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

Electronic Supplementary Information: Bilirubin analogues as model compounds for exciton coupling

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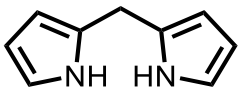
Experimental Details

General

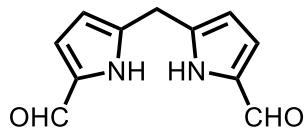
All chemicals were purchased from commercial suppliers and were used without further purification, unless specified. Thin layer chromatography was performed on pre-coated 0.2 mm thick Merck Kieselgel 60 F254 silica gel plates and visualised by absorption of UV light. Dry toluene, dichloromethane, diethyl ether, and tetrahydrofuran were obtained from a Glass Contour Solvent System (SG Water USA). DMF and chloroform were dried and stored over 4Å molecular sieves. ^{1}H NMR and ^{13}C NMR spectroscopy was performed using Agilent MR400 and Varian Inova 600 spectrometers. Chemical shifts (δ) are given in units of parts per million (ppm) relative to tetramethylsilane (TMS), where δ (TMS) = 0.00 ppm. The multiplicity of each signal is indicated by: s (singlet), br.s (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The number of protons (n) for a given resonance is indicated by nH. Coupling constants (J) are quoted in Hz and are recorded to the nearest 0.01 Hz. Absorbance measurements were performed using a Cary 300 Bio UV-visible spectrophotometer. Fluorescence measurements were carried out using a Varian Eclipse spectrophotometer. Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer in the region 4000-650 cm^{-1}.

Synthesis

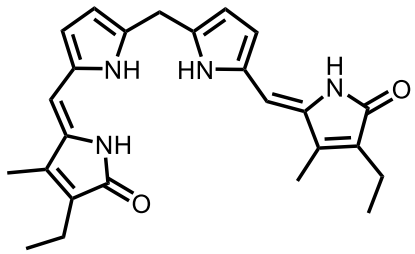


2,2'-Dipyrromethane. The synthesis of this product has been reported previously and the experimental procedure was adapted from the literature.[1] Freshly distilled pyrrole (200 mL, 2.88 mol) and paraformaldehyde (1.5 g, 0.05 mol) were sequentially added into a flame-dried flask at room temperature. The mixture was degassed with N_2 for 10 min and then

heated to 55 °C. Afterwards, $InCl_3$ (1.1 g, 5.00 mmol) was added in the mixture. The cloudy mixture was stirred at 55 °C for 2.5 h. The mixture was then cooled to room temperature and the reaction was quenched by the addition of powdered NaOH (6 g, 0.15 mol), which was stirred for another 45 min. The resulting mixture was filtered over celite, washed with pyrrole, and evaporated to dryness. The product was further purified by column chromatography (using petroleum spirits/ethyl acetate (9:1) as eluent) to give 2,2'-dipyrromethane as a white solid (1.1 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (s, 1H), 6.04 (m, 2H), 6.15 (q, 2H, J =2.92 Hz), 6.68 (m, 2H), 7.93 (br. s, 2H).

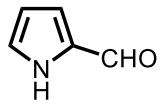


5,5'-Methylenebis(1H-pyrrole-2-carbaldehyde). The synthesis of this product has been reported previously and the experimental procedure was adapted from the literature.[2] To a DMF solution (150 mL) containing 2,2'-dipyrromethane (5.31 g, 36.37 mmol), $POCl_3$ (11.86 mL, 127.30 mmol) was added slowly at 0 °C. The mixture was stirred for 2 h. During that time the mixture was allowed to reach room temperature. Next, the reaction quenched by addition of a saturated solution of Na_2CO_3 (500 mL) and heated to approximately 70 °C. The mixture was vigorously stirred for 30 min and allowed to cool to room temperature. The crude product was filtered off and washed with water and cold methanol. The product was obtained as a yellow solid (6.25 g, 85%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.95 (s, 2H), 6.05 (d, J = 3.64 Hz, 2H), 6.88 (d, J = 3.64 Hz, 2H), 9.34 (s, 2H), 12.00 (s, 2H).

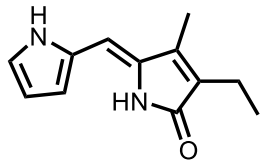


Non-conjugated Phycobilin (main text Figure 1-c). 5,5'-Methylenebis(1H-pyrrole-

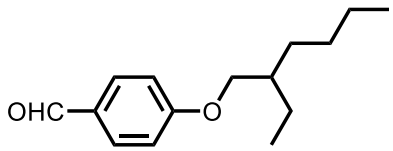
2- carbaldehyde) (0.58 g, 2.86 mmol) and 3-ethyl-4-methyl-1,5-dihydro-pyrrol-2-one (1.43 g, 11.4 mmol) were dissolved in DMSO (10 mL), and the solution was sparged with nitrogen for 15 mins. Potassium hydroxide (11.4 mL, 2 M solution, sparged with nitrogen) was added through a septum and the resulting orange mixture was heated to 60 °C and held under nitrogen for 12 h with stirring. The reaction mixture was then poured into water (200 mL) and the resulting precipitate filtered, taken up in chloroform and dried over $MgSO_4$. Evaporation of solvent under reduced pressure successfully gave the unsubstituted phycobilin as a dark green powder (0.88 g, 74%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.98 (t, J = 7.48 Hz, 6H), 2.00 (s, 6H), 2.23 (q, J = 7.48 Hz, 4H), 3.87 (s, 2H), 5.88 (d, J = 3.48 Hz, 2H), 6.00 (s, 2H), 6.53 (d, J = 3.48 Hz, 2H), 9.61 (s, 2H), 10.88 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 9.6, 13.9, 16.8, 26.5, 100.4, 109.1, 112.6, 127.0, 130.7, 131.4, 133.4, 141.1, 172.0. FTIR (cm^{-1}): 3335, 2964, 1635. HRMS (ESI+) *m/z* 417.2282 (417.2291 calculated for $C_{25}H_{28}N_4O_2$ $(M+H)^+$).



Pyrrole-2-carboxaldehyde. The synthesis of this product has been reported previously and the experimental procedure was adapted from the literature.[3] To a solution of $POCl_3$ (17.13 g, 0.112 mol) and DMF (9.805 g, 0.134 mol) in dry diethylether (100 mL), pyrrole (7.5 g, 0.112 mol) was added dropwise in an ice-bath. After the reaction was stirred for 24 h, the mixture was quenched with saturated $NaHCO_3$ solution until the pH reached 7. Thereafter, extraction was performed with chloroform (200 mL × 3). The solution was then dried over $MgSO_4$ and the solvent removed under reduced pressure to give a crude residue. Separation by column chromatography eluted with ethyl acetate/petroleum spirits (1:3) successively gave pyrrole-2-carboxaldehyde as needle shaped colourless crystals (8.24 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (m, 1H), 7.01 (m, 1H,), 7.18 (s, 1H), 9.50 (s, 1H), 10.51 (br. s, 1H).

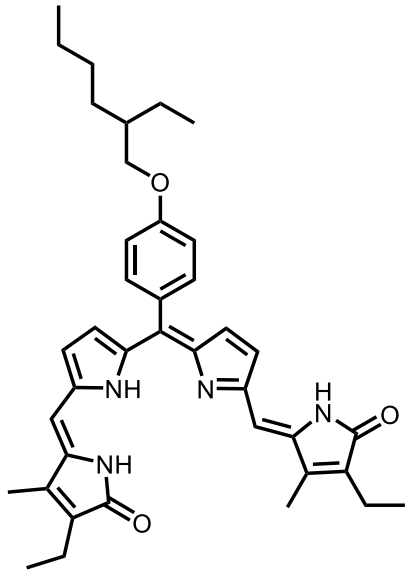


(Z)-5-((1H-pyrrol-2-yl)methylene)-3- ethyl-4-methyl-1,5-dihydro-2H-pyrrol-2-one (main text Figure 1-b). The synthesis of this product has been reported previously and the experimental procedure was adapted from the literature.[4] Pyrrole-2-carboxaldehyde (0.32 g, 3.3 mmol) and 3-ethyl-4-methyl-1,5-dihydro-pyrrol-2-one (0.84 g, 6.7 mmol) were dissolved in DMSO (10 mL) and the solution was sparged with nitrogen. Potassium hydroxide (3.5 mL, 4 M solution, sparged with nitrogen) was added through a septum and the resulting orange mixture was heated to 60 °C and held under nitrogen for 12 h with stirring. The reaction mixture was then poured into water (70 mL) and the resulting precipitate was filtered, taken up in dichloromethane and dried over $MgSO_4$. Evaporation of solvent under reduced pressure gave (Z)-5-((1H-pyrrol-2-yl)methylene)-3-ethyl-4-methyl-1,5-dihydro-2H-pyrrol-2-one as yellow needle shaped crystals (0.62 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, 3H, J = 7.52 Hz), 2.12 (s, 3H), 2.44 (q, 2H, J = 7.52 Hz), 6.15 (s, 1H), 6.28 (m, 1H), 6.44 (m, 1H), 7.04 (s, 1H), 10.63 (br. s, 1H), 10.90 (s, 1H).



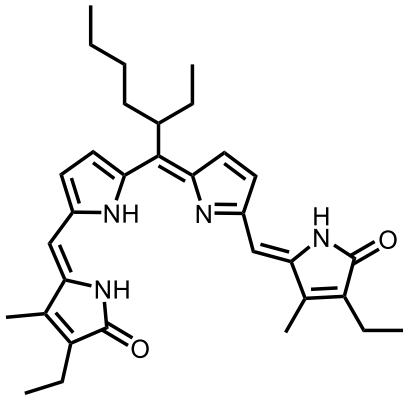
4-(2-ethylhexyloxy)benzaldehyde. The synthesis of this product has been reported previously and the experimental procedure was adapted from the literature.[5] A mixture of 4-hydroxybenzaldehyde (4.9 g, 40 mmol), 2-ethylhexylbromide (9.7 g, 50 mmol) and K_2CO_3 (8.3 g, 60 mmol) in anhydrous DMF (80 mL) were stirred for 24 h at 80 °C. The reaction mixture cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure. To the residue was added to brine and extracted with ethyl acetate. The extract was washed with brine, dried over $MgSO_4$, filtered and concentrated under

reduced pressure. The residue was purified by silica gel column chromatography (using an ethyl acetate/petroleum spirits gradient beginning at 1:9 v/v as eluent) to give 4-(2-ethylhexyloxy) benzaldehyde (7.8 g, 83%) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94–0.85 (m, 6H), 1.53–1.30 (m, 8H), 1.77–1.71 (m, 1H), 3.94–3.91 (m, 2H), 7.00–6.98 (d, J = 8.68 Hz, 2H), 7.82–7.80 (d, J = 8.6 Hz, 2H), 9.87 (s, 1H).



Phenyl-2-ethylhexyloxy-substituted phycobilin analogue (main text Figure 1-d). A solution of 4-(2-Ethylhexyloxy) benzaldehyde (0.234 g, 1 mmol) and (Z)-5-((1H-pyrrol-2-yl)methylene)-3-ethyl-4-methyl-1,5-dihydro-2H-pyrrol-2-one (0.404 g, 2 mmol) in 160 mL of dry chloroform was purged with nitrogen for 15 min. Then $BF_3 \cdot OEt_2$ (0.8 mmol, 10 mL of 0.08 M stock solution in dry chloroform) was added resulting in a colour change from yellow to reddish brown. The solution was stirred for 24 h at room temperature. Thereafter, DDQ (0.23 g in 40 ml chloroform, 1 mmol) was added and the mixture was stirred for an additional 24 h at room temperature resulting in a dark greenish blue solution. The solvent was removed under reduced pressure and flash column chromatography on basic alumina (2% acetone/DCM) gave 0.58 g (94%) of the crude 2-ethylhexyl-substituted phycobilin analogue. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.93 (m, 3H), 0.97 (t, 3H), 1.12 (t, 6H), 1.36 (m, 4H), 1.45-1.59 (m, 4H), 1.78 (m, 1H), 2.16 (Br. s, 6H), 2.38 (q, 4H), 3.93 (m, 2H), 6.09 (s, 2H), 6.57

(d, J = 4.4 Hz, 2H), 6.74 (d, J = 4.4 Hz, 2H), 6.99 (m, 2H), 7.44 (m, 2H), 8.51 (Br. S, 2H). ^{13}H NMR (151 MHz, $CDCl_3$) δ 9.6, 11.3, 13.5, 14.3, 17.2, 23.2, 24.0, 29.3, 29.8, 30.7, 39.6, 70.8, 99.3, 114.0, 119.9, 129.3, 130.4, 133.0, 134.6, 138.4, 141.1, 141.4, 143.0, 150.8, 160.8, 172.3. FTIR (cm^{-1}): 3207, 2925, 1674. HRMS (ESI^+) *m/z* 619.3644 (619.3648 calculated for $C_{39}H_{46}N_4O_3$ $(M+H)^+$). Crystal data: ($C_{39}H_{46}N_4O_3$) M = 618.82, T = 100.1(5) K, λ = 1.54184 Å, triclinic, space group P-1, a = 10.7904(11), b = 10.8858(12), c = 17.103(2) Å, α = 97.947(10)°, β = 102.411(10)°, γ = 92.227(9)°. V = 1938.3(4) Å^3, Z = 2, Dc = 1.034 Mg/m^3, μ(Mo-K_α) 0.521 mm^{-1}, F(000) = 646, crystal size 0.15 × 0.10 × 0.05 mm^3. 20414 reflections measured to a maximum θ = 67.684°, 7712 independent reflections (R_{int} = 0.1336), the final R was 0.1349 [I >2σ(I)] and wR(F2) was 0.3924 (all data).



2-ethylhexyl substituted phycobilin analogue (main text Figure 1-e). A solution of 2-ethylhexanal (0.070 g, 0.55 mmol, 0.85 mL of a 1:10 stock solution in $CHCl_3$) and (Z)-5-((1H-pyrrol-2-yl)methylene)-3-ethyl-4-methyl-1,5-dihydro-2H-pyrrol-2-one (0.200 g, 0.989 mmol) in 50 mL of dry chloroform was purged with nitrogen for 15 min. Then $BF_3 \cdot OEt_2$ (0.50 mmol, 0.62 mL of a 1:10 stock solution in dry chloroform) was added resulting in a deep yellow solution after ∼30 minutes stirring at room temperature under nitrogen. The solution was stirred for 24 h at room temperature, after which time DDQ (0.115 g in 15 ml of chloroform, 0.507 mmol) was added and the mixture was stirred for an additional 24 h at room temperature resulting in a dark greenish blue solution. The reaction mixture was evaporated to dryness, and then purified by column chromatography using basic alumina (2%

acetone/DCM as eluent). A clear blue band was collected and concentrated under reduced pressure to give a blue solid. This was washed with petroleum spirits and then filtered to give the product 3 as a blue solid (0.046 g, 18% yield). ^{1}H NMR (600 MHz, CDCl3) δ 0.83 (t, 3H), 0.89 (t, 3H), 1.12 (t, 6H), 1.20-1.32 (m, 5H), 1.88-1.96 (m, 3H), 2.15 (m, 6H), 2.38 (m, 4H), 2.99 (m, 1H), 6.09 (m, 2H), 6.57 (m, 2H), 7.28 (m, 2H) (+ residual solvent), 8.02 (br. s, 1H), 8.49 (br. s, 1H), 13.16 (br. s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 9.6, 13.37, 13.43, 14.1, 17.1, 22.9, 29.8, 31.0, 31.1, 32.1, 37.5, 46.3, 99.0, 99.7, 117.6, 121.6, 126.0, 129.0, 134.1, 134.7, 138.7, 140.1, 141.2, 141.4, 141.7, 144.8, 144.9, 147.4, 154.9, 172.1, 172.5. FTIR (cm-1): 3223, 2921, 2853, 1671. HRMS (ESI^{+}) m/z 513.3225 (513.3230 calculated for $C_{32}H_{41}N_4O_2$ (M+H)$^{+}$).

NMR Spectra

Figure S1: ^{1}H NMR spectrum of the non-conjugated phycobilin.

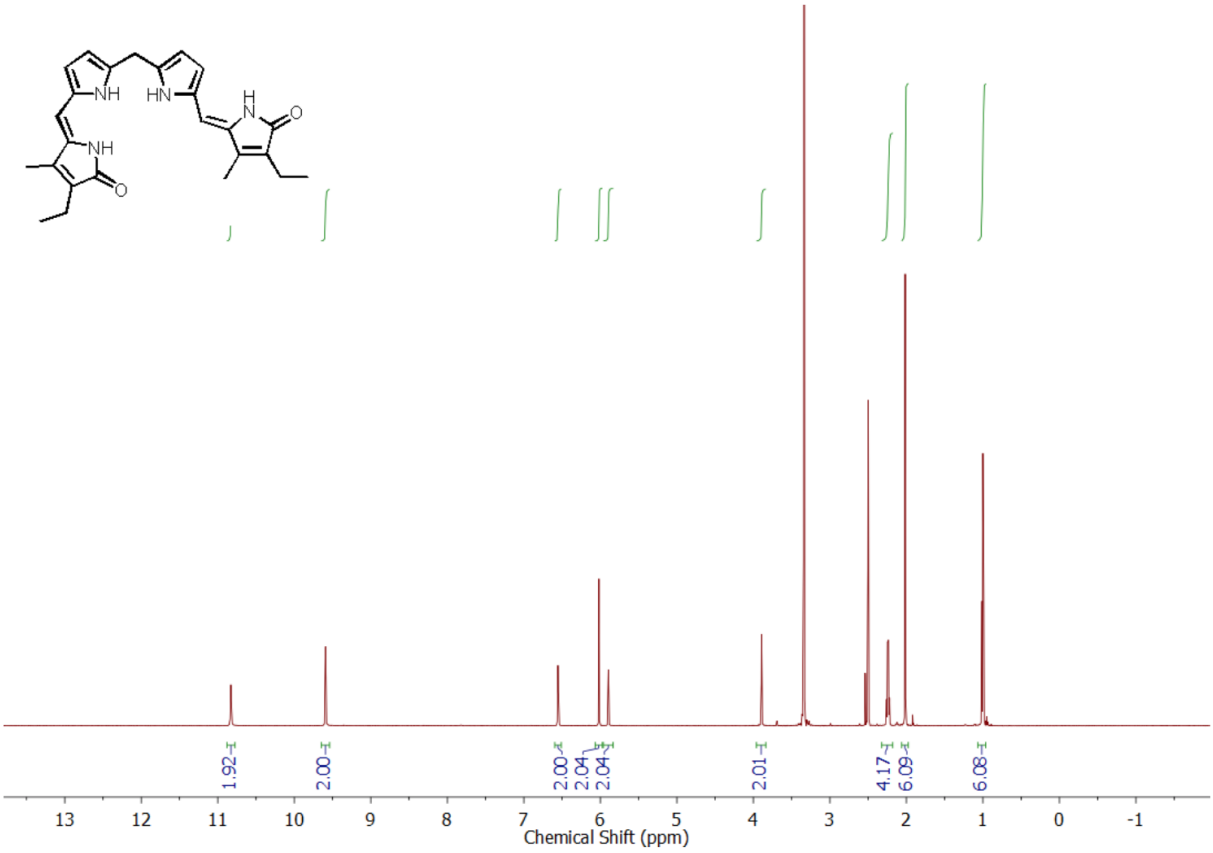


Figure S2: ^{13}C NMR spectrum of the non-conjugated phycobilin.

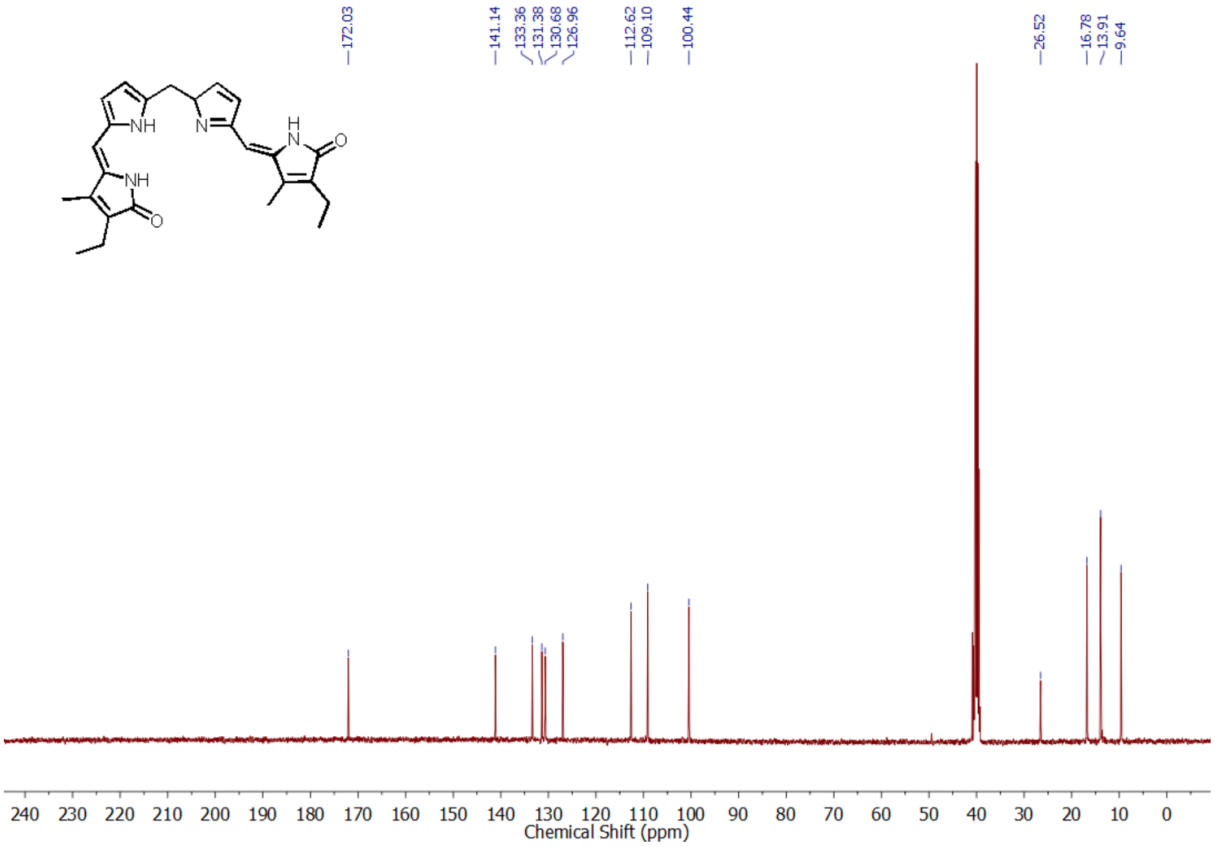


Figure S3: ^{1}H NMR spectrum of a conjugated phycobilin derivative.

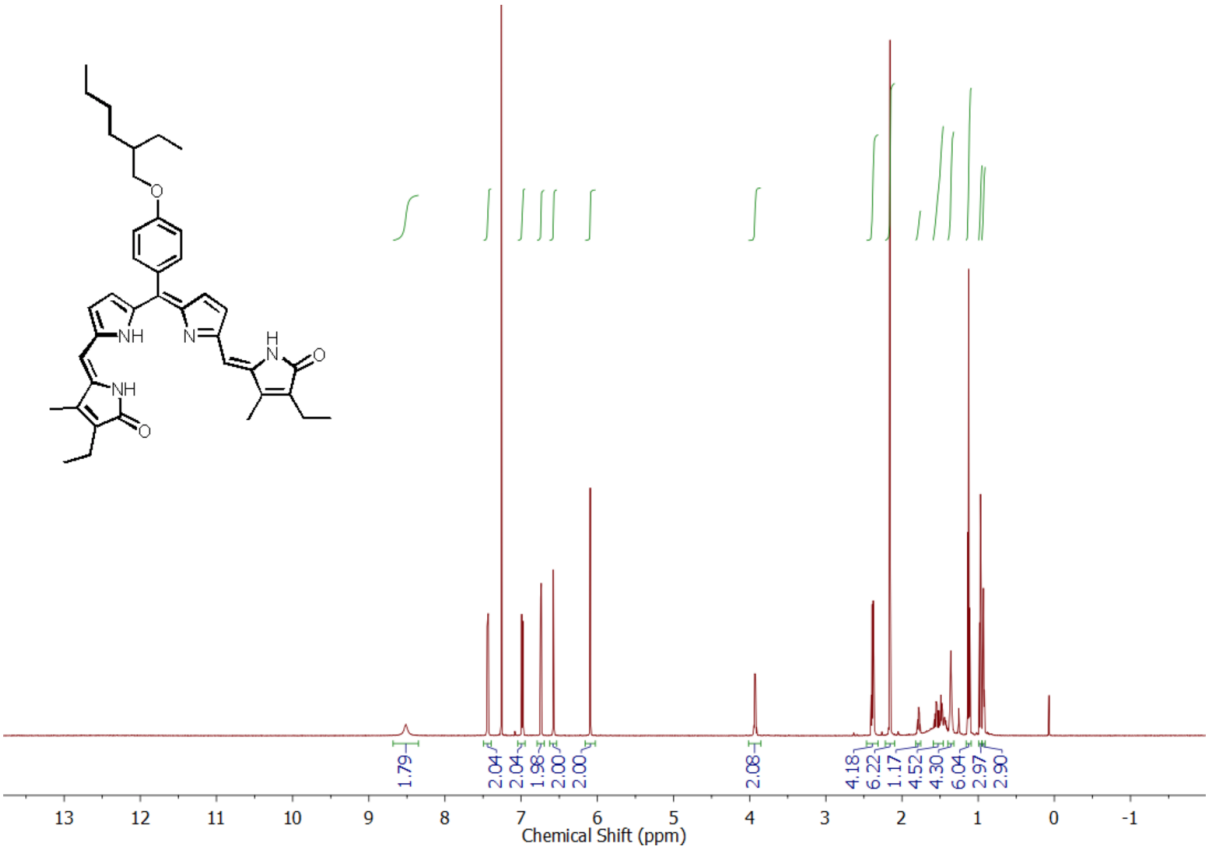


Figure S4: ^{13}C NMR spectrum of a conjugated phycobilin derivative.

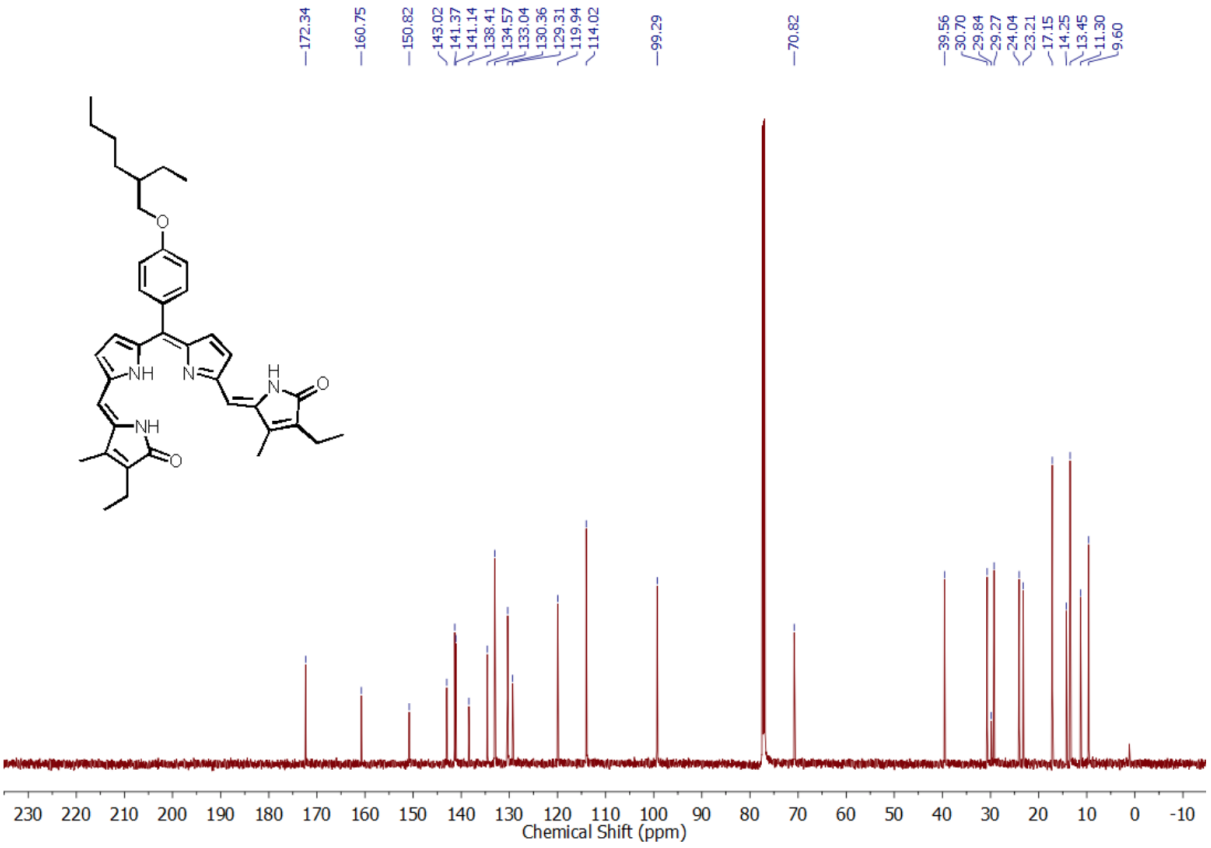


Figure S5: ^{1}H NMR spectrum of a conjugated phycobilin derivative.

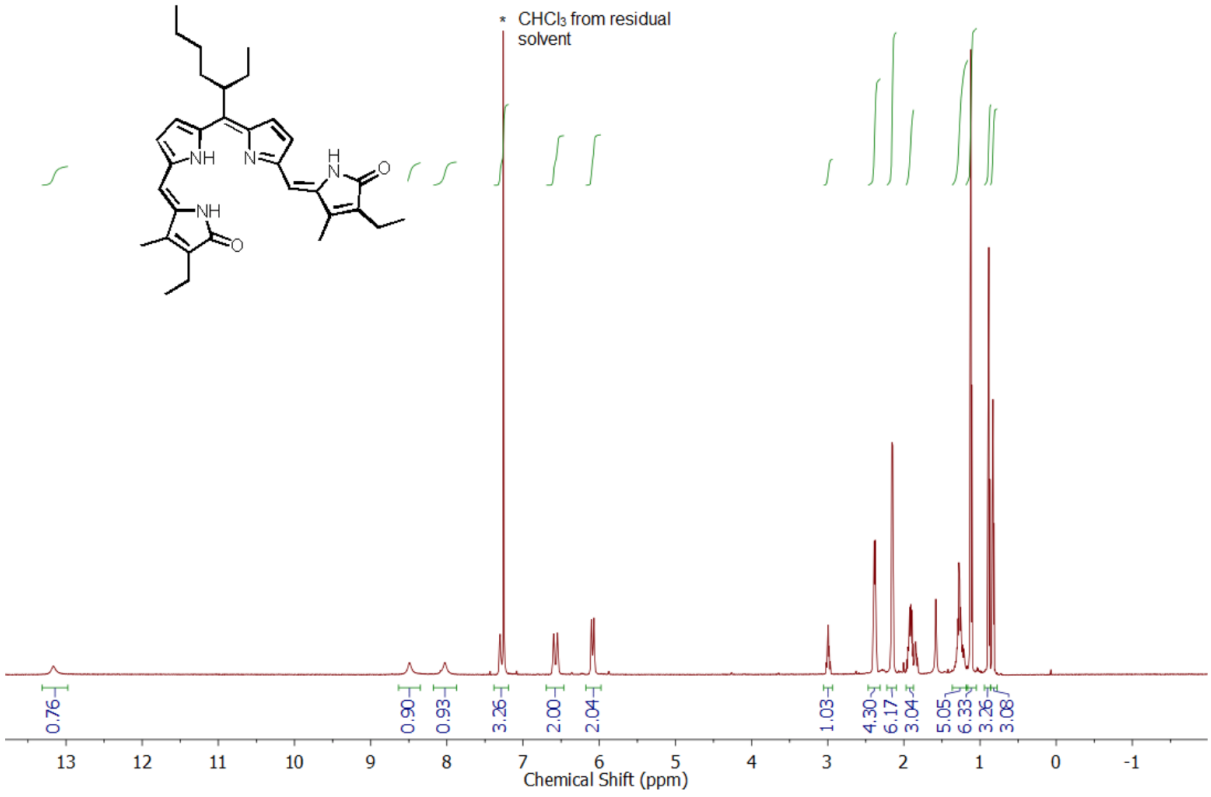
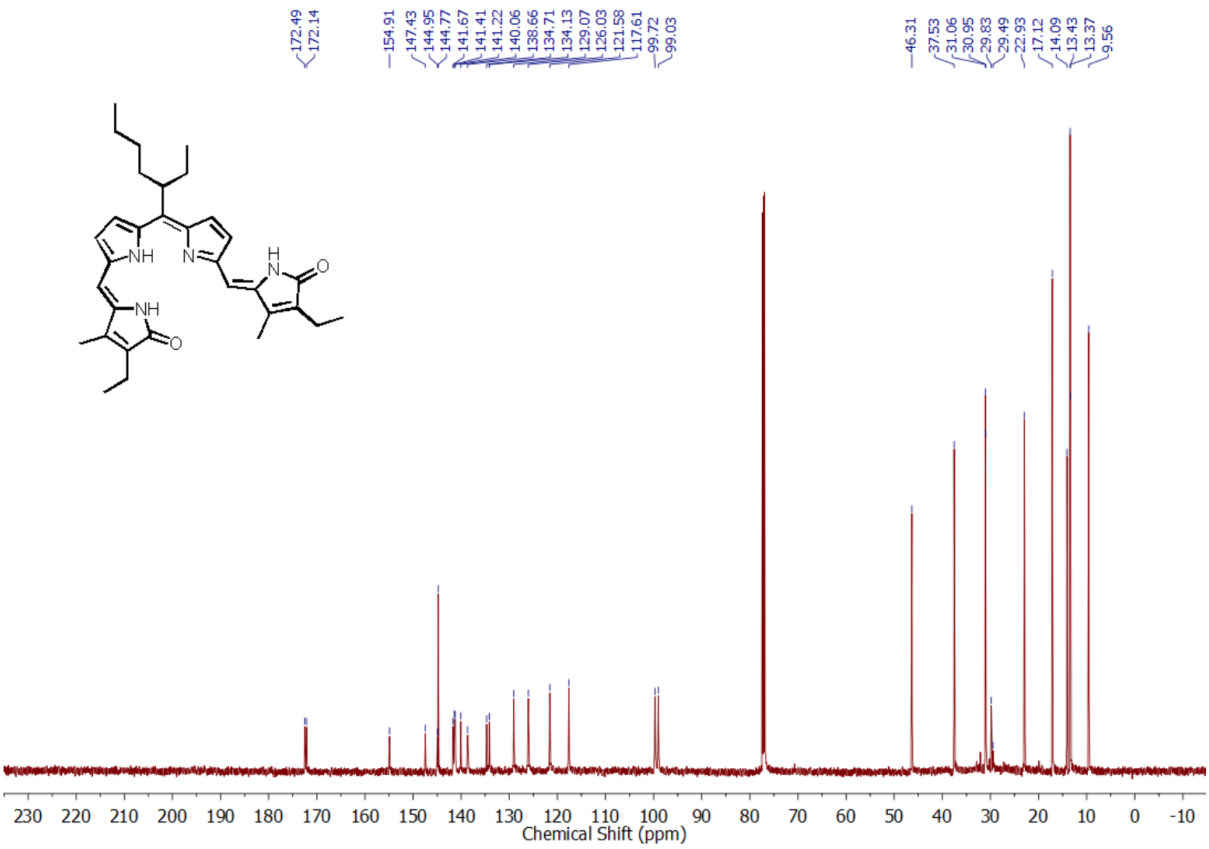


Figure S6: ^{13}C NMR spectrum of a conjugated phycobilin derivative.



Computational Details

In order to locate experimental energies we deconvolute the absorption signals using a two-state gaussian model. The absorption profile s(ω) is represented as follows:

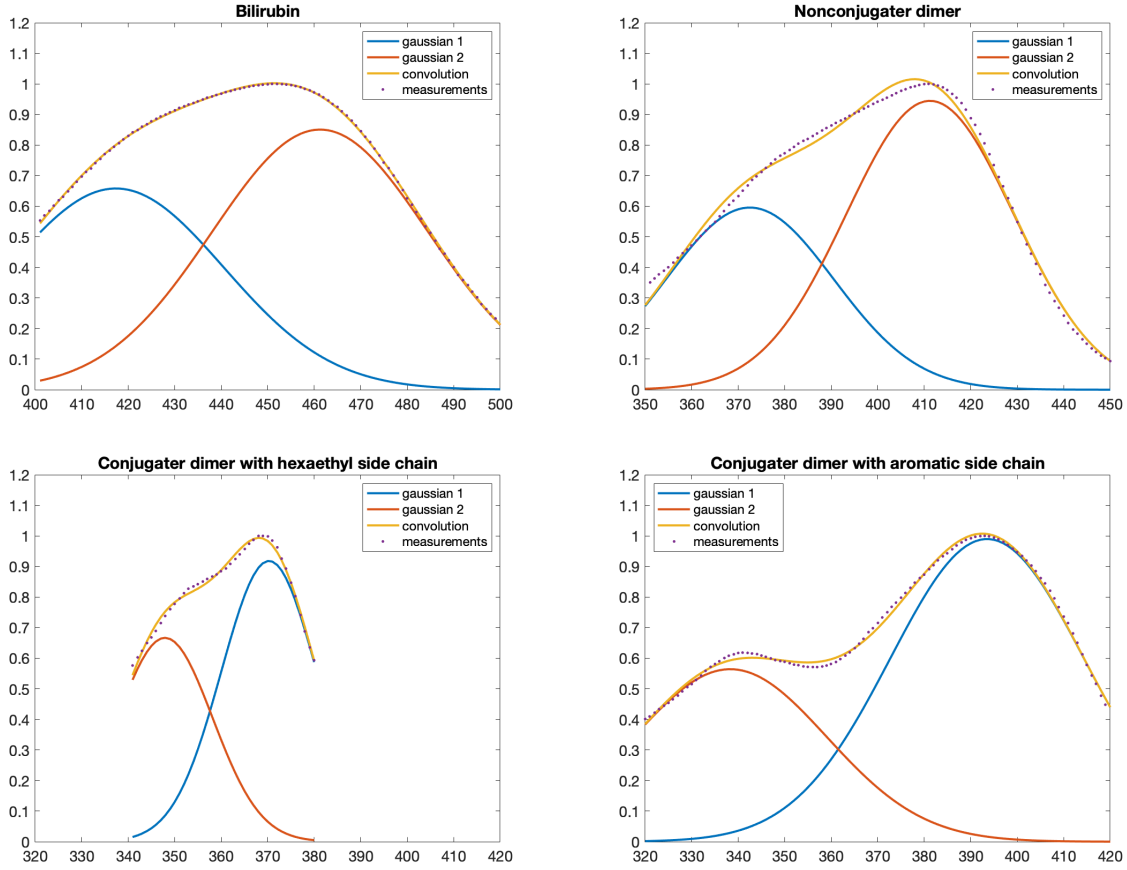
$$s(\omega) = A_1 g_1(\omega) + A_2 g_2(\omega) \tag{1}$$

where expansion coefficients A_1 and A_2 designate the relative intensities. Each of the bands is then given by:

$$g_i(\omega) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\Big(- \frac{(\omega - \omega_i^0)^2}{2\sigma^2} \Big) \tag{2}$$

where σ is a parameter to simulate the homogeneous line broadening, and ω_i^0 are vertical energies. The set of parameters A_1, A_2, σ, ω_1^0, ω_2^0 were iteratively optimized to reproduce the measurements, as shown in Figure S7.

Figure S7: Numerical deconvolution of experimental spectra using two-gaussian model for studied dimers.



The ground state potential energy surface calculation of the nonconjugated bilirubin analogue was performed successively by gradually increasing the complexity of the quantum chemical treatment. We chose two dihedral angles spanning the bridge, see Figure S8, in order to represent key internal coordinates defining the spatial orientation of bys-pyrrole monomers. While keeping α and β fixed we optimized the rest of the system using a semiempirical PM6[6] method. The resulting PM6 configurations served as starting geometries for PBE[7]/SVP[8] optimizations, which draw a potential energy landscape as depicted in Figure S8. This was performed for both cis- and trans- isomers of each of the bis-pyrrole units. We were able to locate eight most stable geometric configurations of the nonconjugated dimer. Finally, each of them was further refined by geometry optimization when unfreezing α and β with a larger basis set (TZVP[9]), and taking into account energy corrections due to ethanol solvent (PCM[10]) and van der Waals forces (D3[11]). We used Gibbs free energies to find the most stable conformer under the normal experimental condition, see Figure S9.

Figure S8: The ground state potential energy landscape of the nonconjugated bilirubin analogue. Labels denote the geometric isomerism for each of the halves.

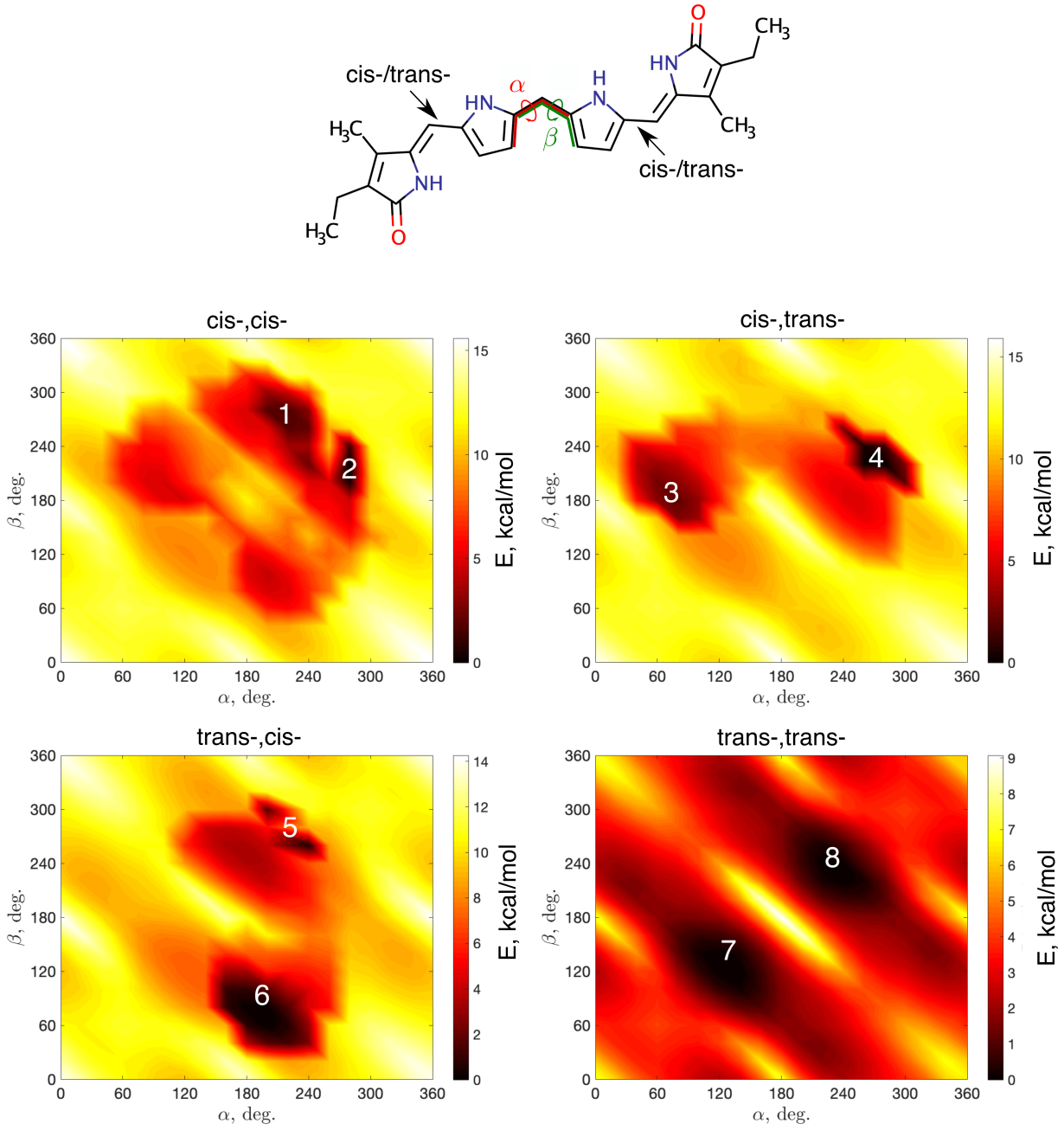
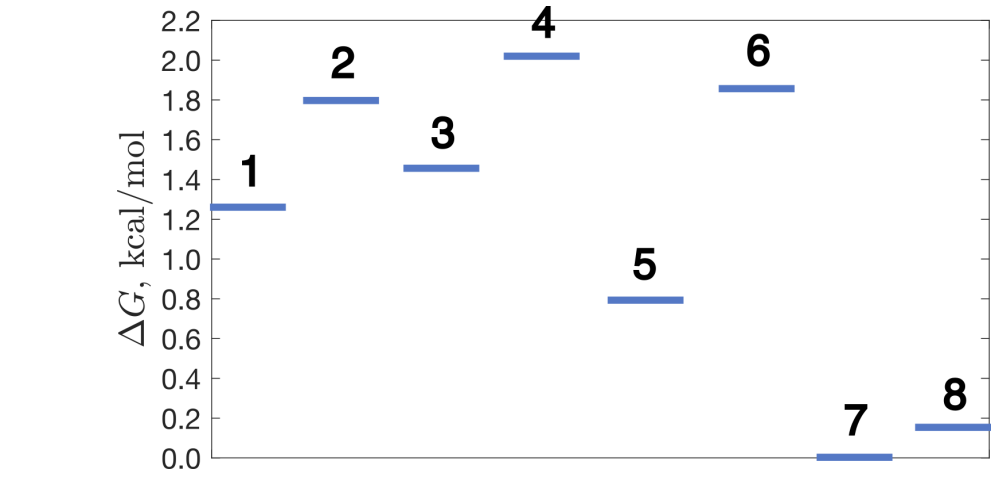


Figure S9: Difference in Gibbs free energy for the most stable isomer configurations of the nonconjugated bilirubin analogue.



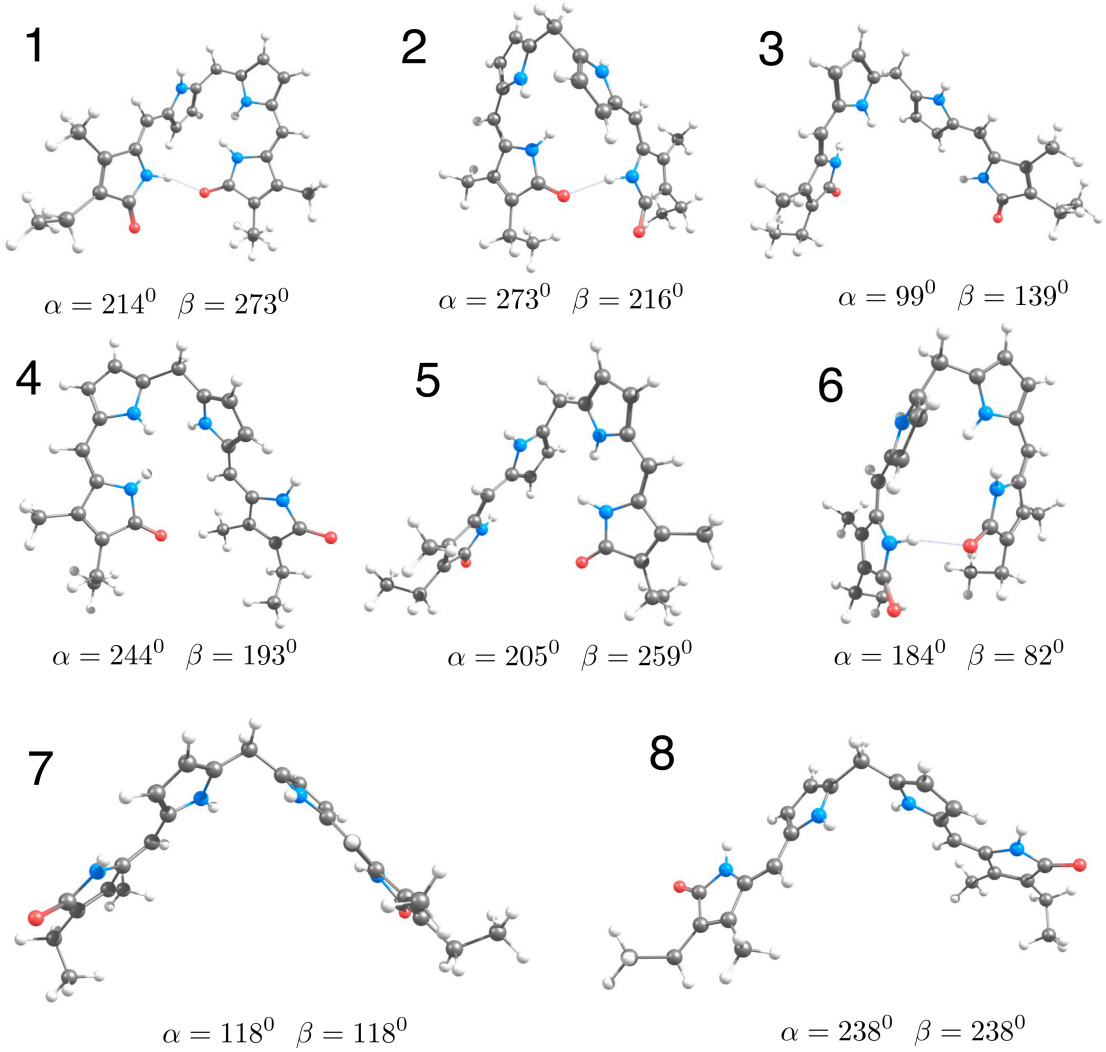


Table S1: The DFT/MRCI vertical singlet and triplet excited-state energies of the bis-pyrrole half.

	cis-					trans-					
	configuration		λ (nm)	E (eV)	f(L)	configuration		λ (nm)	E (eV)	f(L)	exp. (eV)
S_1	0.95	$\pi_1 \rightarrow \pi_1^*$	370	3.35	0.89	−0.95	$\pi_1 \rightarrow \pi_1^*$	371	3.34	0.87	3.25
S_2	−0.60	$\pi_2 \rightarrow \pi_1^*$	293	4.23	0.06	0.72	$\pi_2 \rightarrow \pi_1^*$	292	4.24	0.06	
	0.41	$\pi_3 \rightarrow \pi_1^*$				−0.41	$\pi_3 \rightarrow \pi_1^*$				
S_3	0.72	$n \rightarrow \pi_1^*$	280	4.42	0.02	−0.86	$n \rightarrow \pi_1^*$	280	4.44	0.00	
	0.39	$\pi_3 \rightarrow \pi_1^*$				0.18	$\pi_2 \rightarrow \pi_1^*$				
T_1	0.94	$\pi_1 \rightarrow \pi_1^*$		2.00		0.94	$\pi_1 \rightarrow \pi_1^*$		2.03		
T_2	−0.75	$\pi_2 \rightarrow \pi_1^*$		3.45		−0.79	$\pi_2 \rightarrow \pi_1^*$		3.45		
	0.48	$\pi_3 \rightarrow \pi_1^*$				0.46	$\pi_3 \rightarrow \pi_1^*$				
	−0.75	$\pi_4 \rightarrow \pi_1^*$		3.95		0.75	$\pi_4 \rightarrow \pi_1^*$		3.94		

Figure S10: Frontier molecular orbitals of the bis-pyrrole half.

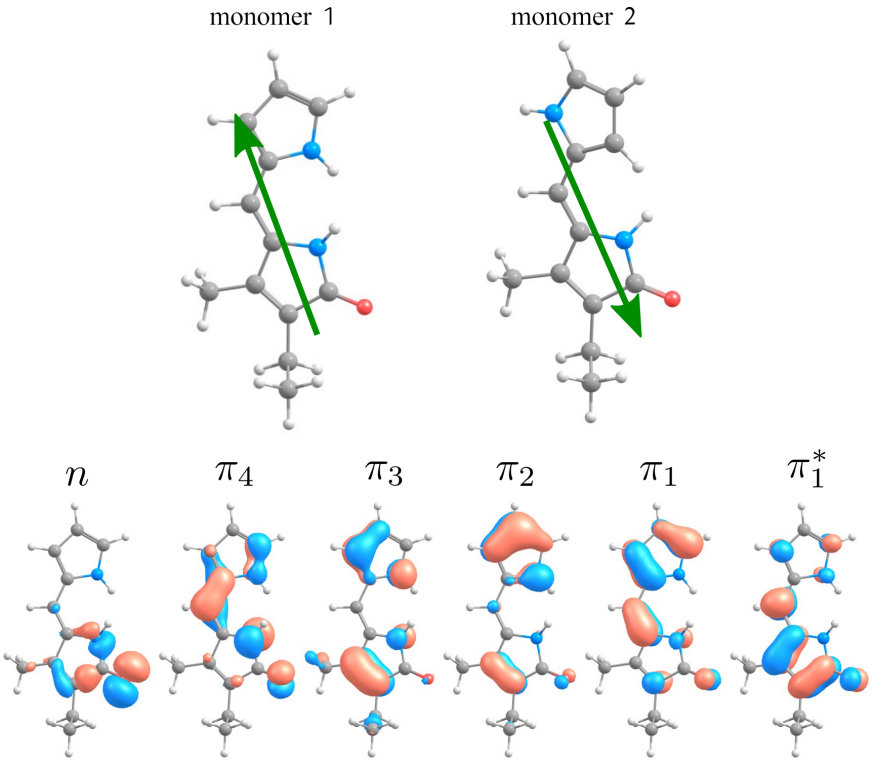


Table S2: The DFT/MRCI vertical singlet and triplet excited-state energies of bilirubin. %D and %T designate percentage of double and triple excitations in a wavefunction.

	configuration	%D	%T	λ (nm)	E (eV)	f(L)	exp. (eV)
S_1	$0.68[\pi_1 \rightarrow \pi_1^*] + 0.43[\pi_2 \rightarrow \pi_2^*] + 0.30[\pi_2 \rightarrow \pi_1^*]$	8	6	489	2.53	1.12	2.70
S_2	$0.73[\pi_1 \rightarrow \pi_2^*] + 0.47[\pi_2 \rightarrow \pi_1^*]$	11	6	460	2.70	0.55	2.99
S_3	$0.58[\pi_1\pi_2 \rightarrow \pi_1^*\pi_2^*] + 0.33[\pi_1^2 \rightarrow \pi_1^*\pi_2^*] - 0.27[\pi_2^2 \rightarrow \pi_1^*\pi_2^*]$	85	6	440	2.82	0.02	
S_4	$0.57[\pi_1 \rightarrow \pi_1^*] - 0.49[\pi_2 \rightarrow \pi_2^*] - 0.47[\pi_2 \rightarrow \pi_1^*]$	13	5	400	3.10	0.04	
S_5	$0.59[\pi_2 \rightarrow \pi_2^*] - 0.47[\pi_2 \rightarrow \pi_1^*] + 0.44[\pi_1 \rightarrow \pi_2^*]$	16	5	392	3.16	0.02	
S_6	$-0.62[\pi_3 \rightarrow \pi_2^*] + 0.35[\pi_3 \rightarrow \pi_1^*] + 0.21[\pi_2\pi_1 \rightarrow (\pi_2^*)^2] + ..$	33	5	379	3.27	0.03	
S_7	$0.67[\pi_4 \rightarrow \pi_1^*] - 0.35[\pi_4 \rightarrow \pi_2^*] + 0.20[\pi_2\pi_1 \rightarrow (\pi_1^*)^2] + ..$	29	5	360	3.44	0.09	
S_8	$0.57[\pi_5 \rightarrow \pi_1^*] - 0.50[\pi_6 \rightarrow \pi_1^*]$	18	6	336	3.69	0.08	
T_1	$-0.55[\pi_2 \rightarrow \pi_1^*] - 0.54[\pi_1 \rightarrow \pi_1^*] + 0.50[\pi_1 \rightarrow \pi_2^*]$	3	6		1.54		
T_2	$0.67[\pi_2 \rightarrow \pi_1^*] + 0.54[\pi_1 \rightarrow \pi_2^*] + 0.31[\pi_1 \rightarrow \pi_1^*]$	3	7		1.57		
T_3	$-0.75[\pi_3 \rightarrow \pi_2^*] + 0.38[\pi_3 \rightarrow \pi_1^*]$	7	6		2.67		
T_4	$-0.56[\pi_1\pi_2 \rightarrow \pi_1^*\pi_2^*] + 0.36[\pi_1\pi_2 \rightarrow (\pi_1^*)^2] + 0.34[\pi_1^2 \rightarrow \pi_1^*\pi_2^*]$	88	6		2.73		
T_5	$0.79[\pi_4 \rightarrow \pi_1^*] + 0.37[\pi_4 \rightarrow \pi_2^*]$	5	6		2.76		

Figure S11: Frontier molecular orbitals of bilirubin.

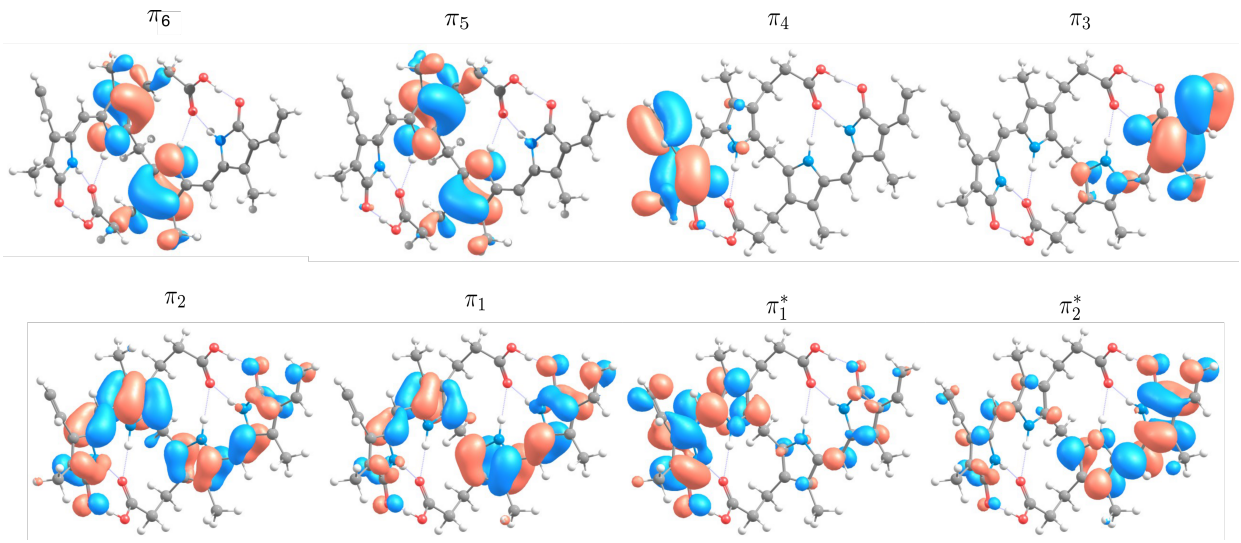


Table S3: The DFT/MRCI vertical singlet and triplet excited-state energies of the nonconjugated bilirubin analogue. %D and %T designate percentage of double and triple excitations in a wavefunction.

	configuration	%D	%T	λ (nm)	E (eV)	f(L)	exp. (eV)
S_1	$-0.73[\pi_1 \rightarrow \pi_1^*] - 0.55[\pi_2 \rightarrow \pi_2^*]$	9	5	427	2.90	0.86	3.03
S_2	$0.71[\pi_1 \rightarrow \pi_2^*] + 0.52[\pi_2 \rightarrow \pi_1^*]$	12	6	408	3.04	0.73	3.35
S_3	$-0.71[\pi_2\pi_1 \rightarrow \pi_1^*\pi_2^*] - 0.29[\pi_1^2 \rightarrow (\pi_2^*)^2] - 0.28[\pi_2^2 \rightarrow (\pi_1^*)^2]$	90	6	401	3.09	0.02	
S_4	$0.73[\pi_2 \rightarrow \pi_2^*] - 0.54[\pi_1 \rightarrow \pi_1^*]$	13	3	337	3.68	0.01	
S_5	$-0.73[\pi_2 \rightarrow \pi_1^*] + 0.55[\pi_1 \rightarrow \pi_2^*]$	12	3	336	3.69	0.02	
S_6	$0.39[\pi_3 \rightarrow \pi_2^*] + 0.37[\pi_4 \rightarrow \pi_1^*] - 0.36[\pi_2\pi_1 \rightarrow \pi_1^*\pi_2^*] + ..$	41	4	326	3.80	0.15	
S_7	$0.44[\pi_3 \rightarrow \pi_1^*] + 0.39[\pi_4 \rightarrow \pi_2^*] - 0.23[\pi_1^2 \rightarrow \pi_1^*\pi_2^*] + ..$	39	4	323	3.83	0.17	
T_1	$-0.66[\pi_1 \rightarrow \pi_2^*] - 0.62[\pi_2 \rightarrow \pi_1^*]$	3	6		1.77		
T_2	$0.67[\pi_1 \rightarrow \pi_1^*] + 0.62[\pi_2 \rightarrow \pi_2^*]$	3	6		1.79		
T_3	$0.50[\pi_1^2 \rightarrow \pi_1^*\pi_2^*] - 0.44[\pi_2^2 \rightarrow \pi_1^*\pi_2^*] + 0.42[\pi_2\pi_1 \rightarrow (\pi_1^*)^2]$	92	6		3.14		
T_4	$-0.57[\pi_3 \rightarrow \pi_2^*] - 0.44[\pi_3 \rightarrow \pi_1^*]$	16	6		3.23		
T_5	$0.55[\pi_4 \rightarrow \pi_2^*] - 0.44[\pi_4 \rightarrow \pi_1^*]$	8	6		3.24		

Figure S12: Frontier molecular orbitals of nonconjugated bilirubin analogue.

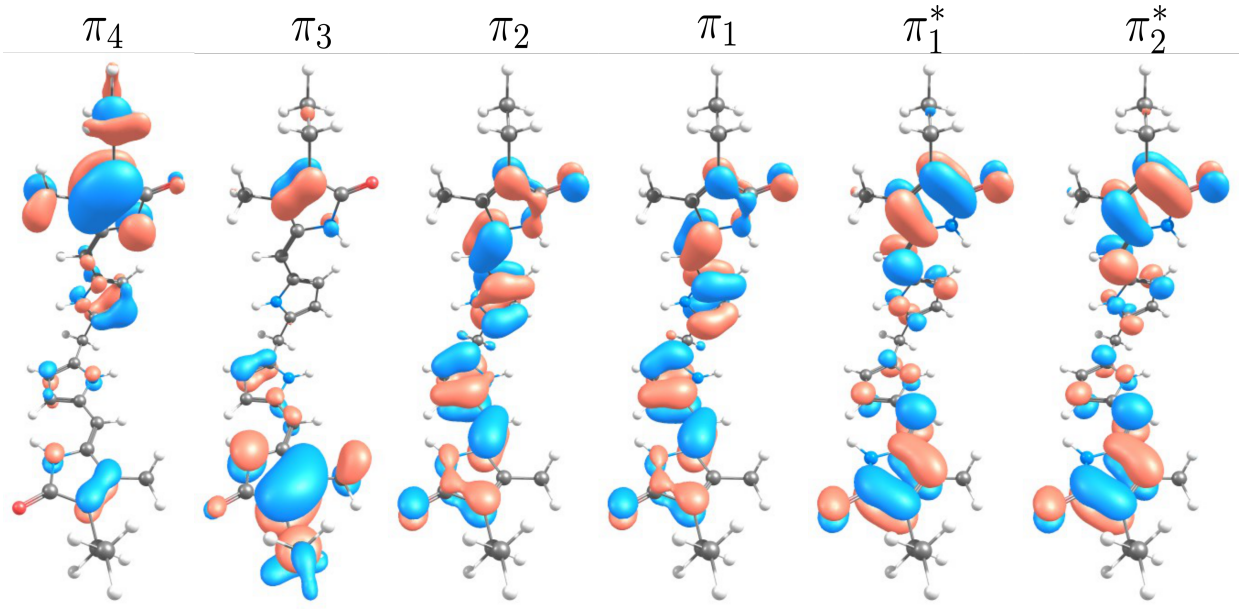


Table S4: The DFT/MRCI vertical singlet and triplet excited-state energies of the conjugated dimer with aromatic side chain. %D and %T designate percentage of double and triple excitations in a wavefunction.

	configuration	%D	%T	λ (nm)	E (eV)	f(L)	exp. (eV)
S_1	$0.91[\pi_1 \rightarrow \pi_1^*]$	10	5	677	1.83	0.57	2.03
S_2	$-0.55[\pi_2 \rightarrow \pi_1^*] + 0.45[\pi_1^2 \rightarrow \pi_1^{*2}] + 0.40[\pi_1 \rightarrow \pi_2^*]$	41	6	554	2.24	0.03	
S_3	$-0.52[\pi_4 \rightarrow \pi_1^*] - 0.38[\pi_3 \rightarrow \pi_1^*] + 0.30[\pi_1 \rightarrow \pi_2^*]$	34	6	449	2.76	0.03	
S_4	$0.46[\pi_1 \rightarrow \pi_3^*] + 0.40[\pi_4 \rightarrow \pi_1^*]$	35	6	434	2.85	0.07	
S_5	$-0.59[\pi_2 \rightarrow \pi_1^*] - 0.42[\pi_1 \rightarrow \pi_2^*] + 0.41[\pi_3 \rightarrow \pi_1^*]$	15	7	422	2.94	1.07	3.17
...							
S_8	$-0.48[\pi_3 \rightarrow \pi_1^*] - 0.46[\pi_1 \rightarrow \pi_2^*] + 0.30[\pi_4 \rightarrow \pi_1^*]$	21	7	361	3.43	0.50	3.68
...							
S_{11}	$-0.44[\pi_5 \rightarrow \pi_1^*] - 0.35[\pi_2 \rightarrow \pi_3^*] - 0.21[(\pi_2)^2 \rightarrow (\pi_1^*)^2]$	43	7	343	3.61	0.19	
T_1	$0.91[\pi_1 \rightarrow \pi_1^*]$	7	6		1.09		
T_2	$-0.68[\pi_2 \rightarrow \pi_1^*] - 0.52[\pi_1 \rightarrow \pi_2^*]$	6	6		1.83		
T_3	$0.52[\pi_1 \rightarrow \pi_3^*] + 0.38[\pi_4 \rightarrow \pi_1^*] + 0.34[\pi_2 \rightarrow \pi_2^*]$	6	7		2.38		
T_4	$-0.58[\pi_1 \rightarrow \pi_2^*] + 0.48[\pi_2 \rightarrow \pi_1^*] - 0.27[\pi_1 \rightarrow \pi_3^*]$	12	6		2.47		
T_5	$-0.56[\pi_4 \rightarrow \pi_1^*] - 0.33[\pi_3 \rightarrow \pi_1^*] + 0.27[\pi_2 \rightarrow \pi_1^*]$	12	7		2.62		

Figure S13: Frontier molecular orbitals of conjugated dimer with aromatic side chain.

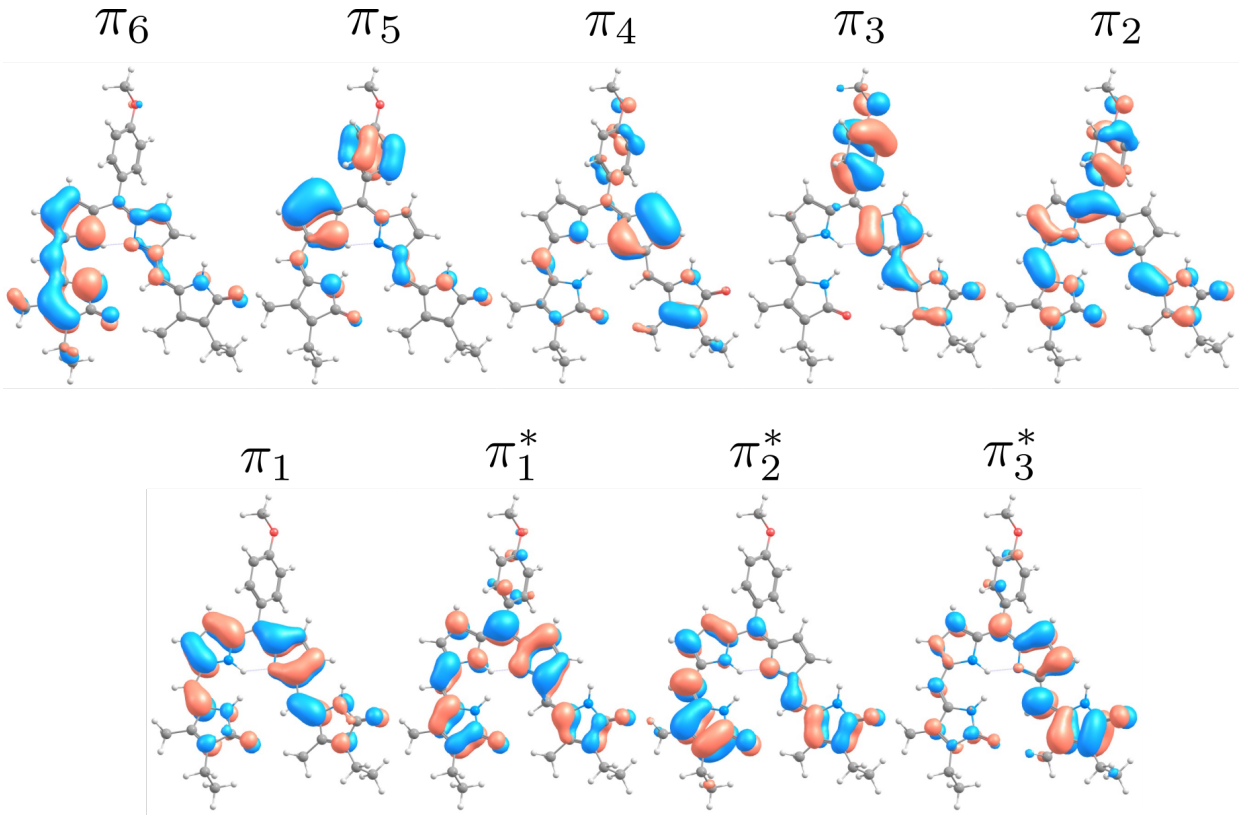


Table S5: The DFT/MRCI vertical singlet and triplet excited-state energies of the conjugated dimer with hexaethyl side chain. %D and %T designate percentage of double and triple excitations in a wavefunction.

	configuration	%D	%T	λ (nm)	E (eV)	f(L)	exp. (eV)
S_1	$0.91[\pi_1 \rightarrow \pi_1^*]$	10	4	659	1.88	0.58	2.03
S_2	$-0.50[\pi_2 \rightarrow \pi_1^*] + 0.47[(\pi_1)^2 \rightarrow (\pi_1^*)^2] + 0.45[\pi_1 \rightarrow \pi_2^*]$	44	6	532	2.33	0.00	
S_3	$-0.48[\pi_3 \rightarrow \pi_1^*] - 0.43[\pi_1 \rightarrow \pi_3^*] + 0.34[(\pi_1)^2 \rightarrow \pi_1^*\pi_2^*]$	41	5	436	2.84	0.06	
S_4	$0.52[\pi_3 \rightarrow \pi_1^*] - 0.38[\pi_1 \rightarrow \pi_3^*]$	30	6	426	2.91	0.03	
S_5	$-0.52[\pi_1 \rightarrow \pi_2^*] - 0.42[\pi_2 \rightarrow \pi_1^*] - 0.34[\pi_5 \rightarrow \pi_1^*]$	18	6	378	3.28	1.01	3.35
S_6	$-0.54[\pi_4 \rightarrow \pi_1^*] + 0.34[\pi_1 \rightarrow \pi_2^*]$	27	6	370	3.35	0.39	3.57
...							
S_8	$-0.48[\pi_6 \rightarrow \pi_1^*] - 0.48[\pi_7 \rightarrow \pi_1^*]$	31	6	350	3.54	0.13	
...							
S_{12}	$-0.38[\pi_2 \rightarrow \pi_3^*] - 0.27[\pi_6 \rightarrow \pi_1^*]$	46	7	330	3.75	0.18	
T_1	$-0.91[\pi_1 \rightarrow \pi_1^*]$	7	5		1.13		
T_2	$-0.70[\pi_2 \rightarrow \pi_1^*] - 0.56[\pi_1 \rightarrow \pi_2^*]$	6	5		1.88		
T_3	$-0.53[\pi_1 \rightarrow \pi_3^*] + 0.44[\pi_3 \rightarrow \pi_1^*] - 0.36[\pi_2 \rightarrow \pi_2^*]$	7	6		2.42		
T_4	$0.48[\pi_1 \rightarrow \pi_2^*] - 0.38[\pi_2 \rightarrow \pi_1^*] - 0.37[\pi_1 \rightarrow \pi_3^*]$	13	5		2.56		
T_5	$-0.66[\pi_3 \rightarrow \pi_1^*] - 0.31[\pi_2 \rightarrow \pi_1^*] + 0.29[\pi_2 \rightarrow \pi_1^*]$	14	6		2.72		

Figure S14: Frontier molecular orbitals of the conjugated dimer with hexaethyl side chain.

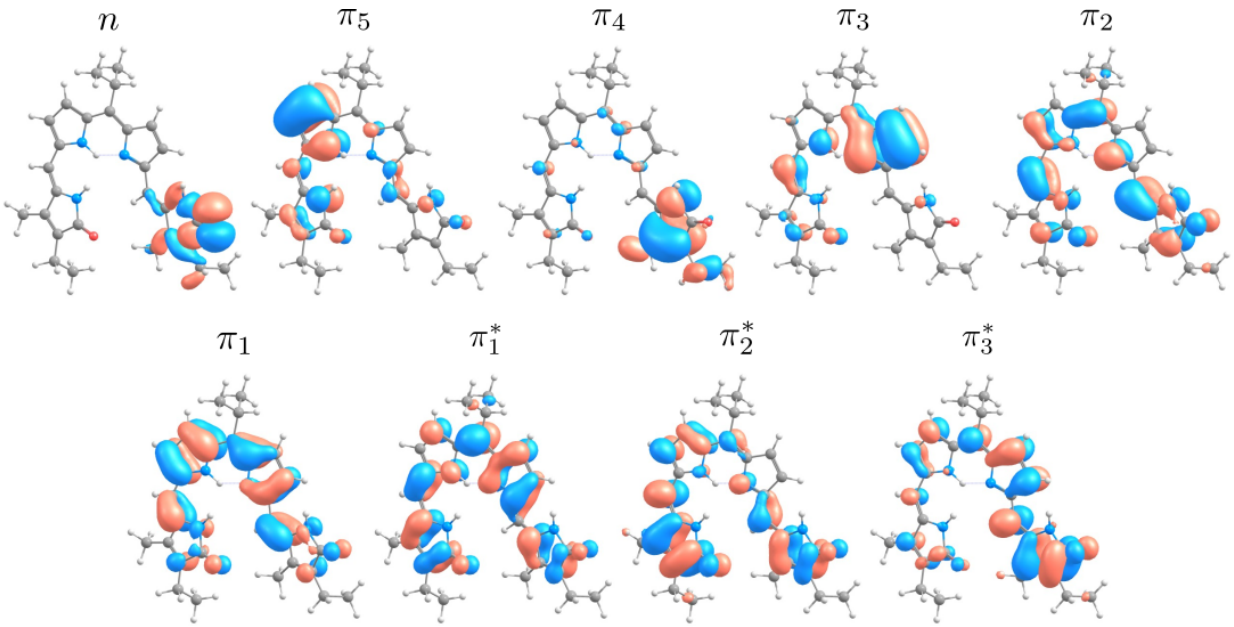


Table S6: The cartesian coordinates of bis-pyrrole half in the ground state.

cis-isomer			
C	-1.3676202	-1.0315768	4.2465564
N	-1.1450215	-0.5873837	2.9663297
C	-0.4080980	-1.5288825	2.2538109
C	-0.1462642	-2.5788285	3.1431386
C	-0.7388389	-2.2603985	4.3881435
C	-0.0622959	-0.2432997	0.1269330
C	0.1337697	-0.1326914	-1.3157320
C	0.0204401	1.1831203	-1.6760857
C	-0.2037166	1.9864926	-0.4521149
N	-0.3360489	1.0518880	0.6003693
C	-0.0478896	-1.3850512	0.8762153
C	0.3610520	-1.3118670	-2.2035873
C	0.1485282	1.8313915	-3.0139739
C	1.5197500	2.5028158	-3.2096970
O	-0.2626111	3.2055219	-0.3182196
H	0.4356956	-3.4642485	2.9034660
H	-0.7110860	-2.8558761	5.2954735
H	-0.0815988	1.3450846	1.5404820
H	0.2673273	-2.3008482	0.3737512
H	-0.5040814	-1.9932442	-2.1951110
H	1.2364433	-1.8952331	-1.8778229
H	0.5347911	-0.9980741	-3.2405122
H	-0.6372411	2.5985945	-3.1072035
H	-0.0263428	1.0921258	-3.8110004
H	1.6865007	3.2634003	-2.4347843
H	1.5771389	2.9946357	-4.1916795
H	2.3317730	1.7635464	-3.1470148
H	-1.6235688	0.1947897	2.5301759
H	-1.9508862	-0.4459036	4.9496939
trans-isomer			
O	1.0083150	-0.3156450	0.2646514
C	2.5684552	-2.9233263	-1.5845786
C	2.8218109	-2.7462479	-0.0770222
C	5.7841628	-1.5399634	0.5262100
C	5.3236174	1.4846727	1.0791177
N	2.9755422	0.9031657	0.6123002
C	2.2310344	-0.2601421	0.3643096
C	3.2326476	-1.3556108	0.2706945
C	4.4690955	-0.8323240	0.5238208
C	4.3258736	0.6056808	0.7695808
C	4.6822061	5.1242882	1.2854611
C	5.9144939	4.9616390	1.9020096
N	6.2248463	3.6264198	1.8620946
C	5.2105675	2.9034499	1.2463731
C	4.2374336	3.8447615	0.8750517
H	2.2424269	-3.9495952	-1.8084934
H	3.4804528	-2.7176284	-2.1640653
H	1.7837050	-2.2337693	-1.9251072
H	3.5850393	-3.4636325	0.2628607
H	1.8921597	-2.9782685	0.4676910
H	5.6468244	-2.6242652	0.4264763
H	6.3422900	-1.3551670	1.4573926
H	6.4213065	-1.2053297	-0.3077890
H	6.3173536	1.0516687	1.2200911
H	2.5401622	1.7669026	0.9182520
H	4.1683733	6.0689207	1.1361572
H	6.5844345	5.6832241	2.3574876
H	7.0470617	3.2061524	2.2803052
H	3.3406897	3.6376826	0.2994926

Table S7: The cartesian coordinates of bilirubin in the ground state.

C	-1.0269735	-0.7365578	-4.9057924
C	-2.1045340	0.0923359	-5.4357827
C	-2.0002917	1.3401945	-4.8423412
C	-0.8955670	1.3024130	-3.8834957
C	-0.5771024	2.2385377	-2.9298357
H	-1.1808528	3.1454899	-2.9577952
C	0.3720660	2.1984972	-1.8736565
C	0.6221324	3.2113376	-0.9157635
C	1.6187287	2.7312679	-0.0228895
C	1.9704113	1.4439152	-0.4582793
C	2.9719701	0.4430846	0.0463561
H	3.5308853	0.8957781	0.8806484
H	3.7081287	0.2262862	-0.7436655
C	2.3582784	-0.8535003	0.4966890
C	2.5367963	-2.1796296	0.0714602
C	1.7296846	-2.9950602	0.9097155
C	1.0541375	-2.1471770	1.8209703
C	0.1183593	-2.5344549	2.8158542
H	-0.0784439	-3.6073233	2.8512540
C	-0.6006225	-1.7809283	3.7125864
C	-1.6296607	-2.2430409	4.6230090
C	-2.1485768	-1.1467612	5.2999993
C	-1.4208709	0.0409385	4.8175029
N	-0.3404362	0.0308273	-3.9964056
H	0.5429031	-0.3282582	-3.6035857
N	1.2190522	1.1445910	-1.5574450
H	1.3311021	0.2523902	-2.0419916
N	1.4676111	-0.8535036	1.5307838
H	1.2256523	0.0125731	2.0152253
N	-0.5327423	-0.3959777	3.8670592
H	0.2080956	0.2479437	3.5516324
O	-0.7339009	-1.9329600	-5.1805709
C	-3.0640854	-0.3890204	-6.4676014
H	-4.0809718	-0.0070203	-6.2924898
H	-3.0948837	-1.4870666	-6.4677241
H	-2.7654776	-0.0683670	-7.4793872
C	-2.8657349	2.4734101	-5.1290213
H	-3.8898515	2.2144518	-5.4211604
C	-2.5170201	3.7724747	-5.1277006
H	-3.2451823	4.5465110	-5.3732714
H	-1.4957964	4.0986243	-4.9236824
C	-0.0405003	4.5515006	-0.8694166
H	0.6607659	5.3277324	-0.5280359
H	-0.9021071	4.5661130	-0.1809590
H	-0.4099404	4.8589075	-1.8577005
C	2.2139464	3.4874851	1.1306158
H	2.6856502	4.4125870	0.7564037
H	3.0204106	2.8945473	1.5858608
C	1.2191099	3.8899819	2.2295352
H	1.7151330	4.5514981	2.9609182
H	0.3776864	4.4726023	1.8302677
C	0.6511040	2.7314689	3.0204689
O	1.1869349	1.6085235	3.0090311
O	-0.4143538	3.0455511	3.7211839
H	-0.8077995	2.2558748	4.3104766
C	3.4325742	-2.6604659	-1.0338192
H	4.1865342	-3.3536853	-0.6224872
H	3.9919739	-1.8121530	-1.4540462
C	2.7091304	-3.3886070	-2.1768977
H	3.4472817	-3.8017219	-2.8862635
H	2.1326286	-4.2507065	-1.8151489
C	1.7799817	-2.5128888	-2.9903722
O	1.8824649	-1.2720272	-2.9789504
O	0.9121829	-3.1871960	-3.7063599
H	0.2705577	-2.5934241	-4.3187721
C	1.6118208	-4.4850573	0.8535674
H	2.5620446	-4.9449762	0.5437679
H	0.8412784	-4.8163572	0.1373353
H	1.3508418	-4.9105261	1.8326768
C	-2.0744771	-3.6641730	4.7301738
H	-1.2263918	-4.3605914	4.6597364
H	-2.7812550	-3.9249496	3.9253901
H	-2.5801001	-3.8523841	5.6860558
C	-3.2094417	-1.1396855	6.2807294
H	-3.6390505	-2.1195391	6.5153708
C	-3.7016228	-0.0550209	6.9125944
H	-4.5062759	-0.1586041	7.6415123
H	-3.3125689	0.9434469	6.7135167
O	-1.5325677	1.2496537	5.1526287

Table S8: The cartesian coordinates of the conjugated bR analogue in the ground state.

C	0.1970801	-1.3793903	-3.4069102
C	0.0948442	-0.9830483	-4.8330947
C	-0.6364667	0.1692806	-4.9039639
C	-1.0206832	0.5659014	-3.5446708
C	-1.7532168	1.6771513	-3.2149376
H	-2.1258192	2.2729436	-4.0491775
C	-2.0977597	2.1602570	-1.9211954
C	-2.9640052	3.2385010	-1.5874247
H	-3.5010659	3.8475480	-2.3093727
C	-2.9941302	3.3546029	-0.1988392
H	-3.5411812	4.0858483	0.3873962
C	-2.1505807	2.3415819	0.3314491
C	-1.7558996	2.0212979	1.6632473
C	-0.7973261	1.0232332	1.9254330
C	-0.3874912	0.5160226	3.2176780
H	-0.7542165	0.8552325	4.1822623
C	0.5328114	-0.4721868	2.9778380
H	1.0874769	-1.0250151	3.7311383
C	0.6735148	-0.5720824	1.5336010
C	1.5169151	-1.4263025	0.7581248
H	1.5740140	-1.1948314	-0.3072550
C	2.2412569	-2.5109775	1.1778032
C	3.1809761	-3.2878907	0.3562224
C	3.6854120	-4.3015707	1.1200100
C	3.0664084	-4.2263125	2.4698279
C	-2.3757988	2.7682614	2.7739079
C	-3.7709803	2.8886844	2.8762821
H	-4.4027513	2.3950654	2.1359952
C	-4.3689471	3.5878004	3.9257564
H	-5.4556215	3.6397469	3.9817552
C	-3.5642295	4.2005816	4.8984229
C	-2.1657068	4.0973208	4.8066668
H	-1.5542659	4.5922483	5.5623939
C	-1.5856556	3.3898123	3.7638130
H	-0.4988234	3.3344604	3.6870406
C	0.7636414	-1.7765948	-5.9036866
H	0.6035201	-2.8466753	-5.6938125
H	0.2976927	-1.5645573	-6.8783064
C	2.2775309	-1.5070043	-5.9752511
H	2.4793051	-0.4497690	-6.2013729
H	2.7464458	-2.1217309	-6.7571601
H	2.7576190	-1.7497600	-5.0169864
C	-0.9904408	0.9616559	-6.1187933
H	-0.6688102	0.4452865	-7.0320072
H	-0.5075430	1.9515138	-6.1057573
H	-2.0762342	1.1296856	-6.1902609
C	4.7083974	-5.3364617	0.7968065
H	4.4018851	-6.2851820	1.2662294
H	4.7415893	-5.5050043	-0.2904459
C	6.1086021	-4.9567568	1.3116810
H	6.4543631	-4.0183851	0.8539041
H	6.8384180	-5.7446791	1.0748930
H	6.0952228	-4.8211069	2.4021427
N	-0.4747631	-0.3829207	-2.6866216
H	-0.6623309	-0.4876190	-1.6935378
N	-1.6384707	1.6425968	-0.7414835
H	-0.8671744	0.9697337	-0.5040199
N	-0.1257692	0.3329324	0.9240823
N	2.2520924	-3.0806793	2.4447808
O	0.7414143	-2.3654836	-2.9110352
O	-4.0394734	4.9149027	5.9601571
O	3.1967742	-4.9795815	3.4291771
H	1.5469667	-2.9164981	3.1547125
C	3.5111509	-2.9440927	-1.0570109
H	4.1721987	-3.7007594	-1.4989505
H	2.6049029	-2.8689094	-1.6773901
H	4.0285065	-1.9728307	-1.1149751
C	-5.4550590	5.0603603	6.0787667
H	-5.8813318	5.5808374	5.2048211
H	-5.9524967	4.0838086	6.2021614
H	-5.6164298	5.6659519	6.9773255

Table S9: The cartesian coordiantes of the conjugated bR analogue with hexaethyl side chain in the ground state.

C	0.1975028	-1.3429096	-3.3901538
C	0.1068137	-0.9628078	-4.8212741
C	-0.5873685	0.2111170	-4.9068224
C	-0.9583999	0.6365886	-3.5522006
C	-1.6666142	1.7671994	-3.2369292
H	-2.0314571	2.3579043	-4.0781501
C	-2.0080133	2.2660234	-1.9476973
C	-2.9029676	3.3229186	-1.6223699
H	-3.4551313	3.9151791	-2.3466359
C	-2.9516783	3.4321464	-0.2353628
H	-3.5516873	4.1383080	0.3270859
C	-2.0783984	2.4479259	0.3102540
C	-1.7139081	2.0890255	1.6417492
C	-0.7918220	1.0544632	1.8876078
C	-0.2914970	0.6022748	3.1713247
H	-0.5492972	0.9975051	4.1498368
C	0.6058127	-0.4021950	2.9201030
H	1.2186332	-0.9131694	3.6578363
C	0.6529120	-0.5689665	1.4764738
C	1.4648233	-1.4552563	0.7007929
H	1.4978803	-1.2638118	-0.3735498
C	2.1922159	-2.5282691	1.1453365
C	3.1278100	-3.3313301	0.3435189
C	3.6352707	-4.3207968	1.1362525
C	3.0208731	-4.2049715	2.4852671
C	0.7447911	-1.7939223	-5.8822569
H	0.5575265	-2.8549284	-5.6500583
H	0.2757863	-1.5875491	-6.8566236
C	2.2646929	-1.5673996	-5.9724022
H	2.4933059	-0.5211063	-6.2225374
H	2.7096907	-2.2111961	-6.7449008
H	2.7468000	-1.8030876	-5.0133435
C	-0.9199843	0.9954964	-6.1327376
H	-0.6069305	0.4597505	-7.0377692
H	-0.4160447	1.9748316	-6.1317765
H	-2.0017397	1.1857917	-6.2101572
C	4.6616795	-5.3610881	0.8439218
H	4.3593301	-6.2958802	1.3429384
H	4.6949306	-5.5633513	-0.2375556
C	6.0601496	-4.9592348	1.3465562
H	6.4055735	-4.0383059	0.8544188
H	6.7917894	-5.7542276	1.1414493
H	6.0439392	-4.7819976	2.4310058
N	-0.4398569	-0.3163848	-2.6815625
H	-0.6311925	-0.4049534	-1.6866024
N	-1.5352304	1.7740953	-0.7661569
H	-0.8081966	1.0550225	-0.5250068
N	-0.1802637	0.3099137	0.8796096
N	2.2105178	-3.0570351	2.4303495
O	0.7088507	-2.3407449	-2.8823192
O	3.1519796	-4.9307207	3.4650166
H	1.5011921	-2.8767532	3.1326471
C	3.4618631	-3.0266378	-1.0776124
H	4.0990337	-3.8114304	-1.5055855
H	2.5566582	-2.9351979	-1.6967033
H	4.0086089	-2.0728673	-1.1559483
C	-2.3252049	2.8314052	2.8177038
H	-1.9049289	2.3780188	3.7248829
C	-1.9232740	4.3174937	2.8520524
H	-2.2885339	4.7809130	3.7807376
H	-0.8299796	4.4278400	2.8220190
H	-2.3392415	4.8813822	2.0071384
C	-3.8500278	2.6371600	2.9099959
H	-4.3815851	3.0989092	2.0679218
H	-4.1083633	1.5688017	2.9228314
H	-4.2273975	3.0913592	3.8383691

Table S10: The cartesian coordinates of the nonconjugated bR analogue in the ground state (isomer 1).

C	-0.2162350	-1.6653479	1.8735289
C	-0.6048040	-2.2534858	0.6589079
N	0.3935770	-3.1644378	0.3329190
C	1.3955879	-3.1547798	1.2704099
C	1.0252129	-2.2319058	2.2523378
C	-2.6924878	-1.1142599	-0.1697950
C	-3.9712067	-1.1274369	-0.8851409
C	-4.6113156	0.0567250	-0.6405570
C	-3.7343277	0.8841179	0.2205850
N	-2.6163338	0.1007750	0.5193130
C	3.4868807	-2.8133168	0.0457560
N	3.2242738	-1.4722049	0.0992320
C	3.9408937	-0.7802469	-0.8641569
C	4.7048916	-1.7443709	-1.5440239
C	4.4067977	-3.0119938	-0.9854629
C	2.7500738	1.4099159	-0.6368810
C	2.6588258	2.8640538	-0.6887199
C	1.4830159	3.2519728	-0.0920470
C	0.7627429	2.0402658	0.3327200
N	1.5946789	0.9646319	0.0328770
C	-1.7835809	-2.1350118	-0.1494920
C	2.7470248	-3.7408587	0.9810679
C	3.7818627	0.6233160	-1.0809399
C	-4.4698377	-2.2907978	-1.6787389
C	-5.9629285	0.5236870	-1.0707429
C	-7.0498125	0.2394650	-0.0175150
O	-3.9165527	2.0463508	0.6106420
C	3.7307087	3.7430387	-1.2447789
C	0.9507639	4.6233186	0.1683790
C	1.3406079	5.1562606	1.5594719
O	-0.3666170	1.9390389	0.8484979
H	-0.7977059	-0.9410569	2.4357908
H	0.4246460	-3.6900507	-0.5366560
H	1.6075089	-1.9956428	3.1397418
H	-1.7320819	0.5549500	0.7927029
H	5.3645756	-1.5389219	-2.3833488
H	4.8019646	-3.9740367	-1.3003879
H	1.1988649	0.0313410	-0.0578380
H	-1.9872058	-2.9679538	-0.8273129
H	3.2952457	-3.8634717	1.9292889
H	2.6770348	-4.7387036	0.5227070
H	4.5597097	1.1137589	-1.6688399
H	-5.3828766	-2.0293218	-2.2287998
H	-4.7060746	-3.1471328	-1.0274089
H	-3.7210637	-2.6362548	-2.4080198
H	-6.2405825	0.0493090	-2.0248398
H	-5.9158095	1.6096189	-1.2536129
H	-7.1448985	-0.8410679	0.1652290
H	-8.0270634	0.6189530	-0.3507270
H	-6.8036025	0.7243499	0.9383809
H	4.0803777	3.3860487	-2.2250618
H	4.6073736	3.7709057	-0.5782680
H	3.3723807	4.7734786	-1.3648799
H	-0.1480240	4.5927916	0.0893210
H	1.3085239	5.3188586	-0.6066350
H	0.9698869	4.4897157	2.3518478
H	0.9149109	6.1562785	1.7286859
H	2.4337298	5.2266566	1.6598699
H	2.6661298	-1.0518189	0.8405209

Table S11: The cartesian coordinates of the nonconjugated bR analogue in the ground state (isomer 2).

C	4.7880536	-0.7428479	-1.8170179
C	3.9403467	-0.0164900	-0.9631729
N	3.4624627	-0.9281469	-0.0355740
C	3.9489817	-2.1837478	-0.2760520
C	4.7775916	-2.0960658	-1.3960669
C	2.3963868	1.8668099	-0.3831550
C	2.0270428	3.2735178	-0.2711170
C	0.8738119	3.3671897	0.4702400
C	0.4434580	2.0034598	0.8216979
N	1.4220919	1.1446259	0.3305010
C	2.0606998	-3.0417538	1.0172749
N	1.0127219	-3.1214048	0.1348440
C	-0.1030850	-2.4498348	0.6213130
C	0.2601890	-1.9501769	1.8824229
C	1.6044779	-2.3244978	2.1264798
C	-2.4017188	-1.6052459	0.0244020
C	-3.6925807	-1.7531299	-0.6541800
C	-4.5100087	-0.7347289	-0.2474270
C	-3.7426497	0.1265020	0.6828679
N	-2.4972298	-0.4829630	0.8531389
C	3.5049097	1.3443919	-0.9983899
C	3.4706927	-3.3279417	0.5868730
C	-1.3346959	-2.4482538	-0.1138490
C	2.8391508	4.3886047	-0.8445699
C	0.0766820	4.5711277	0.8559769
C	-1.1195699	4.8148656	-0.0828160
O	-0.5779710	1.6355539	1.4327079
C	-4.0172827	-2.8728788	-1.5886129
C	-5.9122745	-0.4110730	-0.6482390
C	-5.9760265	0.6135580	-1.7962889
O	-4.1013037	1.1833279	1.2223119
H	5.3093846	-0.3302160	-2.6771278
H	2.9190678	-0.7006559	0.7951469
H	5.2999076	-2.9284948	-1.8598639
H	1.2054159	0.1603440	0.1879210
H	-0.3973330	-1.4140009	2.5600258
H	2.1966758	-2.0938968	3.0087878
H	-1.6923739	0.0731120	1.1787359
H	4.1123487	2.0329398	-1.5884209
H	3.5513127	-4.2681167	0.0209660
H	4.1029217	-3.4395687	1.4826269
H	-1.4353049	-3.2201698	-0.8813319
H	2.3341898	5.3537446	-0.7136669
H	3.0144578	4.2426237	-1.9215769
H	3.8272067	4.4544007	-0.3626400
H	0.7239199	5.4612646	0.8708409
H	-0.2973090	4.4324707	1.8834809
H	-0.7785609	4.9834546	-1.1149379
H	-1.6936489	5.6966296	0.2378860
H	-1.7974789	3.9490937	-0.0846920
H	-3.9502787	-3.8503257	-1.0858959
H	-3.3197517	-2.8995038	-2.4405028
H	-5.0325936	-2.7685788	-1.9914698
H	-6.4432945	-0.0023640	0.2267740
H	-6.4423725	-1.3298519	-0.9431619
H	-5.4711246	1.5482779	-1.5126659
H	-7.0192675	0.8520279	-2.0510558
H	-5.4830166	0.2214700	-2.6980868
H	1.0752719	-3.5200977	-0.7981889

Table S12: The cartesian coordinates of the nonconjugated bR analogue in the ground state (isomer 3).

C	-3.3554077	3.4067397	1.4892799
C	-3.2347818	2.1284168	0.9221179
N	-2.2980568	2.2439868	-0.1011520
C	-1.8164949	3.5279557	-0.1691740
C	-2.4754778	4.2763887	0.8037719
C	-3.9908117	-0.2582040	0.6012100
C	-4.5566717	-1.5116419	1.0891189
C	-4.4379177	-2.4585338	0.1033000
C	-3.8256767	-1.8217909	-1.0791339
N	-3.5076897	-0.5128150	-0.6929569
C	0.2972500	2.8717148	-1.3244469
N	1.2754329	2.6871568	-0.3828950
C	2.0741588	1.5937539	-0.6999609
C	1.5669279	1.0808009	-1.9069409
C	0.4617390	1.8760889	-2.2880618
C	3.9433727	0.1100800	0.1098330
C	5.1078956	-0.1751620	0.9490389
C	5.5885146	-1.4148029	0.6177960
C	4.7278296	-1.9769988	-0.4471970
N	3.7878407	-0.9872589	-0.7386519
C	-3.9023737	0.9208579	1.2904389
C	-0.7716119	3.9116867	-1.1795819
C	3.1758448	1.2409879	0.1426400
C	-5.1156666	-1.6879419	2.4634628
C	-4.8784186	-3.8867047	0.0930020
C	-6.2927265	-4.0660617	-0.4893770
O	-3.6149137	-2.2958678	-2.2045488
C	5.6603056	0.7819929	1.9542009
C	6.7802775	-2.1503268	1.1372699
C	8.0340234	-1.9338029	0.2698330
O	4.7823676	-3.0885008	-0.9919479
H	-4.0290887	3.6618967	2.3034348
H	-1.8442729	1.4636009	-0.5713310
H	-2.3274358	5.3376596	0.9849139
H	-3.3943587	0.2085070	-1.4003339
H	1.9832098	0.2605100	-2.4836148
H	-0.1510510	1.7598189	-3.1782518
H	2.9618168	-1.1739619	-1.2979349
H	-4.4129857	0.9548749	2.2548468
H	-1.2370979	4.0601847	-2.1681678
H	-0.3429020	4.8822946	-0.8868609
H	3.4329687	1.9633519	0.9214919
H	-5.5134176	-2.7011138	2.6014708
H	-5.9332575	-0.9761589	2.6572248
H	-4.3485647	-1.5157019	3.2344288
H	-4.8446136	-4.2984917	1.1135569
H	-4.1647907	-4.4708117	-0.5102140
H	-7.0354525	-3.5210817	0.1117640
H	-6.5773135	-5.1285226	-0.5063240
H	-6.3425165	-3.6826237	-1.5187979
H	4.8802166	1.1450399	2.6406788
H	6.0981105	1.6662269	1.4644989
H	6.4481045	0.3103130	2.5551658
H	6.5437005	-3.2264558	1.1648329
H	6.9907325	-1.8429029	2.1733368
H	7.8535764	-2.2570948	-0.7657439
H	8.8860733	-2.5079098	0.6628099
H	8.3162904	-0.8708769	0.2486410
H	1.3774129	3.2439308	0.4614090

Table S13: The cartesian coordinates of the nonconjugated bR analogue in the ground state (isomer 4).

C	-5.2421346	-1.5598869	0.7150419
C	-4.2246997	-0.7609439	0.1707250
N	-3.1539358	-1.6137419	-0.0756030
C	-3.4641937	-2.9012388	0.2840680
C	-4.7594796	-2.8864778	0.8010779
C	-3.0996708	1.4635319	-0.1783960
C	-3.0949158	2.8835928	-0.5137530
C	-1.7966679	3.3285817	-0.5160220
C	-0.9206079	2.2033378	-0.1352670
N	-1.7549069	1.0848059	-0.0250830
C	-1.1022479	-3.5825417	-0.2245860
N	-0.3911190	-2.7735588	0.6283700
C	0.8330589	-2.4158638	0.0728650
C	0.8852969	-3.0421648	-1.1843599
C	-0.3202830	-3.7581837	-1.3651319
C	2.9429648	-1.0816389	0.4142060
C	3.6834777	0.0321800	1.0066079
C	4.9050646	0.1155620	0.3913140
C	4.9960016	-0.9706669	-0.6096620
N	3.7581177	-1.6170529	-0.5845840
C	-4.1945117	0.6514000	-0.0511010
C	-2.4955078	-4.0375707	0.0780880
C	1.6747219	-1.4712969	0.7406779
C	-4.3296467	3.6619937	-0.8323229
C	-1.2560169	4.6991486	-0.7666569
C	-1.0754029	5.5105906	0.5297480
O	0.3034090	2.1956648	0.0659090
C	3.1113778	0.9406609	2.0448538
C	5.9992025	1.1163939	0.5730170
C	5.8876126	2.2980748	-0.4082320
O	5.9476285	-1.2880549	-1.3370489
H	-6.2083155	-1.1911149	1.0501849
H	-2.3335498	-1.3706499	-0.6253140
H	-5.2865336	-3.7502297	1.1975729
H	-1.4596599	0.2832830	0.5256050
H	1.6762539	-2.9360088	-1.9203339
H	-0.6146540	-4.3305797	-2.2407748
H	3.6131837	-2.5204448	-1.0246009
H	-5.1698376	1.1400389	-0.0956370
H	-2.5171608	-4.6815236	0.9743339
H	-2.8303568	-4.6724906	-0.7577159
H	1.2315059	-0.9586629	1.5980999
H	-4.0962177	4.7193926	-1.0088659
H	-5.0581096	3.6112317	-0.0080520
H	-4.8313106	3.2695088	-1.7305119
H	-1.9190119	5.2455336	-1.4551189
H	-0.2803210	4.6052866	-1.2702969
H	-2.0391658	5.6509316	1.0411099
H	-0.6529920	6.5032195	0.3145560
H	-0.3959420	4.9930746	1.2223809
H	2.7332068	0.3774200	2.9122108
H	2.2647268	1.5148819	1.6341659
H	3.8649897	1.6524039	2.4052848
H	6.9668355	0.6114620	0.4201440
H	5.9954255	1.4943089	1.6072269
H	5.9169255	1.9459519	-1.4497839
H	6.7165715	3.0067718	-0.2643060
H	4.9418856	2.8402718	-0.2613010
H	-0.7005089	-2.4967458	1.5563669

Table S14: The cartesian coordinates of the nonconjugated bR analogue in the ground state (isomer 5).

C	-0.9574389	-1.8029689	1.8120899
C	-1.2211969	-1.9329569	0.4371810
N	-0.2775770	-2.8311528	-0.0499740
C	0.5523520	-3.2660728	0.9512019
C	0.1470690	-2.6288098	2.1240898
C	-3.2531388	-0.5600260	-0.1495920
C	-4.1345017	0.1108690	-1.1067269
C	-5.1066936	0.7770619	-0.4087520
C	-4.8916866	0.5314130	1.0354299
N	-3.7345237	-0.2433650	1.1208859
C	2.8307448	-3.3473357	-0.0404000
N	2.9194348	-1.9854618	0.0873000
C	4.0020727	-1.4916269	-0.6304940
C	4.6101976	-2.6045698	-1.2331209
C	3.8687397	-3.7560687	-0.8771179
C	3.5361757	0.9724879	-0.4465240
C	3.9348997	2.3751858	-0.4096710
C	2.8374508	3.1343868	-0.0883130
C	1.6771819	2.2337138	0.0579820
N	2.1755568	0.9336799	-0.0938510
C	-2.1624008	-1.3256959	-0.4538380
C	1.7547459	-4.1168217	0.6801219
C	4.3333737	-0.1046280	-0.7277239
C	-3.9407837	0.0593400	-2.5871908
C	-6.2621565	1.5822099	-0.9079839
C	-7.5467234	0.7459299	-1.0564649
O	-5.5658616	0.9120749	2.0026168
C	5.3357486	2.8456878	-0.6279920
C	2.7296938	4.6074186	0.1355230
C	2.9284368	4.9984746	1.6116239
O	0.4858730	2.5127368	0.2568390
H	-1.4688099	-1.1448119	2.5075048
H	-0.2108880	-3.1214278	-1.0218789
H	0.6198720	-2.7484648	3.0953368
H	-3.4433567	-0.6912199	1.9833478
H	5.4742776	-2.5590428	-1.8912999
H	4.0557907	-4.7792846	-1.1917799
H	1.5467989	0.1845740	-0.3732290
H	-1.9864748	-1.4896879	-1.5199739
H	2.1330728	-4.4920877	1.6451479
H	1.4941589	-5.0055766	0.0832870
H	5.3417626	0.1136750	-1.0842999
H	-3.9827087	-0.9756849	-2.9611408
H	-2.9617228	0.4697350	-2.8793938
H	-4.7176146	0.6341700	-3.1067508
H	-6.0087455	2.0442368	-1.8746489
H	-6.4491465	2.4057748	-0.2000140
H	-7.4029994	-0.0657480	-1.7848349
H	-8.3837274	1.3716299	-1.3999699
H	-7.8310634	0.2926380	-0.0957650
H	5.7795976	2.3961918	-1.5290799
H	5.9831755	2.5748968	0.2211270
H	5.3721596	3.9370757	-0.7387949
H	1.7317139	4.9390396	-0.1938350
H	3.4656437	5.1383436	-0.4882620
H	2.1874418	4.4983027	2.2522708
H	2.8185978	6.0845415	1.7473599
H	3.9297557	4.7080696	1.9623569
H	2.3601488	-1.4538429	0.7510119

Table S15: The cartesian coordinates of the nonconjugated bR analogue in the ground state (isomer 6).

C	-0.6603169	-2.3288148	1.5563589
C	-0.3326910	-2.4669208	0.1978880
N	-1.5221009	-2.7706108	-0.4563500
C	-2.5771168	-2.8048238	0.4262690
C	-2.0524468	-2.5397638	1.6926569
C	2.0583608	-1.7596829	-0.1533250
C	3.3221887	-1.7921959	-0.8929759
C	4.2445107	-1.0547089	-0.2012690
C	3.5811047	-0.4983500	0.9999839
N	2.2788448	-1.0072259	1.0055529
C	-4.4130327	-1.3556289	-0.3782680
N	-3.4980137	-0.3482940	-0.2714940
C	-4.0481877	0.8775589	-0.6124970
C	-5.3897446	0.6166230	-0.9431739
C	-5.6165776	-0.7726419	-0.7877039
C	-2.0449248	2.2323028	-0.0035890
C	-1.0758679	3.3000917	-0.2074810
C	0.0686410	2.9925908	0.4920450
C	-0.1613760	1.7361389	1.2210899
N	-1.4226619	1.2849959	0.8348319
C	0.8992479	-2.3793088	-0.5296410
C	-3.9997147	-2.7737888	-0.0483230
C	-3.2720318	2.0771718	-0.5988880
C	3.5208017	-2.5479168	-2.1664038
C	5.6641426	-0.7335399	-0.5373930
C	5.8005456	0.6038800	-1.2895399
O	4.0509867	0.2671080	1.8537819
C	-1.3011069	4.4596977	-1.1217709
C	1.3915709	3.6856967	0.5225730
C	2.3916218	3.0753128	-0.4780490
O	0.5750020	1.1481039	2.0353878
H	0.0451270	-2.1269858	2.3565598
H	-1.6058949	-2.8933408	-1.4621499
H	-2.6346958	-2.4831258	2.6087028
H	1.5385969	-0.4992430	1.5058879
H	-6.1182205	1.3677839	-1.2379959
H	-6.5526515	-1.3015719	-0.9451739
H	-1.9363339	0.6531630	1.4456999
H	0.9110189	-2.8512258	-1.5156729
H	-4.1388977	-3.4224177	-0.9291059
H	-4.6570456	-3.1743468	0.7385149
H	-3.6790507	2.9323428	-1.1410249
H	4.5419957	-2.4190268	-2.5465868
H	2.8258578	-2.2043278	-2.9487798
H	3.3432647	-3.6257627	-2.0277538
H	6.1034525	-1.5432559	-1.1404039
H	6.2441165	-0.6794879	0.3980890
H	5.2564086	0.5722030	-2.2451098
H	6.8563165	0.8279739	-1.5022429
H	5.3883056	1.4306589	-0.6932199
H	-2.2870408	4.9195946	-0.9572839
H	-1.2608899	4.1474537	-2.1774878
H	-0.5352430	5.2319796	-0.9746889
H	1.8086279	3.6033827	1.5394469
H	1.2638299	4.7587156	0.3124780
H	2.5507728	2.0074608	-0.2689950
H	3.3668497	3.5803887	-0.4157470
H	2.0205938	3.1684308	-1.5093729
H	-2.5051658	-0.5050510	-0.1191740

Table S16: The cartesian coordinates of the nonconjugated bR analogue in the ground state (isomer 7).

C	2.9747438	2.2591348	-1.3777769
C	2.8931378	1.7379029	-0.0738570
N	1.8172799	2.3822768	0.5282800
C	1.2223119	3.2604028	-0.3382540
C	1.9330079	3.2017988	-1.5364639
C	4.6135616	-0.0831820	0.2019340
C	5.4308636	-0.9887439	1.0095169
C	6.2535455	-1.6951529	0.1715030
C	5.9676215	-1.2782509	-1.2193889
N	5.0039406	-0.2739750	-1.1243639
C	-1.1684759	3.2064358	0.4089720
N	-1.7316009	2.3245608	-0.4747880
C	-2.7795198	1.6259349	0.1158730
C	-2.8768168	2.1150908	1.4311159
C	-1.8721499	3.0940558	1.6075629
C	-4.4313777	-0.2514400	-0.1929280
C	-5.2246116	-1.1654669	-1.0144619
C	-6.0079425	-1.9258369	-0.1856360
C	-5.7255236	-1.5298779	1.2118409
N	-4.8057596	-0.4831480	1.1319479
C	3.6678157	0.7891149	0.6652439
C	0.0104910	4.0590887	0.0425250
C	-3.5189867	0.6633499	-0.6411740
C	5.3505846	-1.0718139	2.4992258
C	7.2492104	-2.7645148	0.4844410
C	6.6472315	-4.1793577	0.3990250
O	6.4549715	-1.6992459	-2.2784238
C	-5.1796236	-1.1916439	-2.5074698
C	-7.0278795	-2.9646118	-0.5207260
C	-8.4522164	-2.3875298	-0.6177350
O	-6.1754005	-2.0019938	2.2658608
H	3.7368387	2.0295798	-2.1165298
H	1.4790189	2.1810918	1.4658699
H	1.7175079	3.7955797	-2.4208868
H	4.5040537	0.0791800	-1.9335759
H	-3.6265457	1.8388179	2.1664198
H	-1.6766669	3.6762697	2.5042298
H	-4.2953107	-0.1486760	1.9428809
H	3.4737297	0.7457639	1.7399439
H	0.2317520	4.7155886	0.8992799
H	-0.2369670	4.7207426	-0.8030309
H	-3.3260657	0.6495090	-1.7168669
H	6.0669295	-1.8040709	2.8924038
H	4.3449687	-1.3763609	2.8295268
H	5.5649096	-0.0998700	2.9699858
H	7.6714114	-2.6034128	1.4884899
H	8.0849044	-2.6858748	-0.2296620
H	5.8297786	-4.3012397	1.1249069
H	7.4104004	-4.9431116	0.6096830
H	6.2404675	-4.3709487	-0.6045270
H	-4.1474297	-1.2692229	-2.8817258
H	-5.6114156	-0.2732670	-2.9358538
H	-5.7484936	-2.0425588	-2.9033468
H	-7.0072015	-3.7413927	0.2607650
H	-6.7650535	-3.4585007	-1.4691119
H	-8.7466583	-1.9111569	0.3288090
H	-9.1814863	-3.1800028	-0.8418719
H	-8.5139063	-1.6292149	-1.4121599
H	-1.3910779	2.1593568	-1.4185119

Table S17: The cartesian coordinates of the nonconjugated bR analogue in the ground state (isomer 8).

C	2.9176418	1.9922538	1.4078389
C	2.7909378	1.3454249	0.1652910
N	1.7202529	1.9588039	-0.4766310
C	1.1860209	2.9537128	0.2983220
C	1.9161219	2.9869228	1.4858699
C	4.6573636	-0.3286810	-0.0956210
C	5.2875766	-1.4841459	-0.7344859
C	6.4537315	-1.7648129	-0.0716490
C	6.6223925	-0.7706489	1.0116199
N	5.4843396	0.0352210	0.9682649
C	-1.1891129	2.9500998	-0.5035400
N	-1.7662489	2.0879138	0.3905640
C	-2.8575708	1.4375019	-0.1755990
C	-2.9528208	1.9191099	-1.4938429
C	-1.9119269	2.8549228	-1.6921909
C	-4.7892636	-0.1149560	0.2772570
C	-5.4637656	-1.1660599	1.0384829
C	-6.6408715	-1.4727219	0.4066610
C	-6.7679305	-0.6045740	-0.7847519
N	-5.5956556	0.1516760	-0.8310049
C	3.4793827	0.2605270	-0.4636070
C	0.0144370	3.7744087	-0.1538600
C	-3.5915207	0.4707650	0.5816120
C	4.7013026	-2.2071868	-1.9032319
C	7.4817364	-2.8140358	-0.3456620
C	8.6223103	-2.3048998	-1.2464279
O	7.5564904	-0.6401410	1.8158049
C	-4.8957906	-1.7954119	2.2685838
C	-7.6656664	-2.5062198	0.7429519
C	-7.4264984	-3.8383397	0.0084030
O	-7.7008054	-0.5204610	-1.5965329
H	3.6181877	1.7379799	2.1974868
H	1.3842529	1.7070119	-1.4026209
H	1.7277099	3.6612827	2.3170678
H	5.4106036	0.9003969	1.4932299
H	-3.6593967	1.5891989	-2.2494628
H	-1.6923819	3.4056457	-2.6030548
H	-5.5002546	0.9646739	-1.4311249
H	3.0090098	-0.1477180	-1.3619109
H	-0.2242040	4.4915327	0.6482890
H	0.2789400	4.3757587	-1.0387649
H	-3.1416858	0.1619880	1.5287079
H	5.3316466	-3.0552788	-2.1987618
H	4.6030206	-1.5429849	-2.7762968
H	3.6957657	-2.5938358	-1.6761669
H	7.0081525	-3.6922567	-0.8112239
H	7.9052364	-3.1511548	0.6143240
H	8.2355844	-1.9912128	-2.2272598
H	9.3739723	-3.0914668	-1.4090069
H	9.1256423	-1.4410349	-0.7885119
H	-4.5806597	-1.0391939	3.0036178
H	-4.0100117	-2.4059888	2.0318478
H	-5.6320376	-2.4508768	2.7510528
H	-8.6595773	-2.1174468	0.4680770
H	-7.6806474	-2.6822268	1.8297949
H	-7.4322314	-3.6905437	-1.0814239
H	-8.2098744	-4.5693267	0.2575060
H	-6.4534185	-4.2693007	0.2865050
H	-1.4449279	1.9481649	1.3450169

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