Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Cationic Cyanine Dyes: Impact of Symmetry-Breaking on Optical Absorption and Third-Order Polarizabilities

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Supporting Information

Figure S1: Energy differences between symmetric and asymmetric structures of **1-*n*** cyanine series as a function of ***n*** obtained at HF/6-31G** level.

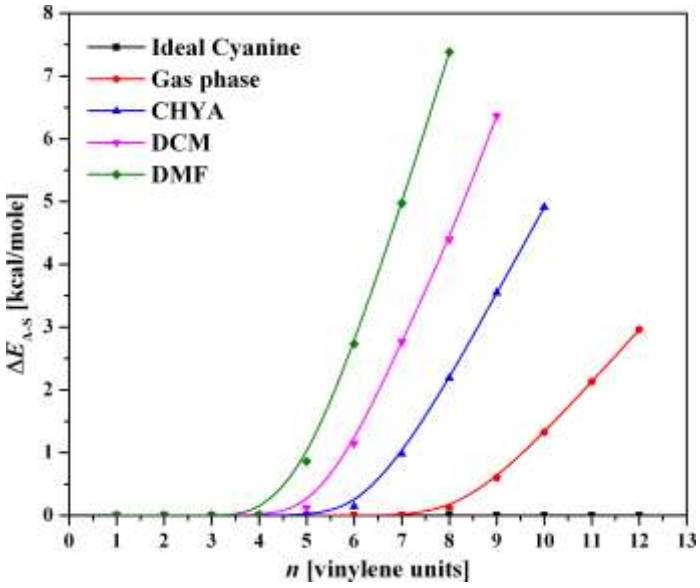

Figure S2: The solitonic structure (top) and local bond length alternations (bottom) of the bare cyanine (***n*** = 50 and 60) obtained at M06-HF/6-31G** level.

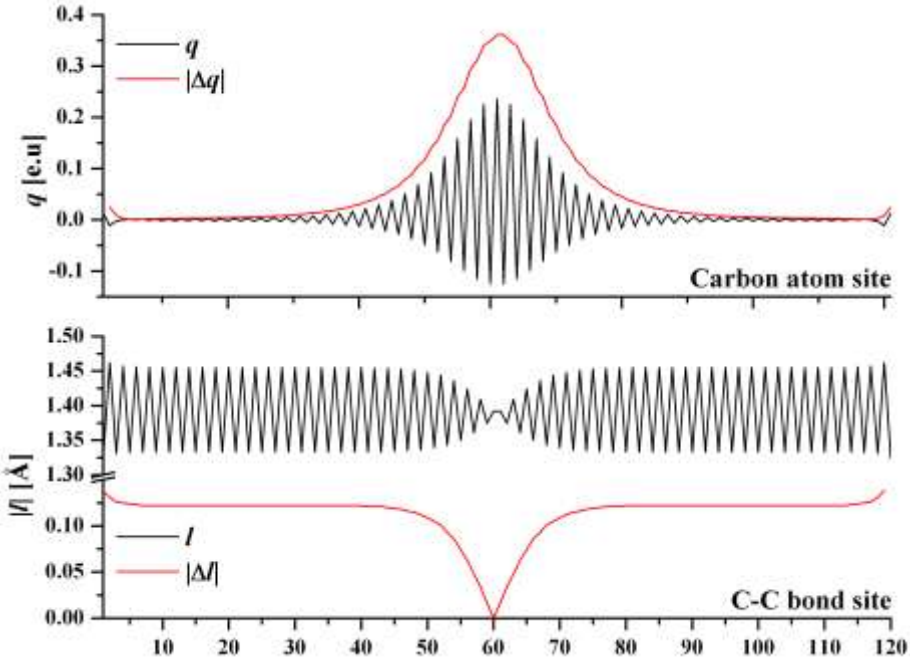

Figure S3: Comparison of the static average third-order polarizabilities (⟨γ⟩) obtained at INDO/MRD-CIS and SAC-CI/6-31G** for **1-*n*** and **2-*n*** series of cyanines as a function of ***n***.

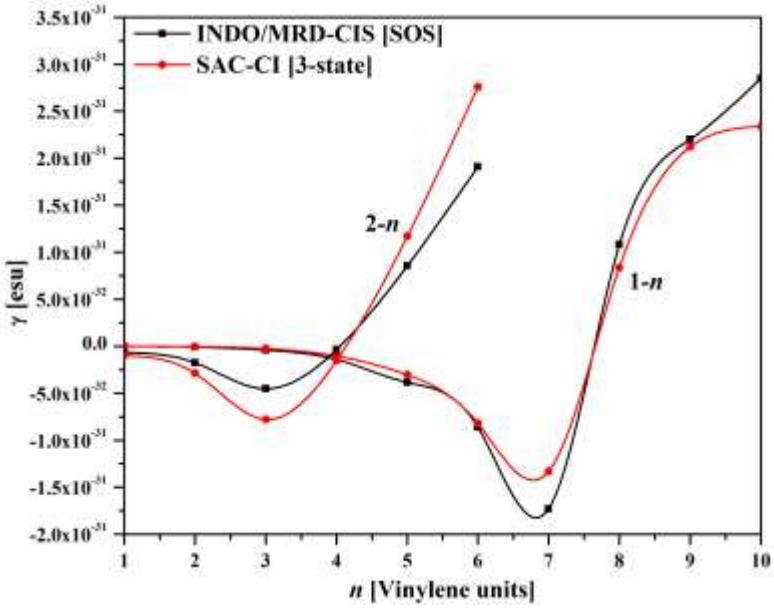

Table S1: Comparison of $S_0 \rightarrow S_1$ transition energies (E_{01}, eV), oscillator strengths (f) and transition dipole moments (μ_{01}, Debye) obtained from INDO/MRD-CIS, SAC-CI/6-31G** and TD-B3LYP/6-31G** level along with the available experimental values (E_{01}^{expt}, eV).

n	INDO/MRD-CIS			SAC-CI/6-31G**			TD-B3LYP/6-31G**			E_{01}^{expt}
	E_{01}	f	μ_{01}	E_{01}	f	μ_{01}	E_{01}	f	μ_{01}	
1-*n* series										
1	3.39	0.856	8.1	4.17	0.837	7.3	4.87	0.947	7.2	3.99(0.69)[a]
2	2.54	1.201	11.1	2.87	1.079	10.0	3.89	1.418	9.8	2.98(1.08)[a]
3	2.01	1.543	14.2	2.11	1.215	12.3	3.29	1.874	12.2	2.39(1.23)[a]
4	1.68	1.812	16.8	1.81	1.454	14.6	2.88	2.320	14.6	1.98(1.5)[a]
5	1.44	2.054	19.4	1.54	1.633	16.7	2.57	2.757	16.8	1.69[a]
6	1.28	2.282	21.7	1.31	1.730	18.7	2.33	3.179	19.0	1.46[a]
7	1.15	2.474	23.8	1.17	1.863	20.5	2.14	3.581	21.0	
8	1.13	1.788	20.4	1.10	1.523	18.7	1.79	2.550	19.4	
2-*n* series										
1	1.89	1.776	15.7	1.98	1.933	16.0	2.29	1.821	14.5	1.64[b]
2	1.69	2.214	18.6	1.68	2.226	18.7	2.10	2.404	17.4	1.41[b]
3	1.49	2.589	21.4	1.48	2.518	21.2	1.94	2.940	20.0	1.24[b]
4	1.40	2.853	21.4	1.36	2.030	19.9	1.72	2.890	21.0	

The values in the parenthesis correspond to the oscillator strengths obtained experimentally.

[a]Ref.[1], [b]Ref.[2].

References

1. W. Werncke, M. Pfeiffer, A. Lau, W. Grahn, H. H. Johannes and L. Dahne, *J. Opt. Soc. Am. B*, 1998, **15**, 863-870.
2. W. Werncke, M. Pfeiffer, T. Johr, A. Lau, W. Grahn, H. H. Johannes and L. Dähne, *Chem. Phys.*, 1997, **216**, 337-347.