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

Supporting Information

Unusual response to environmental polarity in a nonlinear-optical benzylidene-type chromophore containing 1,3-bis(dicyanomethylidene)indane acceptor fragment

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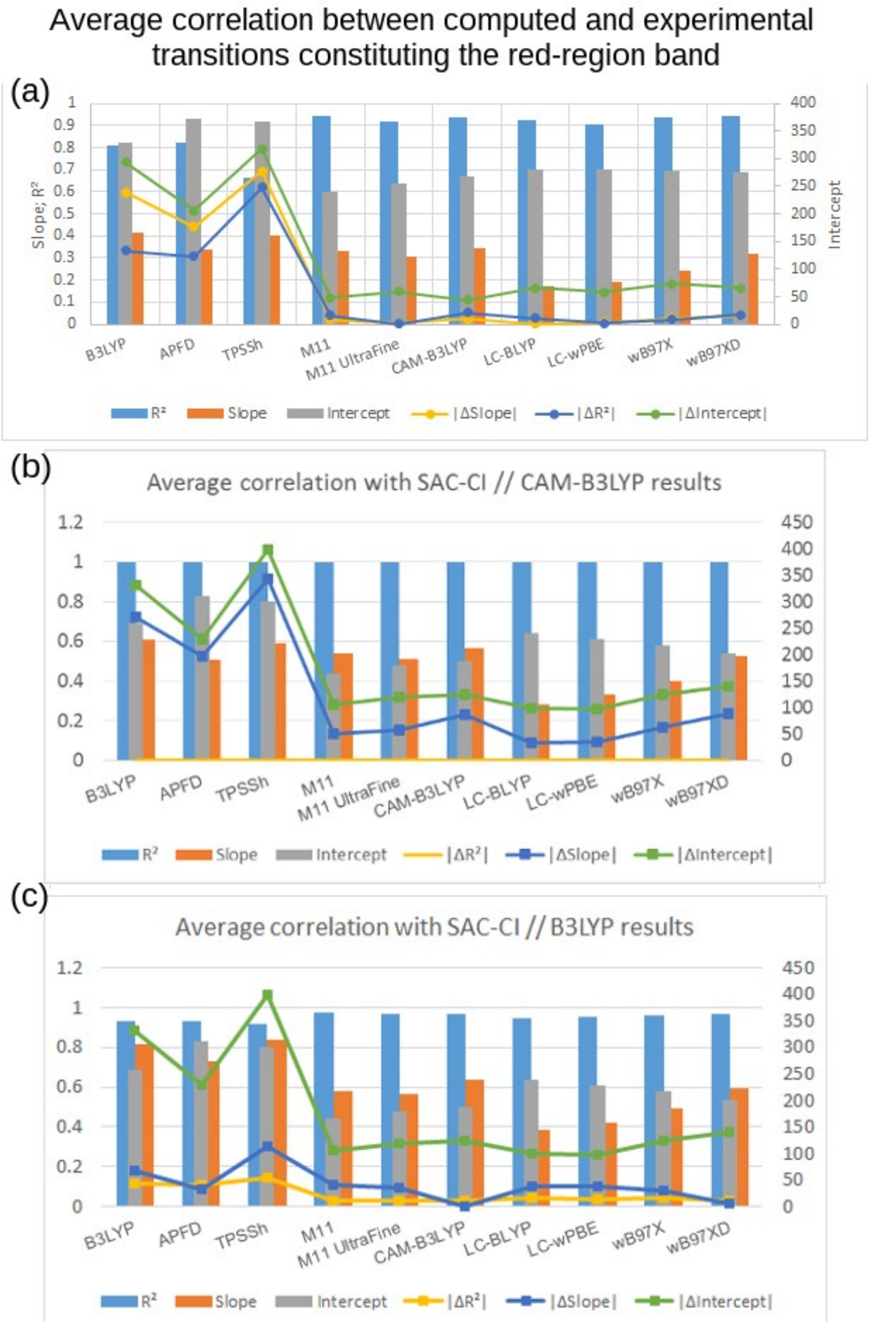

Fig. S1 (a) Correlation between **IND-1** red-region transitions modelled by various functionals and those extracted from experimental band shapes by deconvolution. Average correlation parameters (R^2, slope and intercept) for both valence transitions S_1 and S_2 are shown, complemented with differences in description quality for both deconvoluted transitions. The last ones help to mitigate coincidentally good description of just one band on the expense of mimicking the other one. Each correlation was drawn for 8 data points (solvents where no vibrational fine structure was detected – CCl_4, toluene, THF, DCM, acetic anhydride, $MeNO_2$, DMFA and DMSO).The results of comparison indicate that CAM-B3LYP facilitates the best description, closely followed by ωB97XD. (b, c) Correlation between transitions modelled by various functionals and those computed with SAC-CI/6-31G(d') method on geometries optimized with either CAM-B3LYP/6-311G(d,p) (b) or B3LYP/6-311G(d,p) (c). CPCM was used for solvent modelling, but only three points (vacuum, toluene, DCM) were used for correlations with SAC-CI//B3LYP geometries, due to high computational cost of such calculations. For the CAM-B3LYP-optimized geometry we were able to obtain only two points for the same and other technical reasons, hence $R^2 = 1$ for these correlations. The conclusions about the best DFT method are the same, though; notice that the experimental relative intensity of both transitions that constitute the band is well-mimicked by SAC-CI.

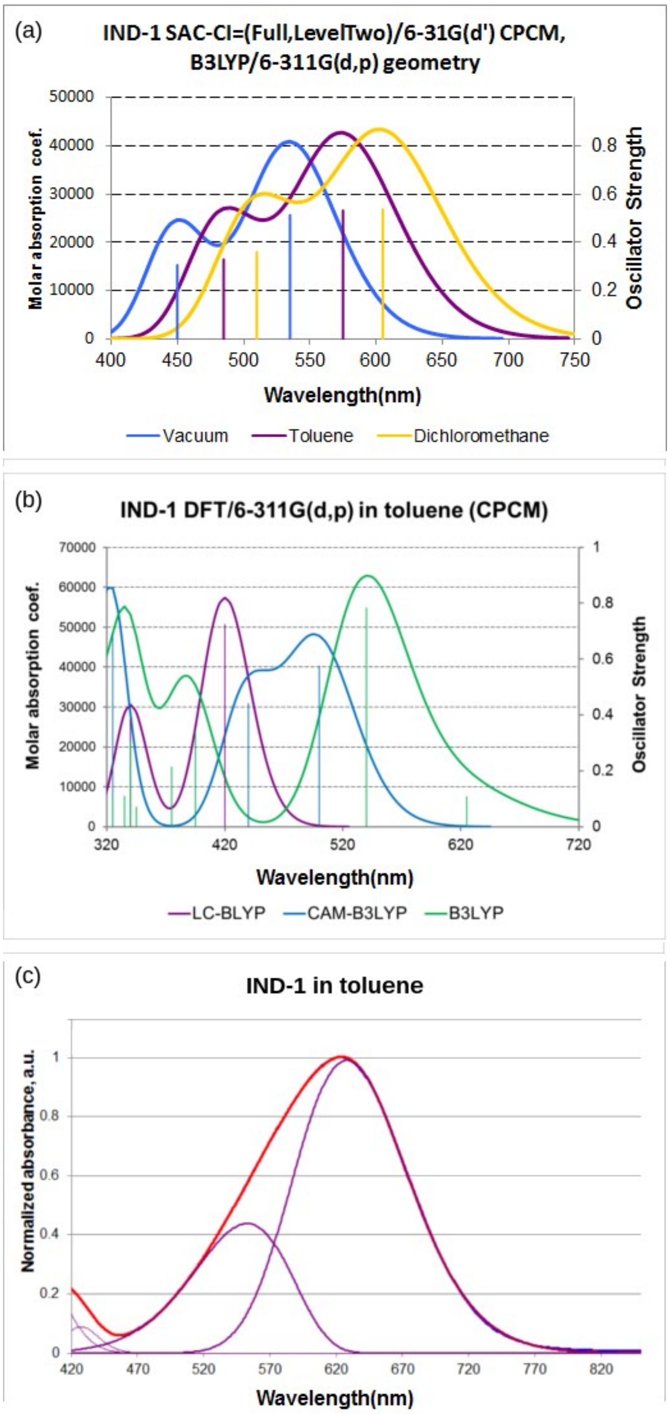

Fig. S2. (a) Reference theoretical red-region absorption bands of **IND-1** in vacuum, toluene and DCM. Theoretical spectra have been computed with SAC-CI/6-31G(d') // B3LYP/6-311G(d,p) using full orbital space and *LevelTwo* accuracy option as well as CPCM; Gaussian broadening of FWHM 0.34 eV was applied. (b) Exemplary theoretical red-region absorption bands of **IND-1** in toluene, obtained with three density functionals, with the same method for spectrum and geometry. (c) Experimental spectrum of **IND-1** in toluene that has been deconvoluted into two skewed Gaussian functions in the energy scale, as it was impossible to reasonably approximate the band with conventional Gaussians.

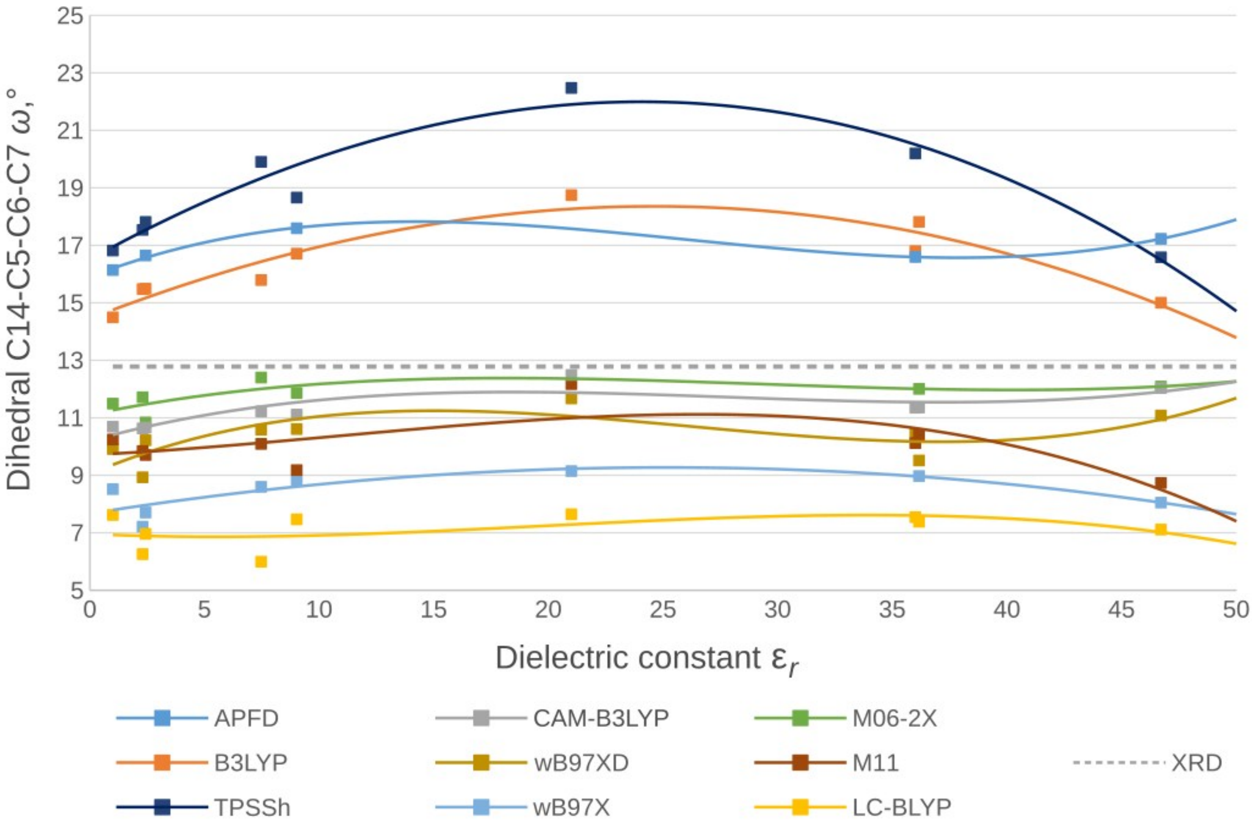

Fig. S3. Dependence of the pivotal dihedral C14-C5-C6-C7 from the dielectric constant of surrounding medium when using full optimization and C-PCM with SAS cavity non-electrostatic terms in the model. Very similar results were obtained with van der Waals cavity. Full lines are cubic fits to actual computation results (squares). The dashed line corresponds to the results of crystallographic examination (to check how our calculations converge to the supposed limit). The weak dependence urged us to use partial optimization scan to check how properties depend on the actual value for this dihedral, which is considered the main coordinate of internal rotation in the molecule studied.

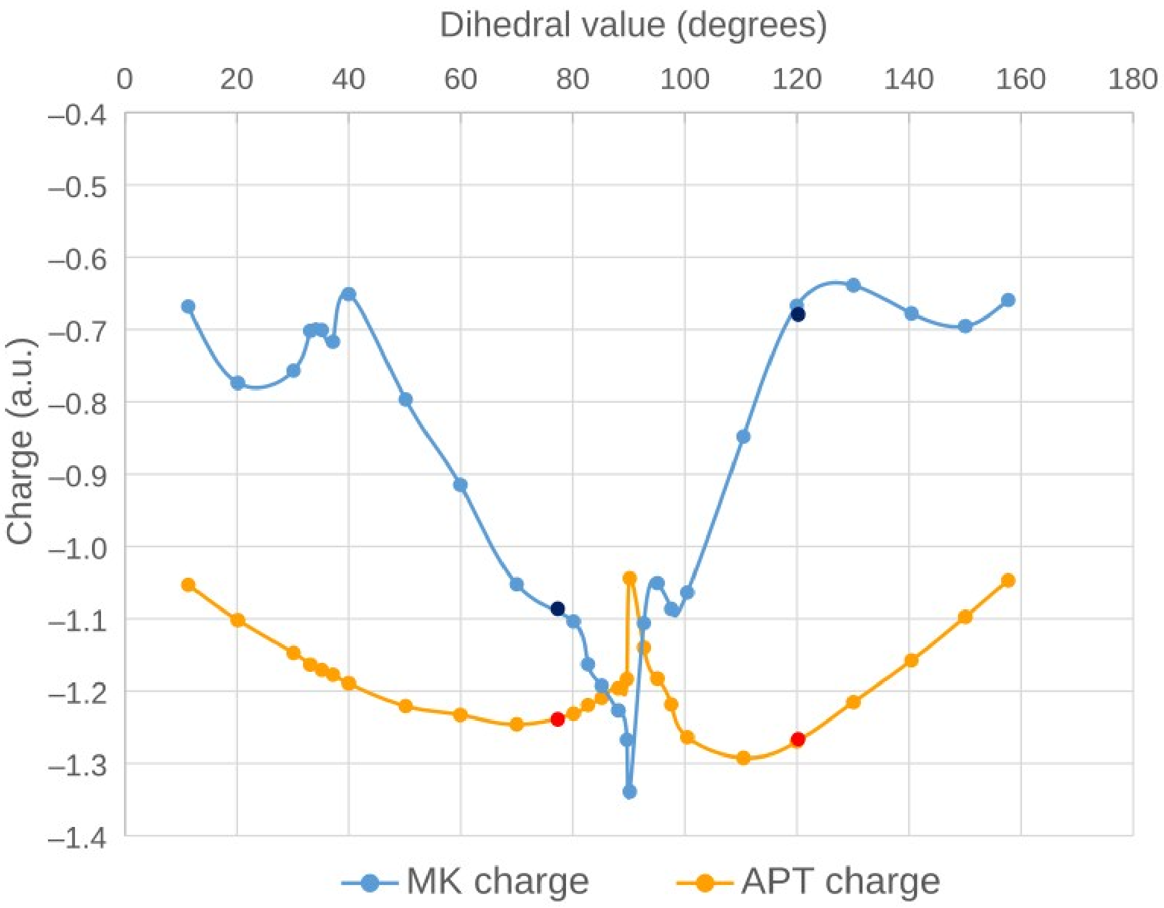

Fig. S4. Dependence of total atomic charge on the indane (the acceptor) part of the molecule IND-1 on the value of the pivotal dihedral C14-C5-C6-C7 when using partial optimization and C-PCM (acetonitrile) with SAS cavity and non-electrostatic terms in the model. The differently colored points refer to sister optimizations run to check dependence on initial geometry. This is the same information as in Table S1, given here graphically for convenience.

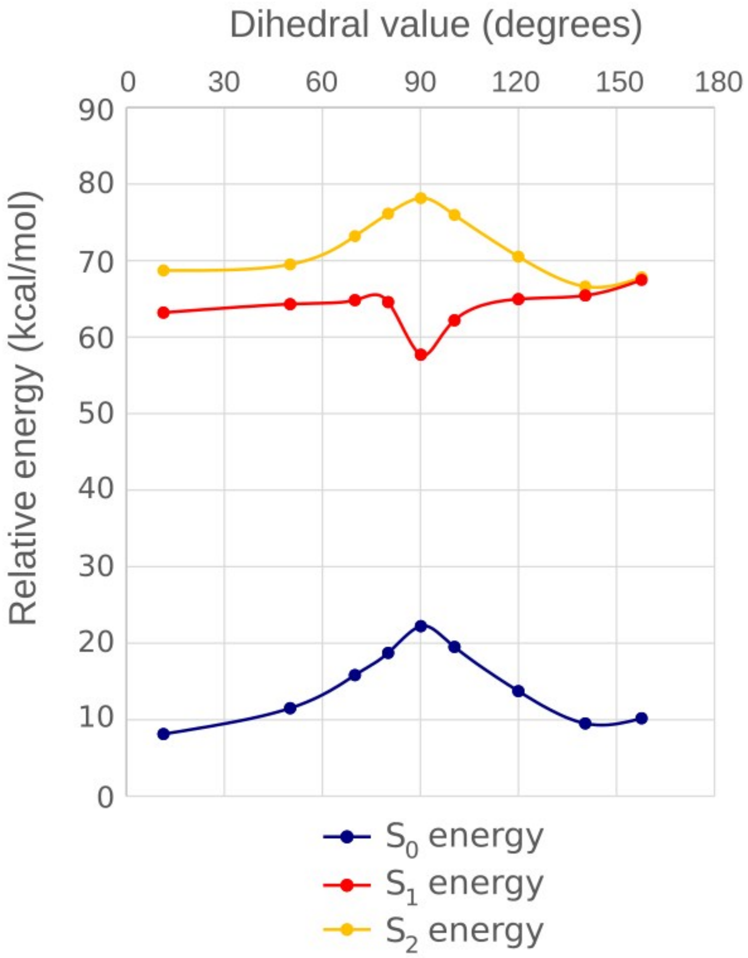

Fig. S5. Computed potential energy surfaces for S_0, S_1 and S_2 states of **IND-1** in acetonitrile (CAM-B3LYP/6-311G(d,p) // TPSSh/6-311G(d,p)). The trends are basically the same as for CAM-B3LYP geometry (except that the 'saw-tooth' of S_1 around the $\omega = 90^{\circ}$ point is less obvious due to lack of calculations in the very vicinity of the saddle point. The lack of 'saw-tooth' in the ground state is interpreted as follows: the change of conformers in the ground state can be described quite well just by rotation around the dihedral ω, while in the state S_1 it is strongly coupled with other transformations in the non-planar 5-membered ring of indane.

Table S1 Computed properties (CAM-B3LYP/6-311G(d,p) + CPCM (acetonitrile, SAS cavity, non-electrostatic terms of dispersion, Pauli repulsion and cavity formation)) of **IND-1** conformations corresponding to different values of torsion angle *ω* (C14-C5-C6-C7).

ω [°]	ISDI [°]	BLA(1)	APT charge on Indane	MK charge on Indane	ΔE[a] [kcal/mol]	ΔE[b] [kcal/mol]	λ_{S1} [nm]	f_{S1}	λ_{S2} [nm]	f_{S2}	$\beta_{HRS}(0)$, 10^{-30} esu
11.3[c]	52.70	0.035	–1.05	–0.67	0.00	0.00	507	0.32	458	0.43	76.2
20.1	47.50	0.030	–1.10	–0.77	0.22	0.22	505	0.40	462	0.39	75.1
30.1	41.35	0.023	–1.15	–0.76	0.98	1.08	508	0.46	466	0.33	69.6
40.0	40.06	0.016	–1.19	–0.65	2.24	2.43	507	0.55	468	0.26	63.1
50.1	26.75	0.005	–1.22	–0.80	3.84	4.16	526	0.53	474	0.20	51.6
59.9	23.91	–0.004	–1.23	–0.91	5.74	6.29	548	0.48	475	0.19	40.2
70.0	23.41	–0.014	–1.25	–1.05	8.24	8.94	573	0.42	478	0.20	29.9
80.1	20.05	–0.025	–1.23	–1.10	11.11	12.11	617	0.31	480	0.22	29.5
89.6	21.59	–0.038	–1.18	–1.27	14.08	-	696	0.17	482	0.24	46.9
90.1	7.27	–0.056	–1.04	–1.34	14.44	16.03	848	0.02	493	0.26	25.8
100.4	12.78	–0.031	–1.26	–1.06	11.93	12.96	672	0.20	487	0.23	35.1
110.4	9.00	–0.014	–1.29	–0.85	8.84	9.60	588	0.35	486	0.20	25.1
120.0	14.39	0.000	–1.27	–0.67	6.11	6.66	603	0.35	480	0.21	37.4
130.1	23.07	0.011	–1.22	–0.64	3.77	3.97	517	0.51	484	0.19	51.6
140.5	36.60	0.021	–1.16	–0.68	1.70	1.89	482	0.23	495	0.52	63.2
150.2	47.65	0.030	–1.09	–0.71	0.65	0.66	479	0.29	494	0.43	69.3
157.7[d]	53.69	0.034	–1.05	–0.66	0.41	0.32	478	0.29	492	0.42	73.2

[a] Relative energy of conformation from the bottom of *E* isomer well.

[b] The same parameter but calculated for the corresponding conformations in benzene.

[c] *E* isomer; [d] *Z* isomer

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