Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Ultrafast Excited State Dynamics and Spectroscopy of 13,13'-Diphenyl-β-carotene

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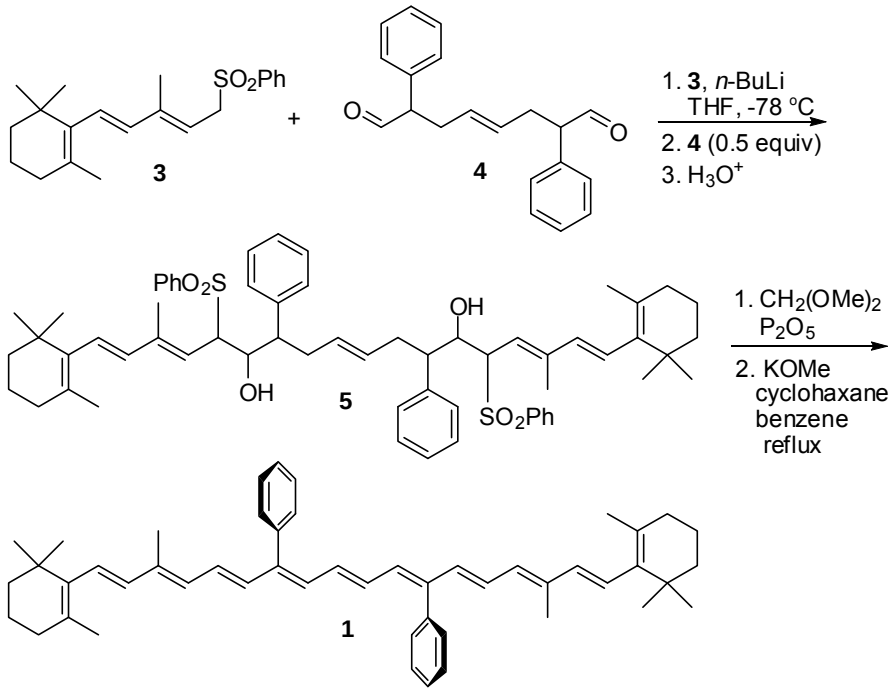
Synthesis



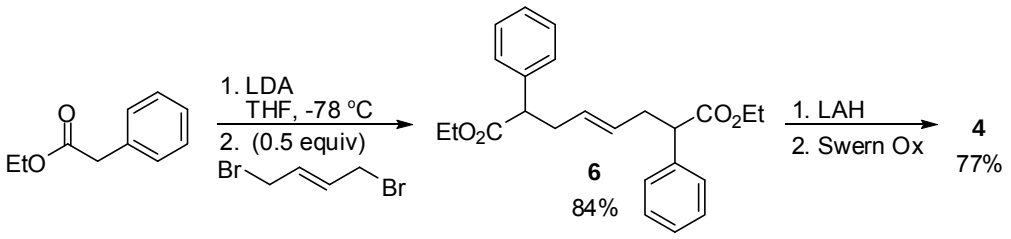
Scheme S1. Coupling of C_{15} sulfone **3** and dialdehyde **4**, and the double-elimination protocol for the synthesis of 13,13′-β-carotene (**1**).

(1*E*,3*E*,9*E*,15*E*,17*E*)-5,14-Bis(benzenesulfonyl)-3,16-dimethyl-7,12-diphenyl-1,18-bis(2,6,6-trimethylcyclohex-1-enyl)octadeca-1,3,9,15,17-pentaene-6,13-diol (5). To a stirred solution of C_{15} sulfone **3** (4.43 g, 12.86 mmol, 2.4 equiv) in THF (25 mL) at –78 °C was added 1.6 M hexane solution of *n*-BuLi (8.71 mL, 13.94 mmol, 2.6 equiv). The resulting red-orange solution was stirred for 30 min, and a solution of dialdehyde **4** (1.57 g, 5.36 mmol, 1 equiv) in THF (10 mL) was added for 5 min period. The mixture was stirred at –78 °C for 2 h, and 1 M HCl was added to quench the reaction. The reaction mixture was warmed up to room temperature, extracted with EtOAc (20 mL × 2), washed with 1 M HCl (15 mL × 2), dried over anhyd Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to give the diol **5** (3.61 g, 3.67 mmol) in 69% yield.

Data for **5**: ^{1}H NMR δ 0.99 (s, 12H), 1.44–1.50 (m, 4H), 1.55 (s, 6H), 1.58–1.66 (m, 4H), 1.66 (s, 6H), 2.02 (t, *J* = 6.0 Hz, 4H), 2.07–2.22 (m, 2H), 2.30–2.44 (m, 2H), 2.58–2.80 (m, 2H), 3.83 (d, *J* = 2.8 Hz, 2H), 4.00 (dd, *J* = 11.2, 8.0 Hz, 2H), 4.25–4.36 (m, 2H), 4.91–5.05 (m, 4H), 5.84 (A of ABq, *J* = 16.0 Hz, 2H), 5.96 (B of ABq, *J* = 16.0 Hz, 2H), 7.04–7.09 (m, 4H), 7.12–7.23 (m, 6H), 7.40–7.47 (m, 4H), 7.56–7.62 (m, 2H), 7.68–7.74 (m, 4H) ppm; IR (KBr) 3503, 3030, 2935, 1717, 1648, 1653, 1624, 1448, 1305, 1148 cm^{-1}; HRMS (FAB^+) calcd for $C_{56}H_{69}O_5S_2$ [$C_{62}H_{77}O_6S_2 - (C_6H_6 + H_2O)$] 885.4586, found 885.4571.

All-(*E*)-13,13'-Diphenyl-β-carotene (1). To a stirred solution of the diol **5** (3.61 g, 3.67 mmol, 1 equiv) in dimethoxymethane (16.28 mL, 50 equiv) was added P_2O_5 (1.57 g, 11.04 mmol, 3 equiv). The mixture was stirred at room temperature for 16 h, and extracted with CH_2Cl_2 (40 mL). The reaction mixture was washed with saturated aqueous $NaHCO_3$ solution (10 mL × 2), dried over anhyd. Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (deactivated by 1% Et_3N) to give the bis-MOM ether (2.99 g, 2.79 mmol) in 76% yield.

The above bis-MOM ether (2.99 g, 2.79 mmol, 1 equiv) was dissolved in cyclohexane (24 mL) and benzene (6 mL) under Ar atmosphere, and KOMe (1.96 g, 28.01 mmol, 10 equiv) was added. The resulting mixture was heated at 80~90 °C for 16 h, and then cooled to room temperature. Most of solvent was removed under reduced pressure, and the mixture was diluted with CH_2Cl_2. The mixture was washed with H_2O, dried over anhyd Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product (1.64 g, 2.47 mmol, 88% yield) which was practically pure and contained less than 15% of stereoisomers, was recrystallized from THF and MeOH to give all-(*E*)-13,13′-diphenyl-β-carotene (**1**) as a red solid.



Scheme S2. Preparation of (*E*)-2,7-diphenyl-oct-4-enedial (**4**).

Diethyl (*E*)-2,7-diphenyl-oct-4-enedioate (6): To a stirred solution of diisopropylamine (70.0 mmol, 9.8 mL) in THF (70 mL) was added 1.6 M hexane solution of *n*-BuLi (70.0 mmol, 43.7 mL) at 0 °C. The mixture was stirred at 0 °C for 20 min, and cooled to –78 °C. A solution of ethyl phenylacetate (60.0 mmol, 9.6 mL) in THF (20 mL) was added to the above mixture. The resulting mixture was stirred at –78 °C for 40 min, and a solution of 1,4-dibromo-2-butene (20.0 mmol, 4.28 g) in THF (5 mL) was added. Stirring at –78 °C for 1 h, the mixture was warmed to room temperature, and quenched with 1 M HCl solution. The mixture was extracted with CH_2Cl_2, washed with 1 M HCl, dried over anhyd Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography (Hexanes:EtOAc = 9:1) to give diester **6** (16.74 mmol, 5.70 g, a 1:1 mixture of stereoisomers) in 84% yield. Data for **6**: R_f = 0.51 (Hexanes:EtOAc = 4:1); ^{1}H NMR δ 1.86 (t, *J* = 7.1 Hz, 6H), 2.33–2.45 (m, 2H), 2.65–2.78 (m, 2H), 3.49 (ddd, *J* = 8.7, 6.7, 3.8 Hz, 2H), 4.00–4.18 (m, 4H), 5.31–5.46 (m, 2H), 7.20–7.34 (m, 10H) ppm; ^{13}C NMR δ 14.1, 36.4(36.5),* 51.8(51.9),* 60.7, 127.9, 128.5, 129.4, 138.6, 173.4 ppm; IR (KBr) 2923, 1738, 1452, 1366, 1059, 700 cm^{-1}; HRMS (CI$^+$) calcd for $C_{24}H_{29}O_4$ 381.2066, found 381.2066.

*: ^{13}C NMR peaks in parenthesis are from the diastereoisomer.

(*E*)-2,7-Diphenyl-oct-4-enedial (4). To a stirred suspension of $LiAlH_4$ (14.68 mmol, 0.56 g) in THF (50 mL) at 0 °C was added a solution of diester **6** (7.34 mmol, 2.50 g) in THF (5 mL). Stirring for 30 min, the mixture was warmed to room temperature, and quenched with 1 M NaOH solution. The mixture was extracted with EtOAc, washed with 1 M HCl, dried over

anhyd Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography (Hexanes:EtOAc = 13:7) to give the corresponding diol (6.24 mmol, 1.85 g, a 1:1 mixture of stereoisomers) in 85% yield.

To a stirred solution of DMSO (9.84 mmol, 0.77 g) in CH_2Cl_2 (70 mL) was added oxalyl chloride (8.43 mmol, 0.74 mL) at –78 °C. The mixture was stirred for 15 min, and a solution of the above diol (2.81 mmol, 1.00 g) in CH_2Cl_2 (5 mL) was added. The resulting mixture was stirred at –78 °C for 40 min, and Et_3N (28.10 mmol, 3.91 mL) was added. Stirring at –78 °C for 20 min, the mixture was warmed to room temperature, and quenched with 1 M HCl solution. The mixture was extracted with CH_2Cl_2, washed with 1 M HCl, dried over anhyd Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash column chromatography (Hexanes:EtOAc = 17:3) to give dial **4** (2.57 mmol, 0.75 g, a 1:1 mixture of stereoisomers) in 91% yield. Data for **4**: R_f = 0.66 (Hexanes:EtOAc = 3:2); ^{1}H NMR δ 2.32–2.43 (m, 2H), 2.68–2.78 (m, 2H), 2.47 (ddd, *J* = 8.3, 7.9, 6.8 Hz, 2H), 5.26–5.43 (m, 2H), 7.06–7.13 (m, 4H), 7.26–7.40 (m, 6H), 9.62 (d, *J* = 1.8 Hz, 2H) ppm; ^{13}C NMR δ 32.8, 58.9(59.0),* 127.6, 128.8(128.9),* 129.0, 129.2, 135.6, 200.3 ppm; IR (KBr) 3030, 2915, 2820, 2718, 1722, 1601, 1494, 700 cm^{-1}; HRMS (CI$^+$) calcd for $C_{20}H_{21}O_2$ 293.1541, found 293.1539.

*: ^{13}C NMR peaks in parenthesis are from the diastereoisomer.

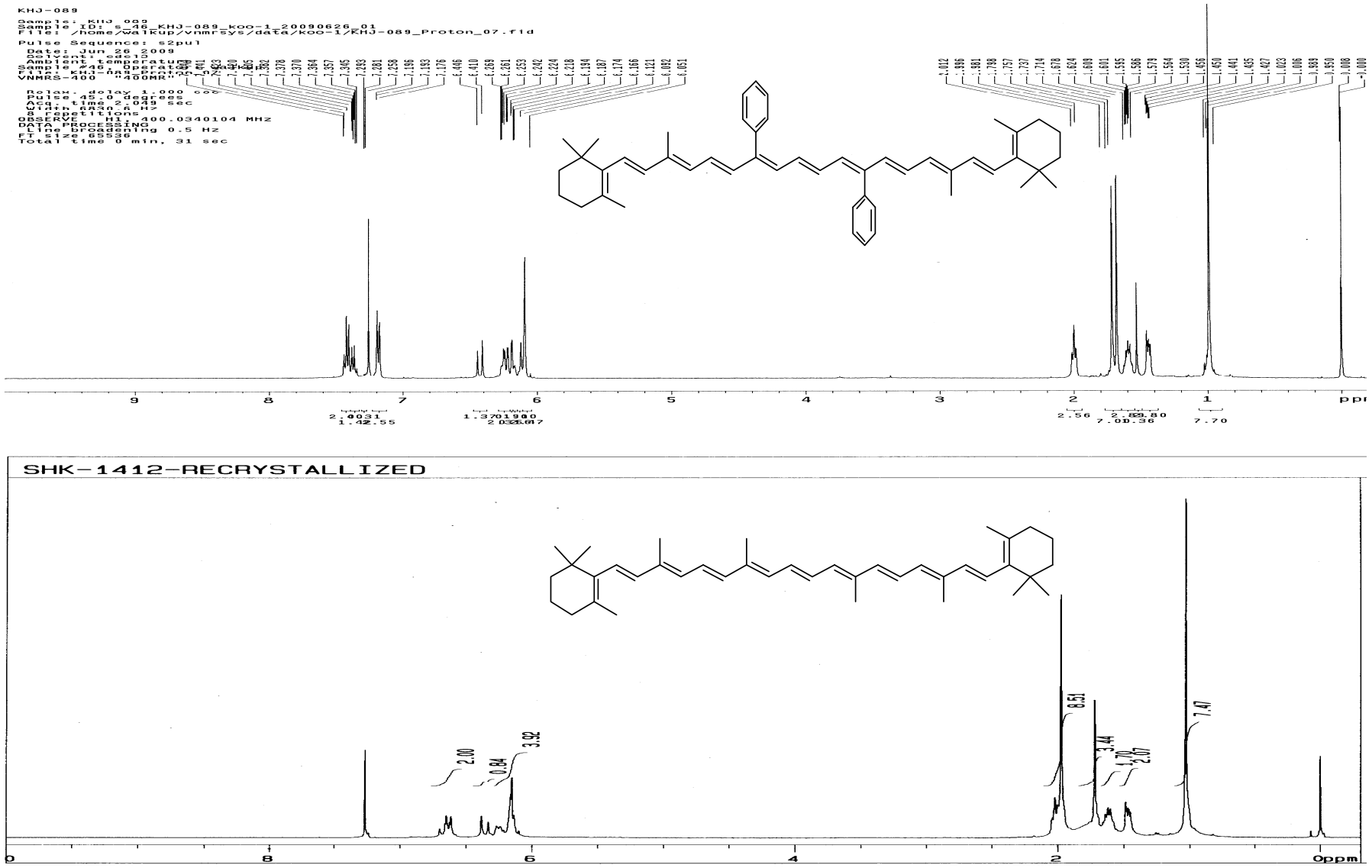
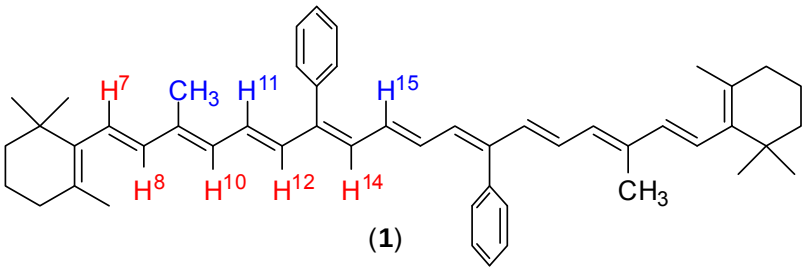
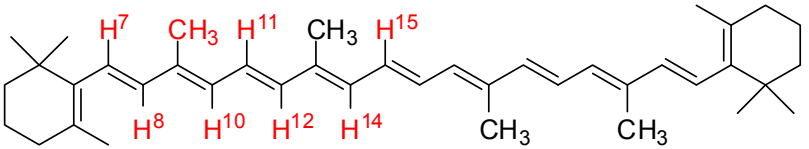


Figure S1. ^{1}H NMR Spectra of 13,13'-diphenyl-β-carotene (**1**) and β-carotene (**2**).

Table S1. Evidence of the close to orthogonal displacement of phenyl groups to the conjugated polyenes chains in 13,13'-diphenyl-β-carotene (**1**) - The ^{1}H NMR chemical shifts of H^{11}, H^{15}, $C^{9}H_3$ are to be up-field shifted compared to those of β-carotene due to the **ring current effect** of benzene.



(**1**)



(**2**)

^{1}H NMR (ppm)	H(7)	H(8)	$C(9)H_3$	H(10)	H(11)	H(12)	H(14)	H(15)
13,13'-diphenyl-β-carotene (1)	6.08	6.09	1.68	6.11	6.22	6.43	6.25	6.18
β-carotene (2)	6.15	6.18	1.98	6.16	6.66	6.37	6.26	6.64
Difference (Δ)	– 0.07	– 0.09	– 0.30	– 0.05	– 0.44	+ 0.06	– 0.01	– 0.46

Table S2. Steady-state absorption spectra of 13,13'-diphenyl-β-carotene (**1**) and β-carotene (**2**) in organic solvents.

solvent	$R(n)$ [a]	λ_{max} [b]			ε_{max} [b]	
		1	**2**	$\Delta\nu_{max}$ (cm^{-1})	**1**	**2**
acetone	0.22	462.3	453.9	416	-	-
n-hexane	0.23	458.4	450.0	406	-	-
THF	0.25	467.1	458.1	421	1.12	-
i-octane	0.24	458.7	-	-	-	-
toluene	0.29	471.2	463.0	374	-	-
acetonitrile	0.21	462.3	453.3	430	-	-
CH_2Cl_2	0.26	471.0	462.5	390	1.32	1.72

[a] Solvent polarizability function: $(n^2-1)/(n^2+2)$. [b] Steady-state absorption maximum (λ_{max}) and absorption coefficient (ε_{max}) for the $S_0 \rightarrow S_2$ (0-1) transition in units nm and 10^5 $L \cdot mol^{-1} \cdot cm^{-1}$, respectively.

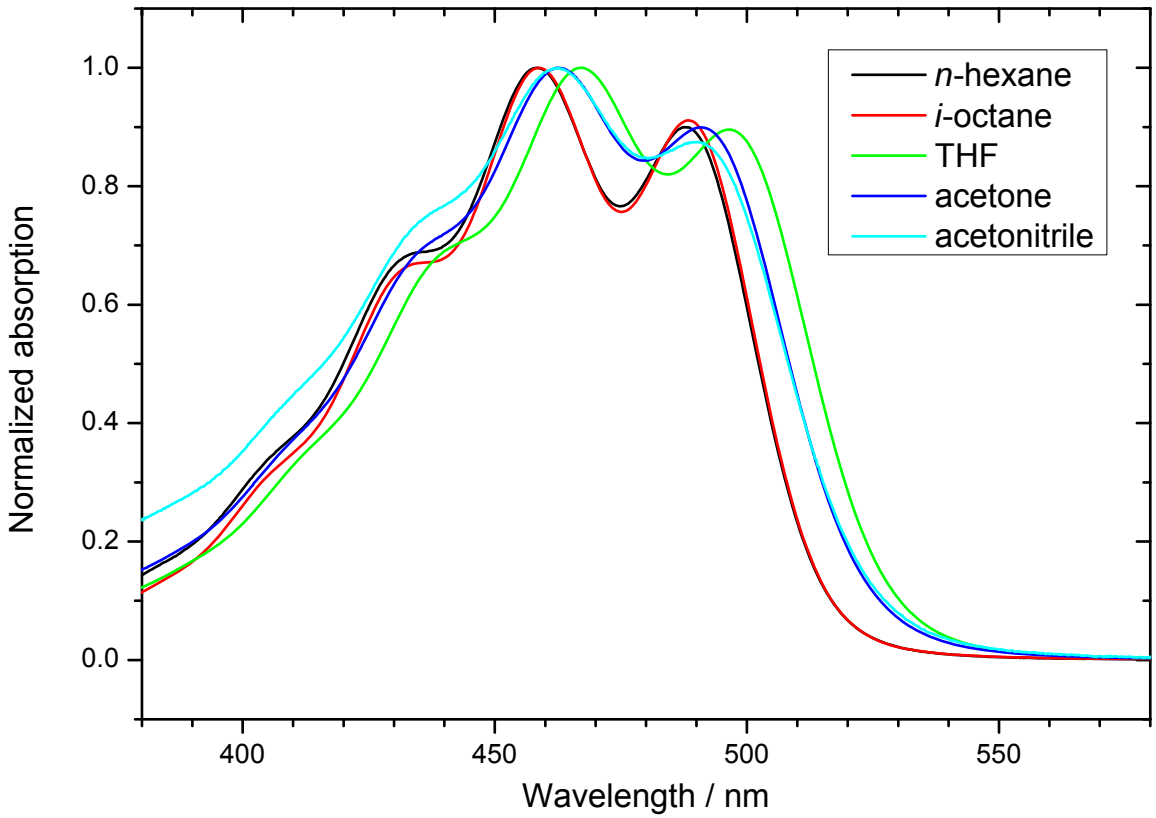


Figure S2. Comparison of steady-state absorption spectra of 13,13'-diphenyl-β-carotene in various organic solvents at room temperature. Each spectrum is normalized to its absorption maximum. Information on absorption maxima and relevant solvent properties are summarized in Table S2.

Additional DFT/TDDFT-TDA calculations

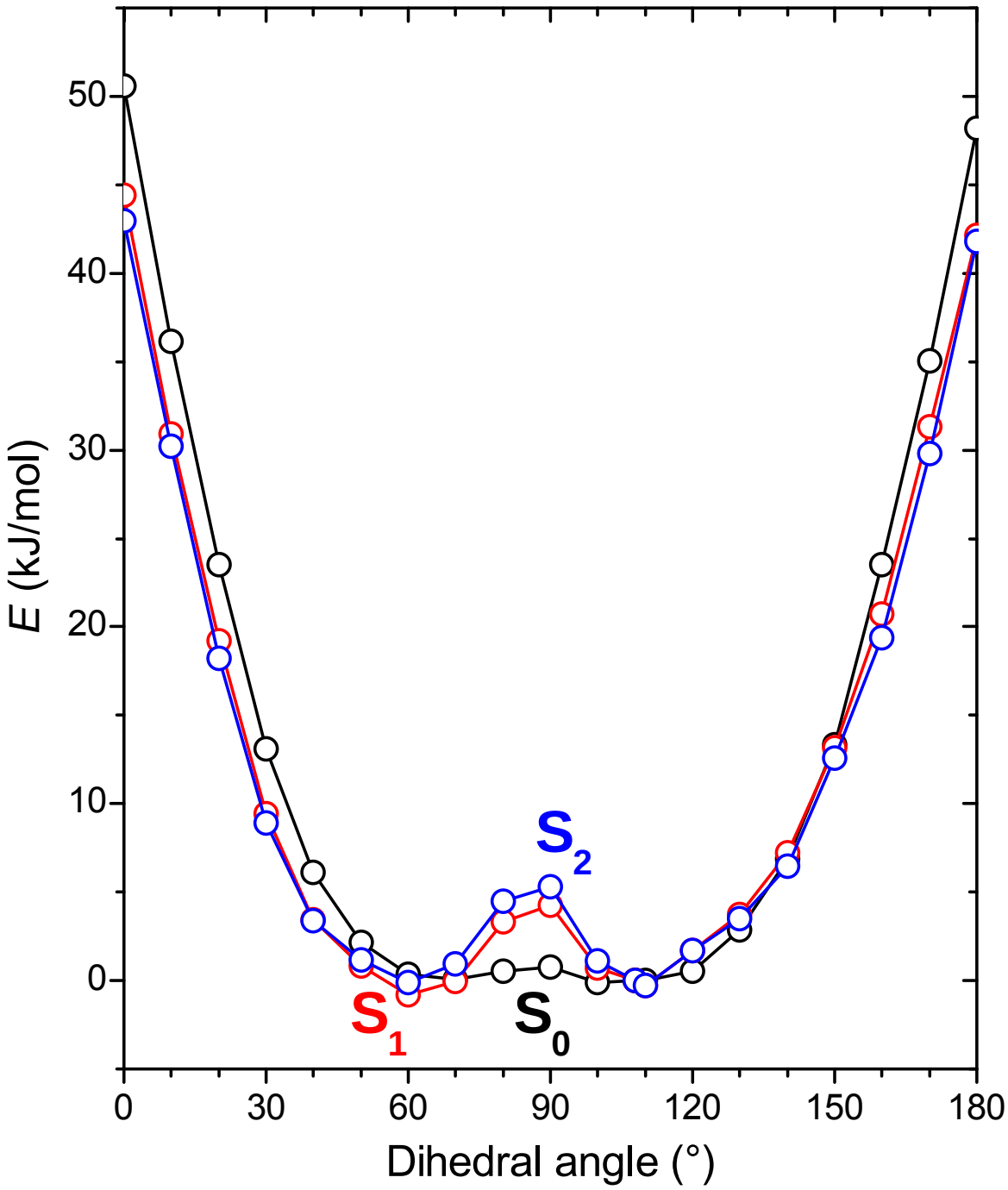


Figure S3. Energy profile for phenyl rotation in S_0 (black), S_1 (red) and S_2 (blue) of 13,13'-diphenyl-β-carotene. One phenyl group was rotated in 10° steps. Functionals: B3LYP (S_0), BLYP (S_1, S_2). Note the large barriers at 0 and 180° and the additional small barrier at ca. 90°, which becomes more pronounced in the excited states.

Table S3. Gas-phase transition energies E, transition wavelengths λ and oscillator strengths f from TDDFT-TDA calculations (BLYP 6-31+G*) for the first five excited singlet states of 13,13'-diphenyl-β-carotene and β-carotene.

	13,13'-diphenyl-β-carotene			β-carotene		
state	E (eV)	λ (nm)	f	E (eV)	λ (nm)	f
S_1	1.98	628	0.0	2.00	618	0.0
S_2	2.09	592	4.5	2.11	587	4.3
S_3	2.57	482	1.3	2.63	472	1.5
S_4	2.74	453	0.0	2.77	448	0.0
S_5	2.81	441	0.5	2.90	427	0.8

Table S4. Same as in **Table S3**, but for the SVWN functional.

	13,13'-diphenyl-β-carotene			β-carotene		
state	E (eV)	λ (nm)	f	E (eV)	λ (nm)	f
S_1	1.96	634	0.0	1.99	624	0.0
S_2	2.07	598	4.3	2.09	592	4.1
S_3	2.56	485	1.7	2.61	476	1.8
S_4	2.69	462	0.0	2.72	456	0.0
S_5	2.80	443	0.5	2.89	429	0.8