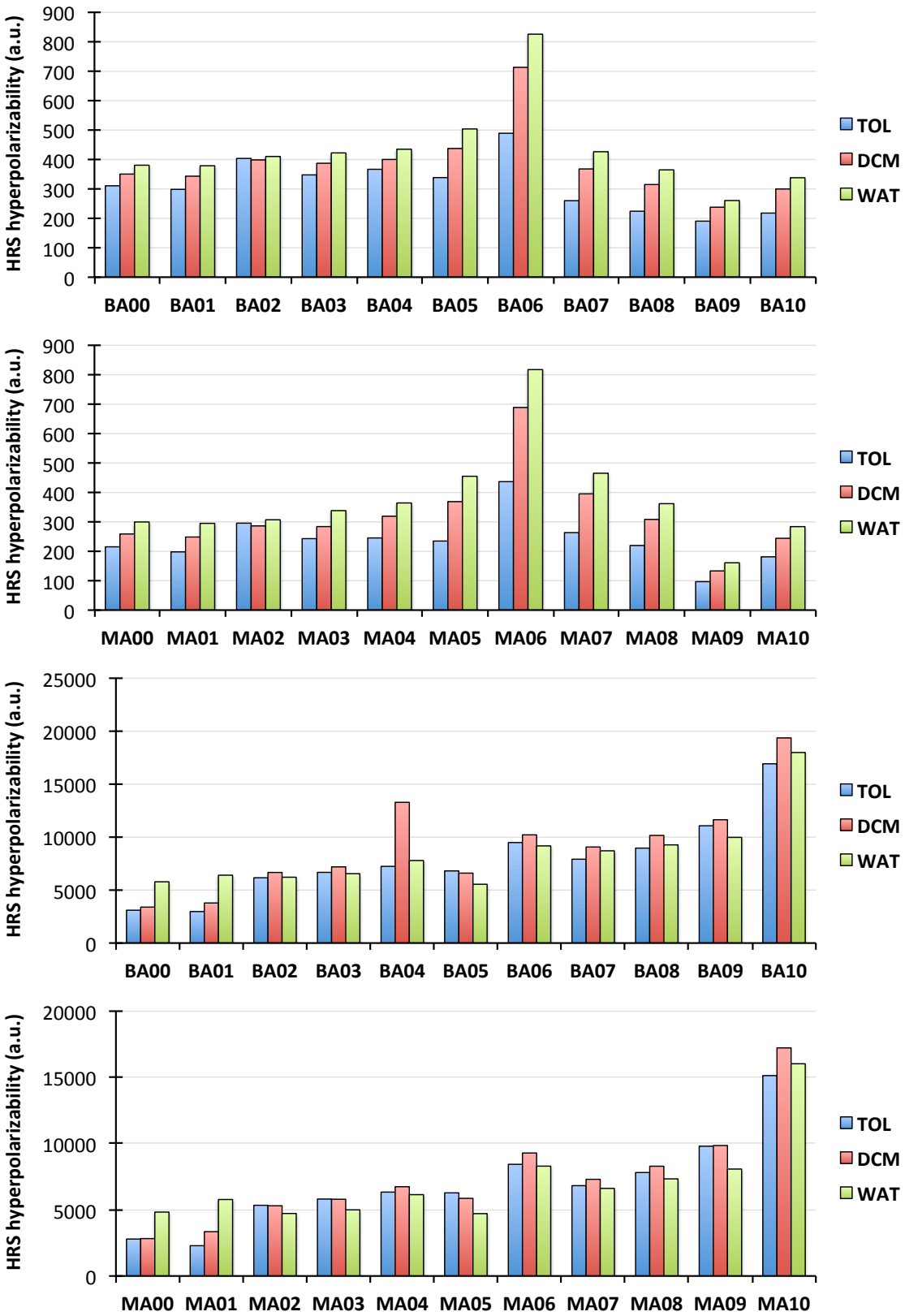


Figure S3: Static β_{HRS} values (a.u.) calculated for closed (top) and open form (bottom) DASAs at the PCM:M06-2X/6-311+G(d) level in toluene (TOL), dichloromethane (DCM) and water (WAT).

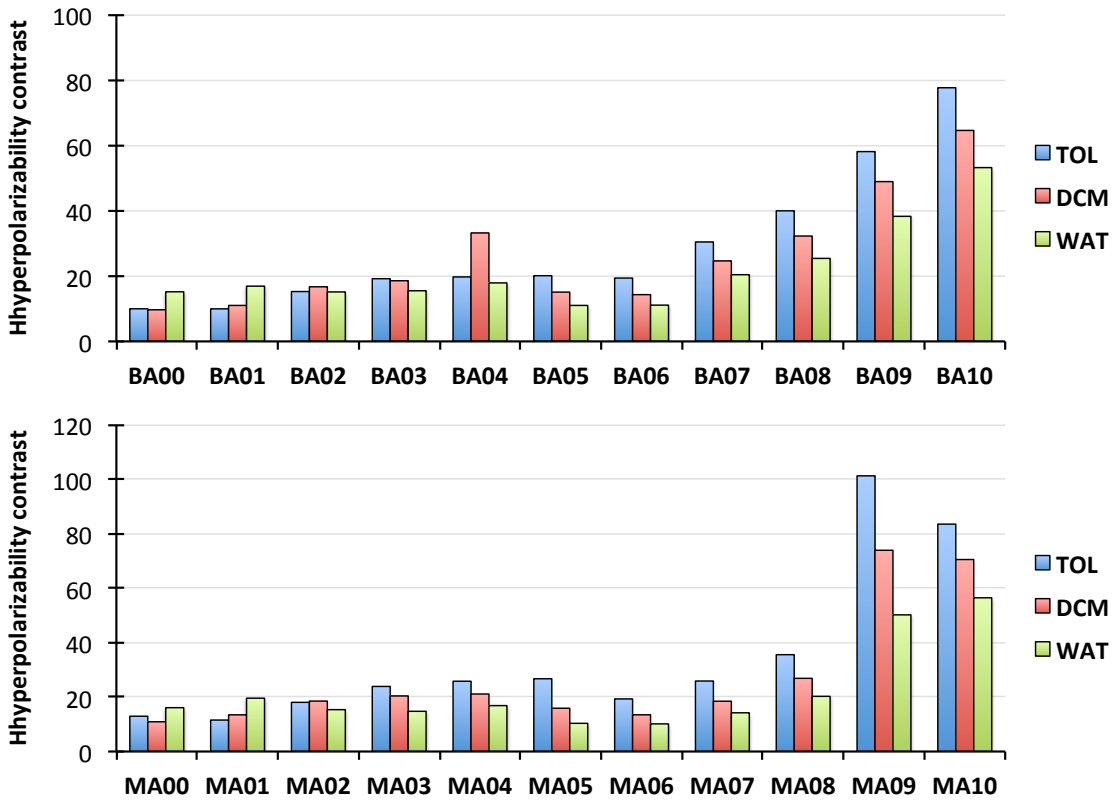


Figure S4: Static β_{HRS} contrasts calculated at the PCM:M06-2X/6-311+G(d) level in toluene (TOL), dichloromethane (DCM) and water (WAT).

Dynamic Second-order NLO responses

Table S13: Dynamic (λ = 1907 nm) β_{HRS} and β_J values (a.u.), as well as ρ and DR, calculated for closed and open form DASAs at the M06-2X/6-311+G(d) level in **toluene**.

	Closed form					Open form					Contrast
Comp.	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	O/C
BA00	321	2.247	377	866	2.297	4336	4.323	7735	7605	0.983	13.51
BA01	308	2.139	340	851	2.504	4153	4.103	7266	7612	1.048	13.50
BA02	433	3.195	674	953	1.413	9201	4.688	16874	14988	0.888	21.25
BA03	367	2.361	455	965	2.120	9914	4.868	18399	15563	0.846	27.02
BA04	386	2.401	487	1007	2.066	10824	4.821	20027	17158	0.857	28.02
BA05	348	1.853	300	1030	3.436	10250	5.048	19231	15501	0.806	29.46
BA06	508	2.372	632	1332	2.106	14863	5.269	28229	21454	0.760	29.27
BA07	278	3.146	429	618	1.441	12115	4.803	22389	19274	0.861	43.59
BA08	237	2.766	336	570	1.695	13944	4.776	25723	22306	0.867	58.87
BA09	197	2.046	205	558	2.725	17490	5.000	32721	26716	0.816	88.62
BA10	229	2.418	290	594	2.045	28117	5.078	52844	42253	0.800	122.99
MA00	222	2.281	265	593	2.240	3662	4.347	6545	6390	0.976	16.52
MA01	205	2.058	215	578	2.694	2959	3.960	5104	5580	1.093	14.43
MA02	323	3.462	524	672	1.283	7497	4.616	13678	12393	0.906	23.24
MA03	256	2.290	308	685	2.227	8130	4.824	15046	12879	0.856	31.71
MA04	259	2.203	297	706	2.375	8943	4.766	16486	14335	0.870	34.50
MA05	237	1.710	161	726	4.500	8935	5.040	16756	13535	0.808	37.75
MA06	453	2.728	637	1099	1.726	12491	5.267	23721	18034	0.760	27.58
MA07	284	4.208	502	510	1.016	9845	4.744	18121	15854	0.875	34.65
MA08	236	3.857	403	455	1.128	11458	4.725	21066	18523	0.879	48.50
MA09	98	3.462	159	204	1.283	14633	4.979	27341	22449	0.821	149.22
MA10	188	4.559	341	314	0.920	23837	5.066	44768	35915	0.802	127.09

Table S14: Dynamic (λ = 1907 nm) β_{HRS} and β_J values (a.u.), as well as ρ and DR, calculated for closed and open form DASAs at the M06-2X/6-311+G(d) level in **dichloromethane**.

	Closed form					Open form					Contrast
Comp.	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	O/C
BA00	265	1.777	205	801	3.899	2396	2.555	3198	6036	1.888	9.03
BA01	259	1.723	181	792	4.363	2701	2.683	3750	6619	1.765	10.44
BA02	321	2.376	400	840	2.100	5671	4.320	10113	9951	0.984	17.68
BA03	296	1.821	244	882	3.612	6261	4.659	11458	10259	0.895	21.18
BA04	307	1.861	267	907	3.397	7293	4.692	13378	11871	0.887	23.77
BA05	323	1.859	281	956	3.407	6203	5.035	11628	9405	0.809	19.18
BA06	557	2.826	804	1325	1.648	11366	5.435	21772	15827	0.727	20.39
BA07	271	3.092	415	610	1.471	8143	4.639	14882	13396	0.900	30.01
BA08	227	2.571	305	571	1.871	8937	4.523	16195	15052	0.929	39.30
BA09	193	2.085	206	542	2.625	11275	5.024	21125	17136	0.811	58.31
BA10	245	2.836	354	580	1.640	21079	5.162	39804	31123	0.782	86.13
MA00	178	1.639	100	558	5.563	2009	2.586	2708	5027	1.856	11.26
MA01	171	1.559	64	544	8.559	2468	2.961	3672	5701	1.553	14.46
MA02	219	2.304	264	583	2.205	4317	4.128	7570	7873	1.040	19.73
MA03	198	1.618	103	621	6.046	4852	4.556	8815	8120	0.921	24.56
MA04	201	1.611	102	632	6.230	5742	4.574	10445	9572	0.916	28.58
MA05	259	2.116	282	719	2.553	5327	5.074	10010	8013	0.800	20.59
MA06	537	3.333	855	1149	1.343	9939	5.428	19032	13862	0.728	18.51
MA07	302	4.438	544	518	0.952	6293	4.540	11419	10564	0.925	20.82
MA08	241	4.081	421	444	1.054	6986	4.408	12549	12043	0.960	28.94
MA09	96	3.306	153	207	1.356	9154	5.015	17141	13940	0.813	95.04
MA10	182	4.321	325	320	0.984	17940	5.157	33866	26515	0.783	98.36

Table S15: Dynamic (λ = 1907 nm) β_{HRS} and β_J values (a.u.), as well as ρ and DR, calculated for closed and open form DASAs at the M06-2X/6-311+G(d) level in **water**.

	Closed form					Open form					Contrast
Comp.	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	β_{HRS}	DR	$\beta_{J=1}$	$\beta_{J=3}$	ρ	O/C
BA00	241	1.666	147	748	5.075	3096	3.206	4830	6798	1.408	12.84
BA01	237	1.649	138	739	5.358	3535	3.372	5667	7504	1.324	14.90
BA02	281	2.136	310	777	2.509	3871	3.835	6589	7484	1.136	13.79
BA03	270	1.739	195	821	4.214	4255	4.315	7585	7474	0.985	15.79
BA04	278	1.755	207	844	4.067	5137	4.434	9246	8808	0.953	18.47
BA05	313	1.959	302	903	2.992	4122	4.910	7671	6415	0.836	13.17
BA06	557	2.997	835	1277	1.529	9268	5.521	17827	12664	0.710	16.64
BA07	258	3.028	390	588	1.510	5880	4.436	10584	10079	0.952	22.77
BA08	215	2.507	283	548	1.940	6037	4.170	10627	10916	1.027	28.04
BA09	186	2.125	204	517	2.532	7761	5.026	14542	11791	0.811	41.62
BA10	240	2.907	353	561	1.589	16608	5.218	31458	24233	0.770	69.18
MA00	163	1.525	40	526	13.129	2674	3.280	4224	5784	1.369	16.38
MA01	158	1.510	25	512	20.889	3362	3.650	5599	6745	1.205	21.23
MA02	186	1.928	174	541	3.104	2813	3.465	4570	5858	1.282	15.12
MA03	187	1.644	107	585	5.459	3121	4.060	5438	5770	1.061	16.66
MA04	194	1.704	131	597	4.566	3894	4.222	6886	6968	1.012	20.04
MA05	265	2.379	331	693	2.096	3422	4.979	6394	5249	0.821	12.92
MA06	547	3.509	894	1128	1.263	8098	5.503	15563	11109	0.714	14.82
MA07	298	4.553	541	498	0.922	4292	4.232	7597	7665	1.009	14.42
MA08	237	4.220	419	424	1.012	4555	3.937	7839	8630	1.101	19.23
MA09	97	3.415	156	203	1.304	6061	5.016	11349	9226	0.813	62.79
MA10	175	4.259	311	311	1.001	14103	5.213	26705	20601	0.771	80.51

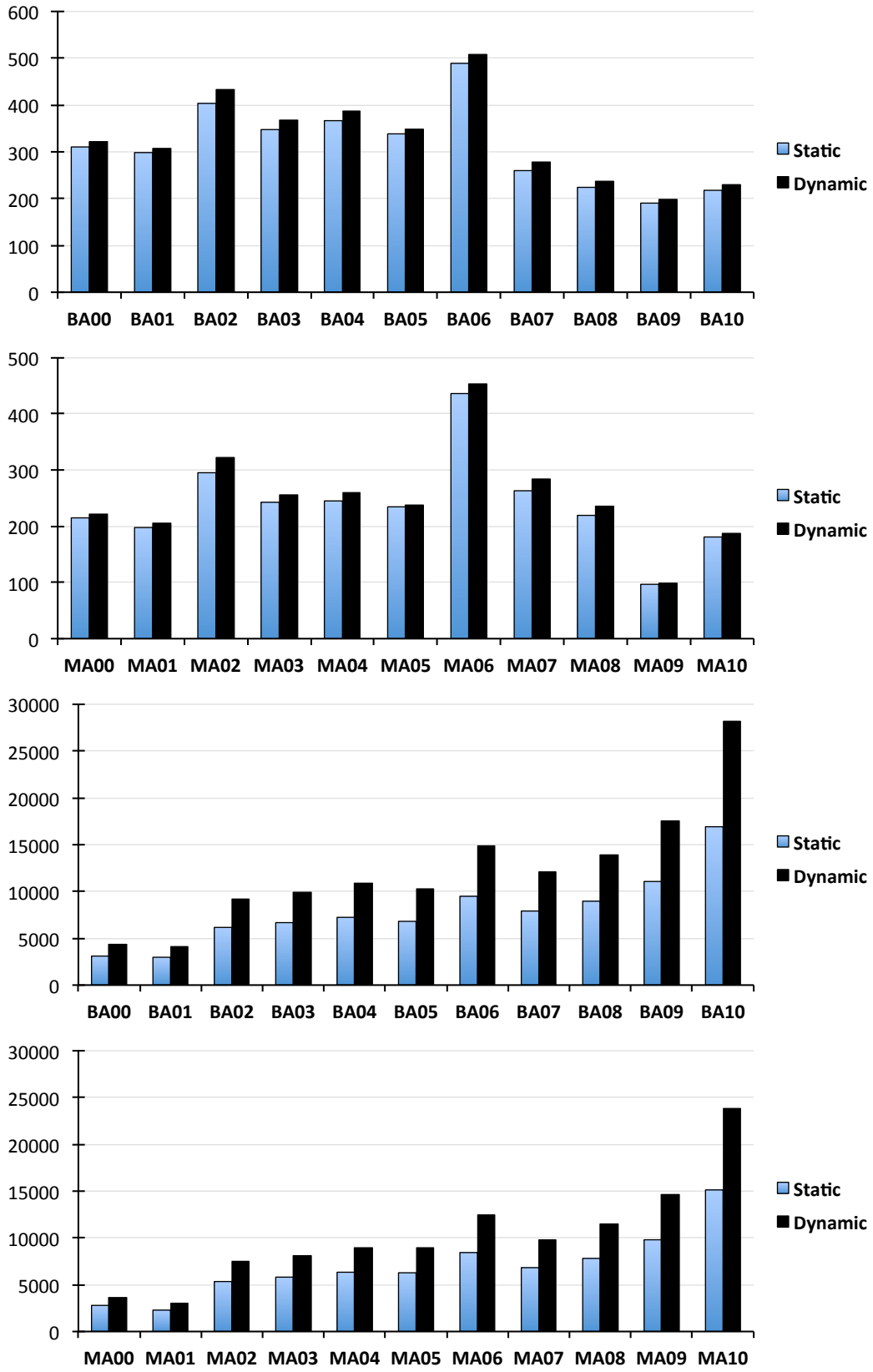


Figure S5: Static and dynamic β_{HRS} values (a.u.) calculated for closed (top) and open form (bottom) DASAs at the PCM:M06-2X/6-311+G(d) level in toluene.

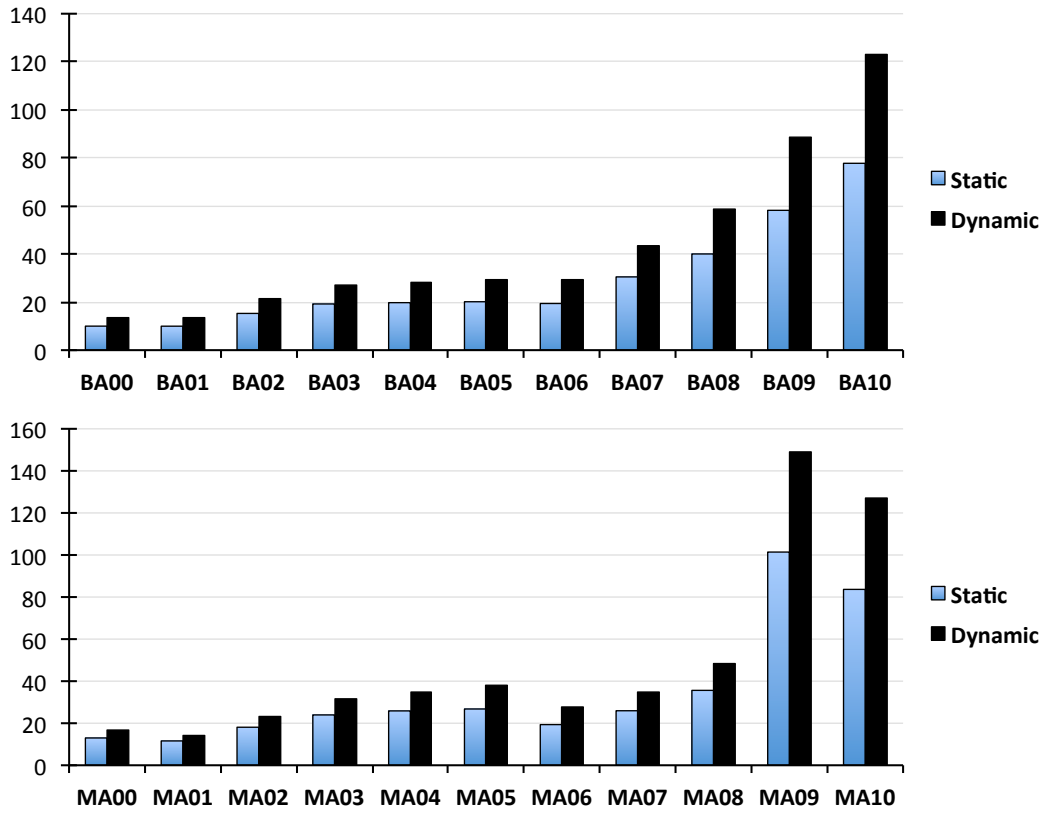


Figure S6: Static and dynamic β_{HRS} contrasts calculated at the PCM:M06-2X/6-311+G(d) level in toluene.

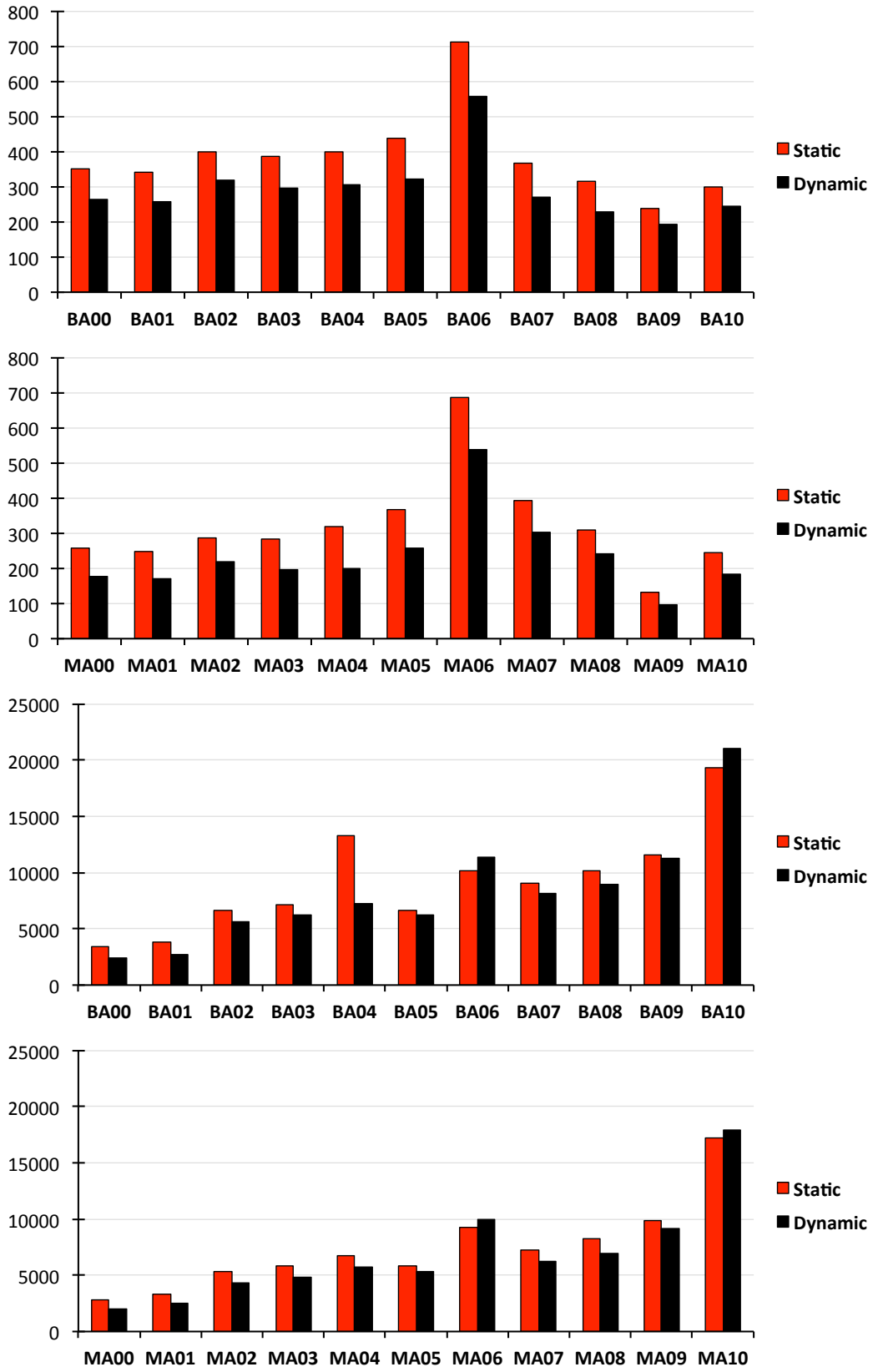


Figure S7: Static and dynamic β_{HRS} values (a.u.) calculated for closed (top) and open form (bottom) DASAs at the PCM:M06-2X/6-311+G(d) level in dichloromethane.

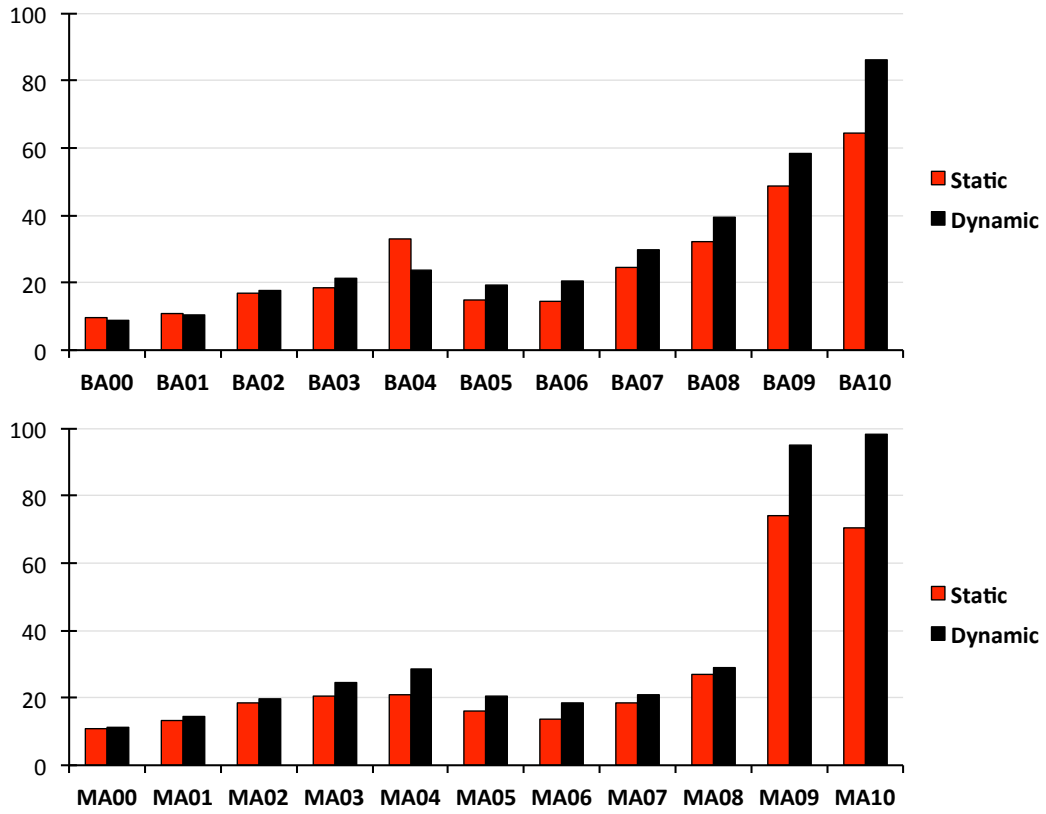


Figure S8: Static and dynamic β_{HRS} contrasts calculated at the PCM:M06-2X/6-311+G(d) level in dichloromethane.

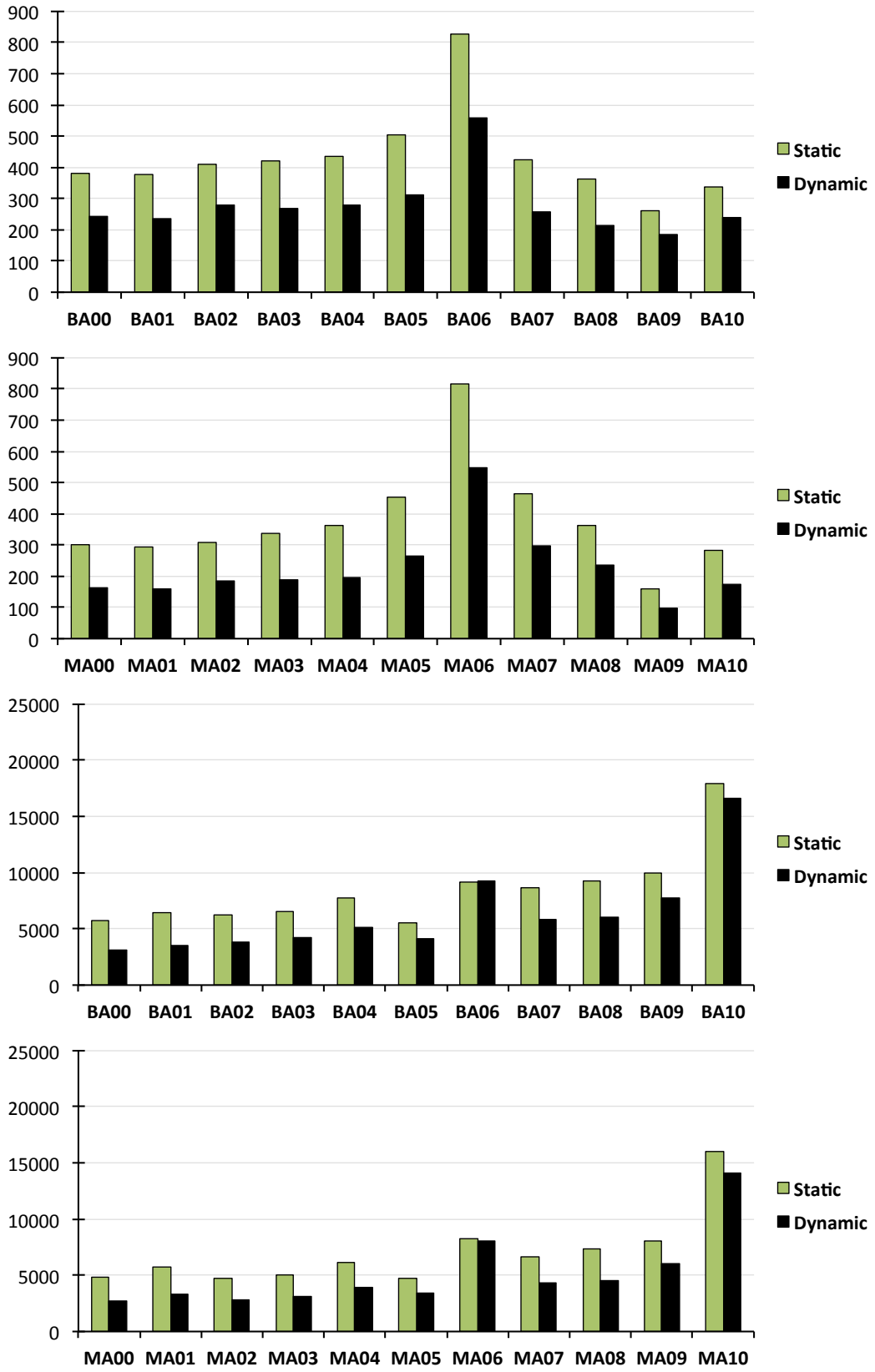


Figure S9: Static and dynamic β_{HRS} values (a.u.) calculated for closed (top) and open form (bottom) DASAs at the PCM:M06-2X/6-311+G(d) level in water.

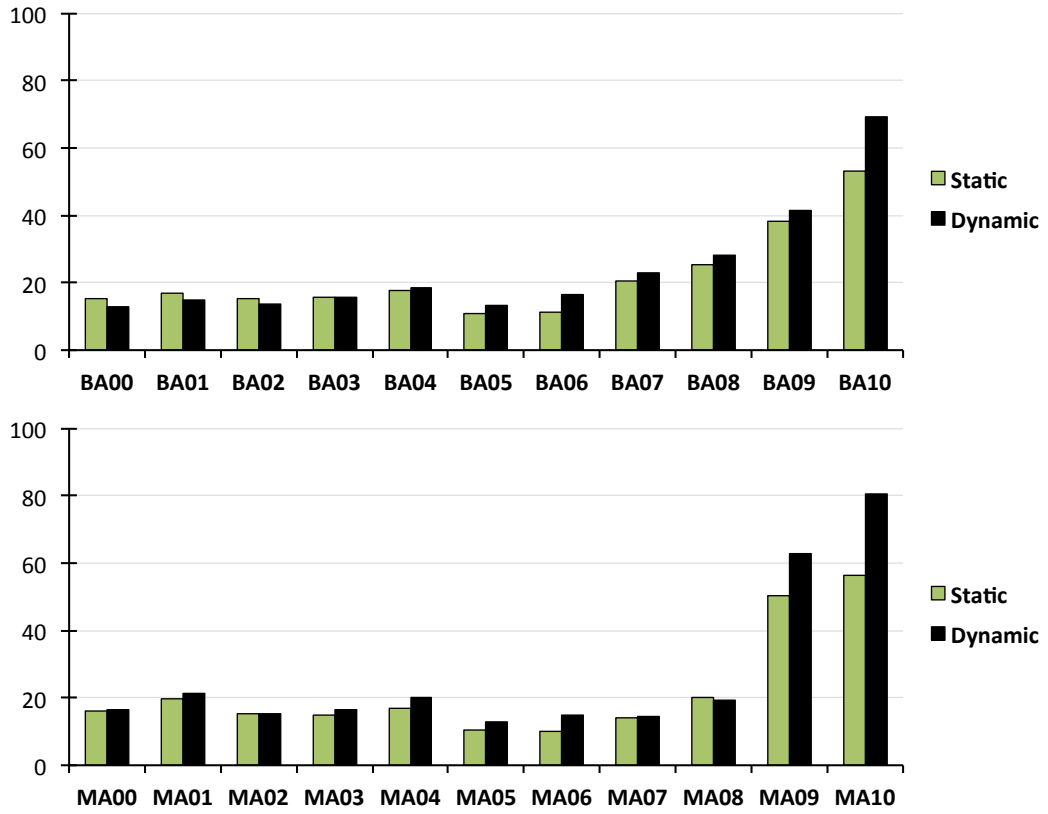


Figure S10: Static and dynamic β_{HRS} contrasts calculated at the PCM:M06-2X/6-311+G(d) level in water.

Unit sphere representation of the second-order NLO responses

The unit sphere representation (USR) is based on the computation of an effective SHG dipole defined as:

$$\overrightarrow{\mu}_{eff} = \beta : \overrightarrow{F}^2(\theta, \phi) \tag{5}$$

where β_{eff} is the first hyperpolarizability tensor and $\overrightarrow{F}(\theta, \phi)$ is a unit vector of the polarization of the incident electric field with polarization defined for convenience in spherical coordinates (θ, ϕ). By sampling all possible incident polarizations defined by (θ, ϕ), a unit sphere is mapped out. Then, at each point (θ, ϕ) on the unit sphere surface, the corresponding $\overrightarrow{\mu}_{eff}$ arrow is plotted. Therefore, the (θ, ϕ) position on the sphere surface corresponds to the polarization of $\overrightarrow{F}^2(\theta, \phi)$, whereas the $\overrightarrow{\mu}_{eff}$ arrow at (θ, ϕ) on the unit sphere provides information about the polarization and magnitude of the generated second harmonic at the particular incident field $\overrightarrow{F}^2(\theta, \phi)$. Unit sphere representations reported in the main manuscript have been generated using the DrawMol software (DrawMol, V. Liégeois, UNamur, www.unamur.be/drawmol) with the following parameters:

- *for the closed forms*:

  Unit sphere radius = 5, multiplying factor for the β vector = 0.03, multiplying factor for the USR = 0.015.

- *for the open forms:*

  MA05: unit sphere radius = 7, multiplying factor for the β vector = 0.001, multiplying factor for the USR = 0.00035;

  MA010: unit sphere radius = 7, multiplying factor for the β vector = 0.0006, multiplying factor for the USR = 0.00035.

The USR is intrinsically linked to the anisotropy factor ρ, which measures the relative magnitude of the octupolar and dipolar contributions of the first hyperpolarizability. The evolution of the USR with ρ is illustrated in Figure S11 for a set of representative compounds.

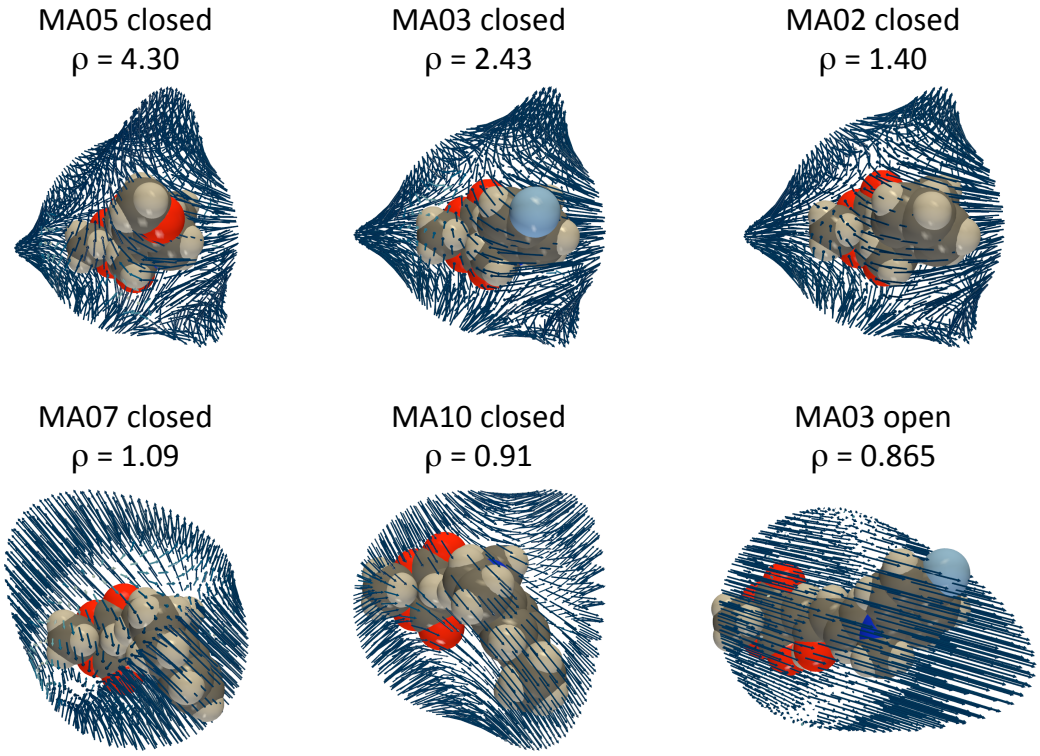


Figure S11: Evolution of the shape of the hyperpolarizability tensor, represented using the USR, with the anisotropy factor ρ.

Effect of the DFT exchange-correlation functional (XCF)

Effect of the XCF used in the calculations of the NLO properties

Table S16: Static β_{HRS} values (a.u.) and β_{HRS} contrasts calculated at the PCM:TDDFT level (in toluene) using different DFT exchange-correlation functionals with the 6-311+G(d) level basis set. Molecular structures are optimized at the PCM:M06/6-311G(d) level.

	M06-2X			ωB97X-D			LC-BLYP		
Comp.	closed	open	Contrast	closed	open	Contrast	closed	open	Contrast
BA00	310	3098	9.99	305	3141	10.28	264	4522	17.11
BA01	298	2971	9.97	291	3035	10.42	258	4236	16.44
BA02	403	6158	15.28	378	5954	15.75	293	8401	28.66
BA03	347	6669	19.22	328	6410	19.53	276	8860	32.06
BA04	366	7233	19.76	339	6909	20.39	282	9488	33.59
BA05	338	6805	20.13	332	6355	19.12	315	8379	26.63
BA06	489	9479	19.38	473	7972	16.85	492	8928	18.15
BA07	260	7908	30.41	263	7632	29.01	266	10162	38.15
BA08	224	8956	39.98	223	8743	39.15	233	11374	48.77
BA09	190	11061	58.21	189	10474	55.38	157	12331	78.74
BA10	218	16906	77.55	214	14721	68.64	162	14349	88.54

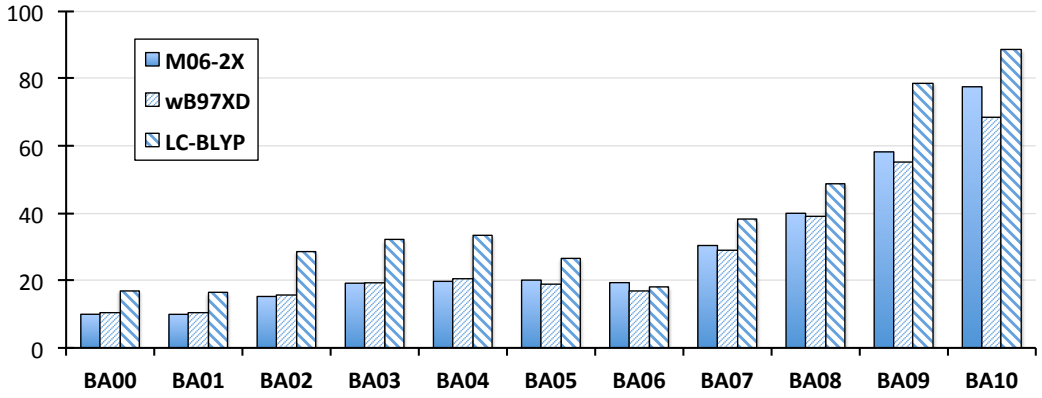


Figure S12: Static β_{HRS} contrasts calculated at the PCM:TDDFT level (in toluene) using different DFT exchange-correlation functionals with the 6-311+G(d) level basis set. Molecular structures are optimized at the PCM:M06/6-311G(d) level.

Effect of the XCF used in the geometry optimizations

Table S17: Static β_{HRS} values (a.u.) and β_{HRS} contrasts calculated at the PCM:M06-2X/6-311+G(d) level (in toluene), using molecular geometries optimized at the PCM:M06/6-311G(d) and PCM:M06-2X/6-311G(d) levels.

	M06 geometry			M06-2X geometry		
Comp.	closed	open	Contrast	closed	open	Contrast
BA00	310	3098	9.99	313	3205	10.26
BA01	298	2971	9.97	301	3124	10.36
BA02	403	6158	15.28	399	6828	17.11
BA03	347	6669	19.22	357	7349	20.59
BA04	366	7233	19.76	365	8128	22.26
BA05	338	6805	20.13	347	7605	21.94
BA06	489	9479	19.38	500	9647	19.30
BA07	260	7908	30.41	251	8633	34.45
BA08	224	8956	39.98	223	9860	44.20
BA09	190	11061	58.21	194	11804	61.00
BA10	218	16906	77.55	206	16342	79.49

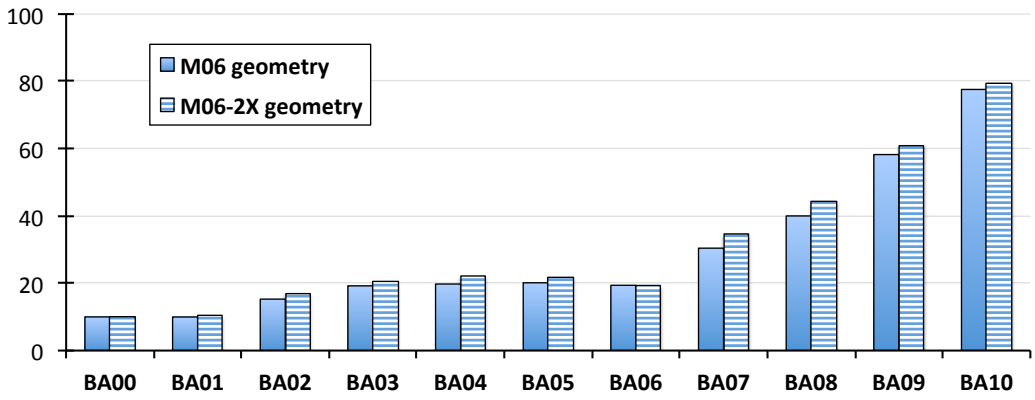


Figure S13: Static β_{HRS} contrasts calculated at the PCM:M06-2X/6-311+G(d) level (in toluene), using molecular geometries optimized at the PCM:M06/6-311G(d) and PCM:M06-2X/6-311G(d) levels..