Anomalous Photophysics of Bis(hydroxystyryl)benzenes—A Twist on the para/meta Dichotomy

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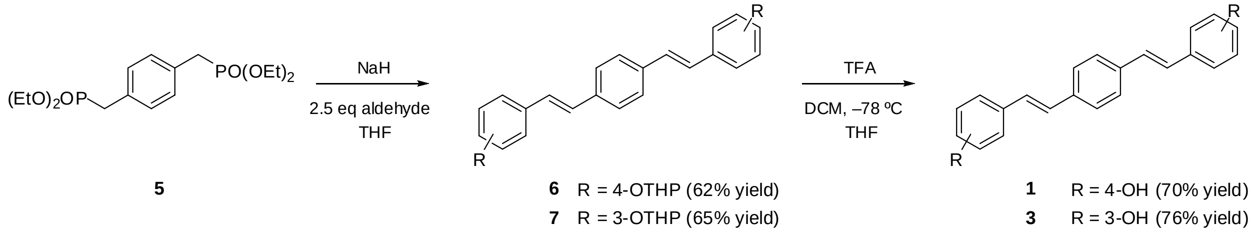
Supporting Information

Materials and Methods

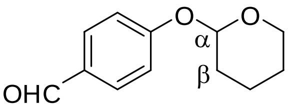
All chemicals were purchased from Aldrich Chemical, Acros, TCI America, or Fisher Scientific and used without purification unless otherwise specified. Column chromatography was performed using standard grade silica gel 60 Å, 32-63 μm (230 x 450 mesh) from Sorbent Technologies (Atlanta, GA) and the indicated eluent. Elution of the fluorophores was readily monitored using a handheld UV lamp (365 nm). Melting points were obtained using a Mel-Temp apparatus fitted with a Fluka 51K/J digital thermometer. All IR spectra were obtained using a Shimadzu FTIR-8400s spectrometer. Unless otherwise specified, NMR spectra were recorded at 298 K on a Bruker (500 MHz/400 MHz) or Varian Mercury spectrometer (300 MHz). Chemical shifts are reported in parts per million (ppm), using residual solvents (chloroform-*d*) or (THF-*d5*) as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, and integration. Mass spectral analyses were provided by the Georgia Institute of Technology Mass Spectrometry Facility.

Scheme 1. Synthetic sequence for 1,4-bis(*p*-hydroxystyryl)benzene (**1**) and 1,4-bis(*m*-hydroxystyryl)benzene (**3**).

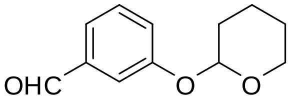


Note: The synthesis of compound **5** has been already previously reported.[1]

Synthesis of the THP-protected hydroxybenzaldehydes:



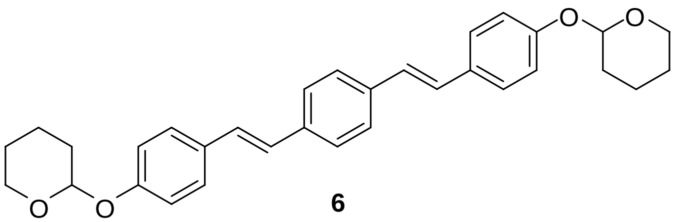
Synthesis of 4-(tetrahydropyran-2-yloxy)benzaldehyde: 4-Hydroxybenzaldehyde (5.80 g, 47.5 mmol) and 3,4-dihydro-2H-pyran (6.40 g, 76.1 mmol) were dissolved in dichloromethane (100 mL) in a 250 mL round bottom flask. Para-toluenesulfonic acid (0.430 g, 2.50 mmol) was added to the reaction mixture along with pyridine (1 mL). The pyridine was added drop wise over a 5 min period. The reaction solution was stirred for 24 h. The crude reaction mixture was washed three times with water, dried with magnesium sulfate and reduced until a dark brown oil was obtained. The product was washed with a solution of dilute NaOH and water to remove unreacted starting material. The final product was obtained as a dark brown oil (8.23 g). Yield: 84%. *^{1}H NMR (500 MHz, CDCl$_3$):* δ = 9.90 (s, 1H, Ar-CHO), 7.84 (d, 2H, Ar-H, $J_{H,H}$ = 9 Hz), 7.17 (d, 2H, Ar-H, $J_{H,H}$ = 8.5 Hz), 5.55 (s, 1H, α-C-H), 3.85 (m, 1H, ε-CH), 3.64 (m, 1H, ε-C-H), 2.01 (m, 1H, β-C-H), 1.90 (m, 2H, γ-C-H) 1.71 (m, 2H, δ-C-H), 1.62 (m, 1H, β-C-H). *^{13}C NMR (125 MHz, CDCl$_3$):* δ = 191.19, 162.48, 132.11, 130.77, 116.82, 96.41, 62.34, 30.36, 25.35, 18.77.



Synthesis of 3-(tetrahydropyran-2-yloxy)benzaldehyde: 3-Hydroxybenzaldehyde (5.80 g, 47.5 mmol) and 3,4-dihydro-2H-pyran (6.40 g, 76.1 mmol) were dissolved in dichloromethane (100 mL) in a 250 mL round bottom flask. Para-toluenesulfonic acid (0.430 g, 2.50 mmol) was added to the reaction mixture along with pyridine (1 mL). The pyridine was added drop wise over a 5 min period. The reaction mixture was stirred for 24 h. The crude reaction mixture was washed three times with water, dried with magnesium sulfate and reduced until a light brown oil was obtained. The product was washed with a solution of dilute NaOH and water to remove unreacted starting material. The final product was obtained as a light brown oil (8.35 g). Yield: 85%. *^{1}H NMR (500 MHz, CDCl$_3$):* δ = 9.97 (s, 1H, Ar-CHO), 7.56 (s, 1H, Ar-H,), 7.50 (dt, 1H, Ar-H, $J_{H,H}$ = 7.5 Hz, *with long range coupling*), 7.44 (t, 1H, Ar-H, $J_{H,H}$ = 8 Hz), 7.31 (md, 1H, Ar-H, $J_{H,H}$ = 8 Hz, *with long range coupling*), 5.49 (s, 1H, α-C-H), 3.88 (m, 1H, ε-CH), 3.63 (m, 1H, ε-C-H), 2.01 (m, 1H, β-C-H), 1.90 (m, 2H, γ-C-H) 1.71 (m, 2H, δ-C-H), 1.62 (m, 1H, β-C-H). *^{13}C NMR (125 MHz, CDCl$_3$)*: δ = 192.19, 157.90, 138.10, 130.10, 123.63, 123.18, 116.59, 96.59, 62.21, 30.47, 25.40, 18.92.

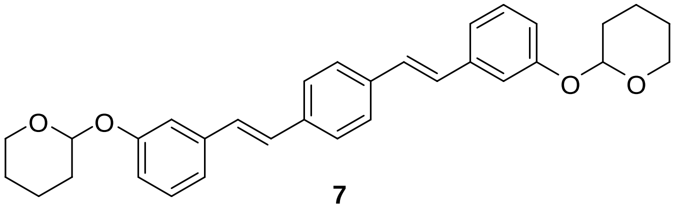
Synthesis of intermediates 6 and 7:

General Procedure: An oven dried Schlenk flask cooled under nitrogen was charged with **1** (0.500 g, 1.32 mmol), potassium *tert*-butoxide (60 mg, 2.5 mmol), and THF (50 mL). The flask was closed with a septum, a nitrogen-filled balloon was fitted to the arm and the stopcock was opened. Upon addition of the potassium *tert*-butoxide, the solution turned purple-red. 4-(Tetrahydropyran-2-yloxy)benzaldehyde (0.409 g, 1.98 mmol) or 3-(tetrahydropyran-2-yloxy)-benzaldehyde (0.409 g, 1.98 mmol) was then added dropwise over a 10 min period. The reaction was allowed to stir overnight before work-up. The small excess potassium *tert*-butoxide was quenched with water and the mixture was extracted three times with dichloromethane. The organic layer was washed three times with water and dried with magnesium sulfate and reduced until a pale yellow precipitate was formed. The yellow precipitate was purified by chromotagraphy eluting with 80:20 dichloromethane/hexanes to give yellow crystals.



6

Compound 6: Yield: 62%. *MP:* 270-272 ºC. *IR:* 2923, 2867, 1600, 1514, 1234, 1174, 1108, 964, 837. ^{1}*H NMR (500 MHz, CDCl$_3$):* δ = 7.50 (s, 4H, Ar-H), 7.48 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.11 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.08, (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.01 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 5.49 (s, 2H, α-C-H), 3.95 (m, 2H, ε-C-H), 3.65 (m, 2H, ε-C-H), 2.04 (m, 2H, β-C-H), 1.91 (m, 4H, γ-C-H) 1.71 (m, 4H, δ-C-H), 1.64 (m, 2H, β-C-H). ^{13}*C NMR (75 MHz, CDCl$_3$):* δ = 156.9, 136.9, 131.3, 128.4, 128.2, 127.8, 126.8, 116.9, 96.56, 62.2, 30.1, 25.5, 18.9.



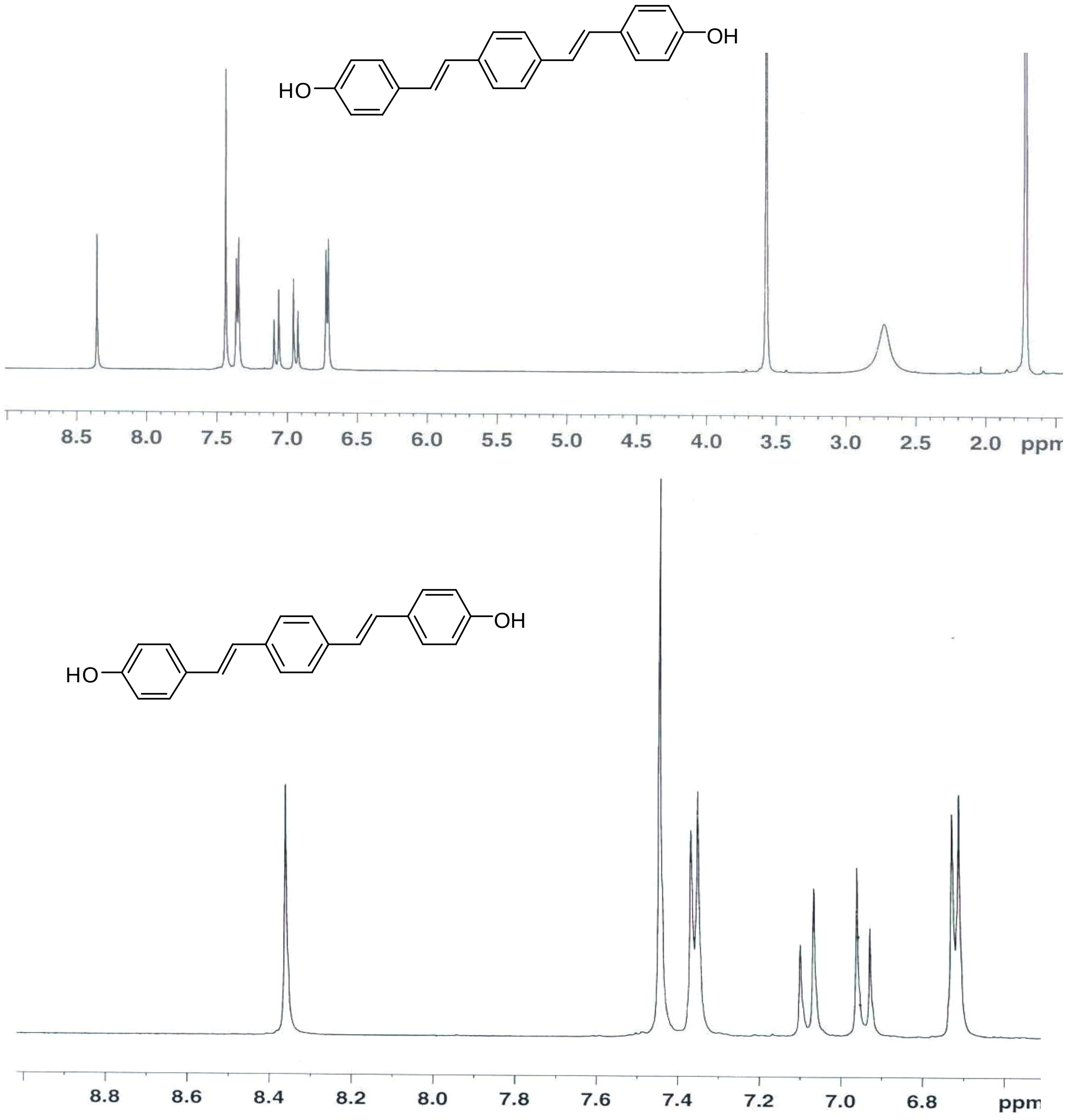
7

Compound 7: Yield: 65%. *MP:* 248-250 ºC. *IR:* 2924.8, 2871.8, 1593.5, 1574.7, 1446.9, 1201.1, 1158.1, 1108.9, 1003.4, 964.3. . ^{1}*H NMR (500 MHz, CDCl$_3$):* δ = 7.52 (s, 4H, Ar-H), 7.30 (t, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.26 (s, 2H, Ar-H), 7.18 (d, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.12 (s, 4H, C=C-H), 7.00 (d, 2H, Ar-H, $J_{H,H}$ = 8.5 Hz), 5.51 (s, 2H, α-C-H), 3.97 (m, 2H, ε-C-H), 3.67 (m, 2H, ε-C-H), 2.06 (m, 2H, β-C-H), 1.91 (m, 4H, γ-C-H) 1.73 (m, 4H, δ-C-H), 1.65 (m, 2H, β-C-H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 157.8, 139.1, 137.1, 129.9, 128.9, 127.2, 120.5, 116.2, 114.7, 96.7, 62.4, 30.8, 25.6, 19.1

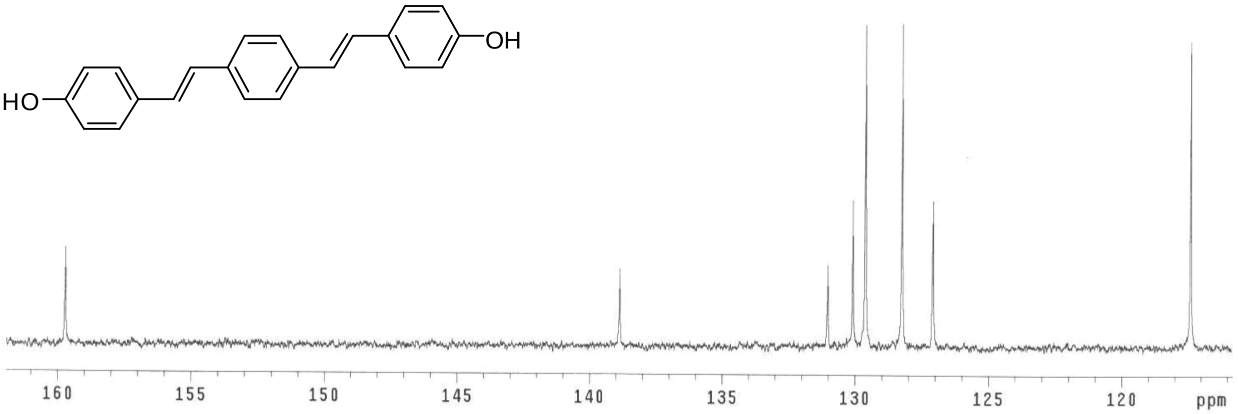
Synthesis of bis(hydroxystyryl)benzenes 1 and 3:

Compounds **6** and **7** were deprotected by trifluoroacetic acid in a dry ice acetone bath. The products were obtained by extracting with ethyl ether or ethyl acetate. The yields reported reflect the amount of pure material that was recovered after deprotection and recrystallization.

1,4-Bis(*p*-hydroxystyryl)benzene 1: 6 (0.200 g, 0.414 mmol) was dissolved in dichloromethane (30 mL) and trifluoroacetic acid (1 mL) was added into a 100-mL round bottom flask kept in a dry ice acetone bath. The solution was allowed to stir at -78 °C for 2 h. The product was extracted with ethyl ether, washed three times with water, dried with magnesium sulfate and reduced until a dark green powder was formed. The powder was washed with dichloromethane and collected by suction filtration and dried under vacuum. Yield: 70%. *MP:* 300 ºC. *IR:* 3278, 3010, 1676, 1602, 1514, 1448, 1377, 1249, 960, 831. ^{1}*H NMR (500 MHz, THF-d5):* δ = 8.36 (s, 2H, Ar-OH), 7.45 (s, 4H, Ar-H), 7.36 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.08 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 6.94 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 6.72 (d, 2H, Ar-H, $J_{H,H}$ = 8.5 Hz). ^{13}*C NMR (75 MHz, THF-d5):* δ = 159.7, 138.8 131.1, 130.1, 129.6, 128.3, 127.07, 117.4. *MS (EI, 70-SE) ($C_{22}H_{18}O_2$)*: m/z = 314. HRMS ($C_{22}H_{18}O_2$) m/z calcd. 314.13068. Found 314.13124.

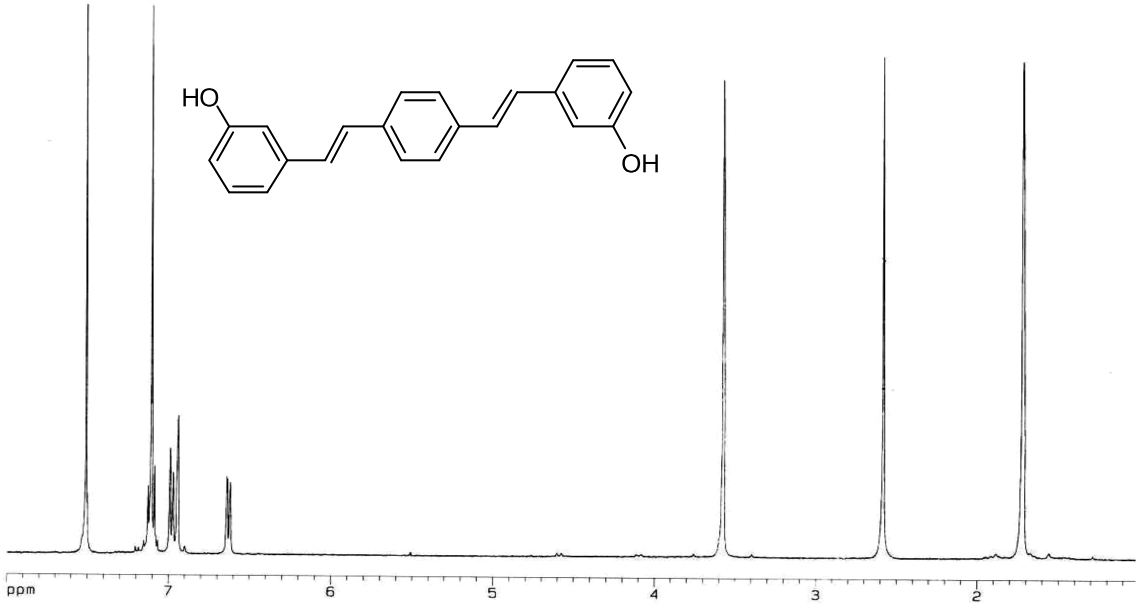


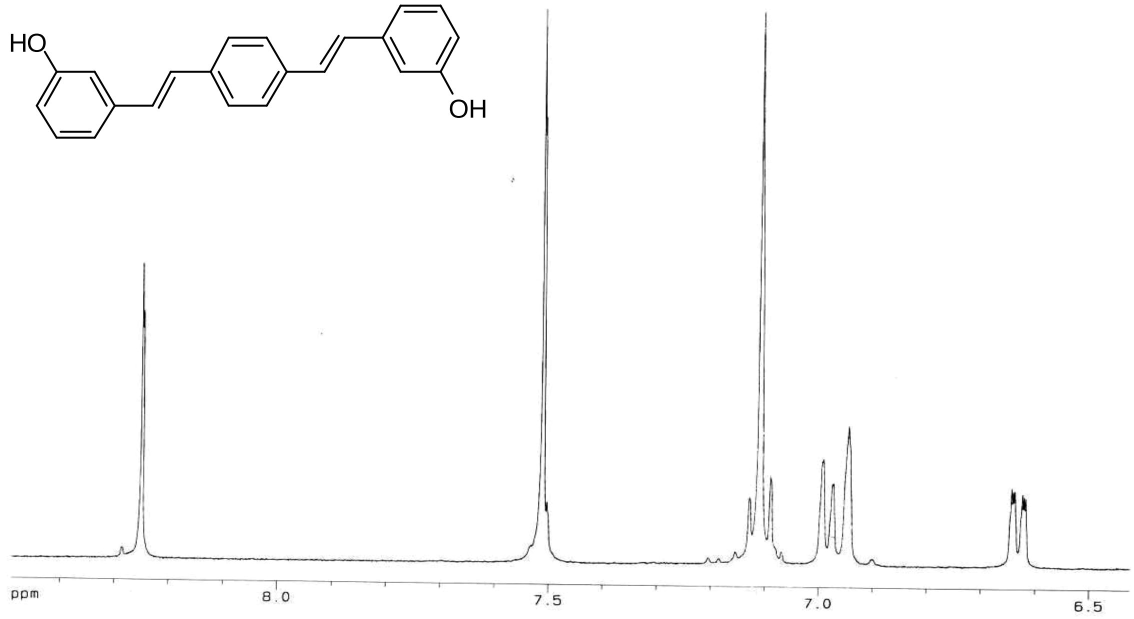
^{1}H NMR of compound **1** in THF d-8. Signals at 3.6 and 1.7 ppm are due partially deuterated THF.



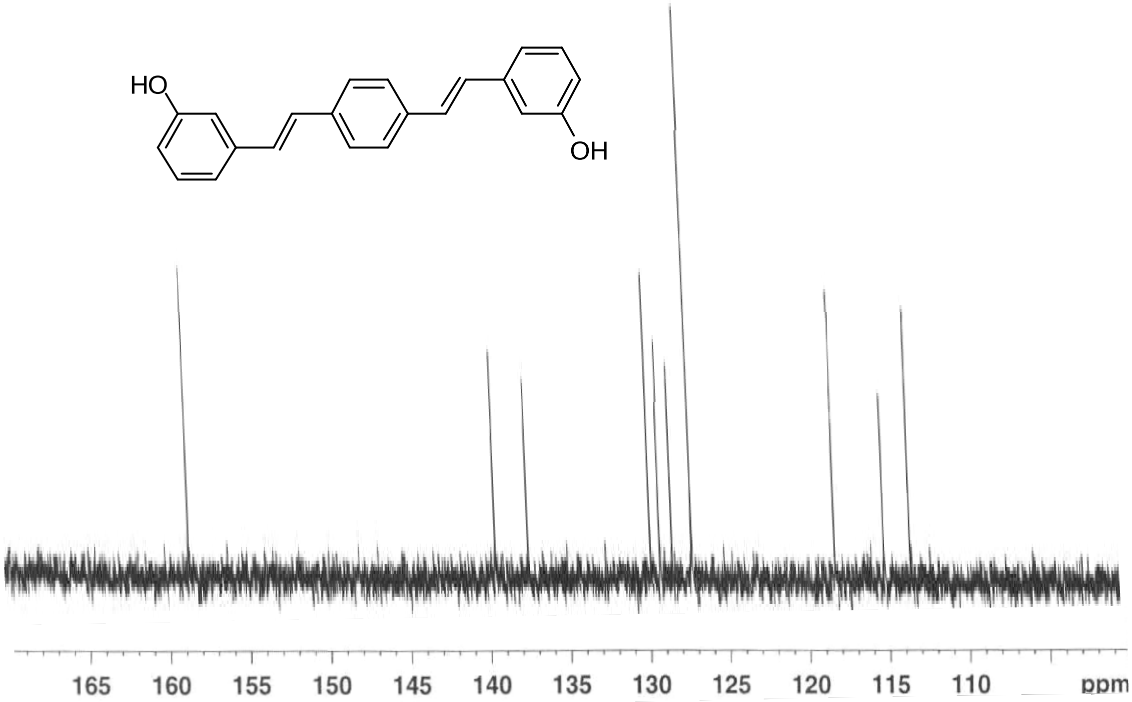
^{13}C NMR of compound **1** in THF d-8.

1,4-Bis(*m*-hydroxystyryl)benzene 3: 7 (0.200 g, 0.414 mmol) was dissolved in dichloromethane (30 mL) and trifluoroacetic acid (1 mL) was added into a 100-mL round bottom flask kept in a dry ice acetone bath. The solution was allowed to stir at -78 °C for 2 h. The product was extracted with ethyl ether, washed three times with water, dried with magnesium sulfate and reduced until a yellow powder was formed. The powder was recrystallized by dissolving in hot ethyl acetate and adding an excess amount of hexanes. Yield: 76%. MP: 240 ºC IR: 3345.7, 3025.4, 1645.2, 1590.2, 1447.4, 1301.2 1157.6, 962.4, 800.3. *^{1}H NMR (400 MHz, THF-d5):* δ = 8.22 (s, 2H, Ar-OH), 7.51 (s, 4H, Ar-H), 7.10 (t, 2H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.10 (s, 4H, C=C-H), 6.98 (d, 2H, Ar-H, $J_{H,H}$ = 8.5 Hz), 6.94 (s, 2H, Ar-H), 6.63 (d, 2H, Ar-H, $J_{H,H}$ = 7.5 Hz). ^{13}C NMR (*125 MHz*, *THF-d5*): δ= 158.4, 139.2, 137.23, 129.5, 128.9, 128.2, 126.9, 118.0, 114.9, 113.3. *MS (EI, 70-SE) ($C_{22}H_{18}O_2$)*: m/z = 314. HRMS ($C_{22}H_{18}O_2$) m/z calcd. 314.13068. Found 314.13176.





^{1}H NMR of **3** in THF d-8. Signals at 3.6 and 1.7 ppm are due partially deuterated THF.



^{13}C NMR of **3** in THF d-8.

Determination of p*K*a Values: Measurements were performed with a combination glass microelectrode (Orion, Thermo Electron Corp, Waltham). The electrode was precalibrated in aqueous buffers at pH 4, 7, and 10. Solution pH measurements were performed in 2/1 v/v methanol-water mixtures. For the determination of the pK_a's, a series of UV-vis spectra were acquired for which $-\log[H_3O^+]$ was varied between 5 and 12. It was demonstrated[4] that the pH can be measured directly in alcohol-water mixtures using glass electrodes precalibrated in aqueous buffers. In this case for 2/1 v/v methanol/water mixtures the observed pH values are 0.18 pH units higher than the real ones for this mixture. The raw spectral data were processed via non-linear least squares fit analysis using the SPECFIT software package,[2] providing deconvoluted spectra for each species present as well as the acidity constants for the relevant protonation equilibria.

Results from principal component analysis:

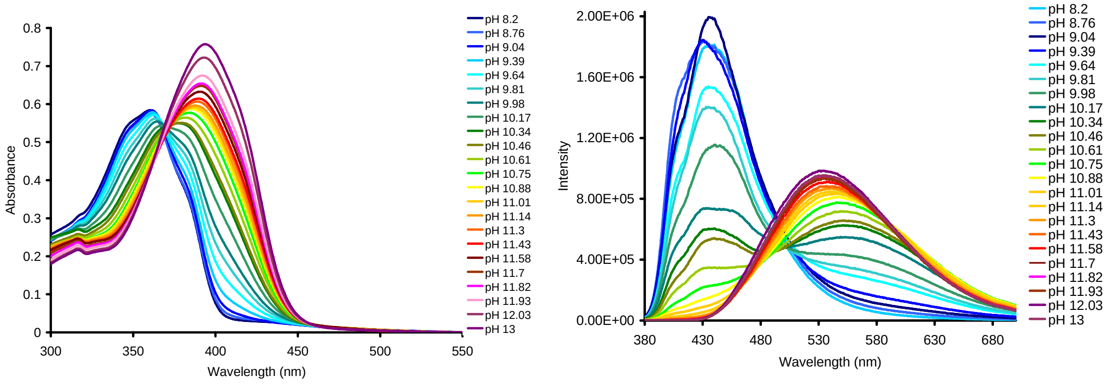


Figure S1. Spectrophotometric pH titration of fluorophore **1** in MeOH/H_2O (2:1, v/v). pK_{a1} = 10.16 ± 0.04; pK_{a2} = 11.77 ± 0.28

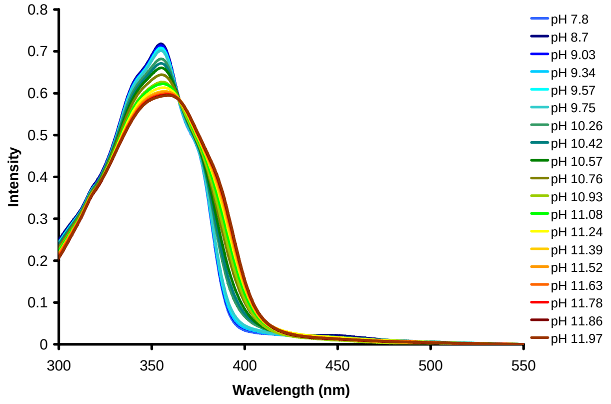


Figure S2. Spectrophotometric pH titration of fluorophore **3** in MeOH/H_2O (2:1, v/v). Left: deconvoluted UV-vis spectra for the diprotonated (H_2L), monoprotonated (HL^-) and fully deprotonated (L^{2-}) species. Right: Calculated species distribution diagram.

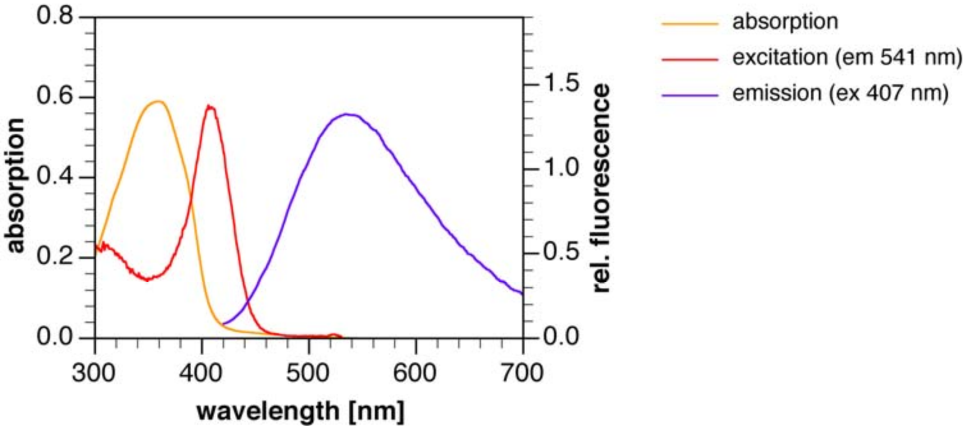


Figure S3: Absorption, excitation and emission spectra for compound **3**$^{=}$ in basic methanol-water solution. Excitation at the red-edge of the absorption spectrum (407 nm) gives rise to fluorescence emission from the lowest excited singlet state (λ_{max} = 541 nm). The excitation spectrum (red) acquired at 541 nm has a maximum at 407 nm.

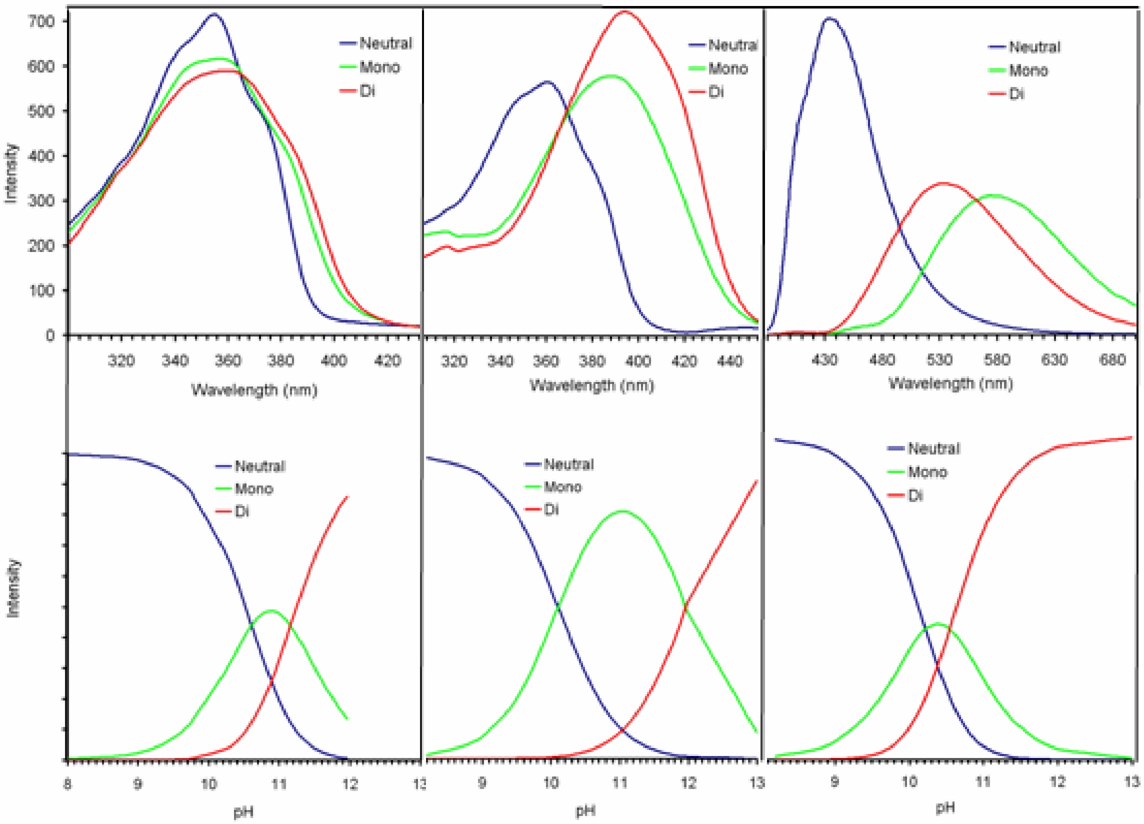


Figure S4. Spectrophotometric pH titration of fluorophores **3** and **1** in MeOH/H_2O (2:1, v/v). Top: deconvoluted UV-vis spectra for the diprotonated (H_2L), monoprotonated (HL^{-}) and fully deprotonated (L^{2-}) species. Bottom: Calculated species distribution diagram.

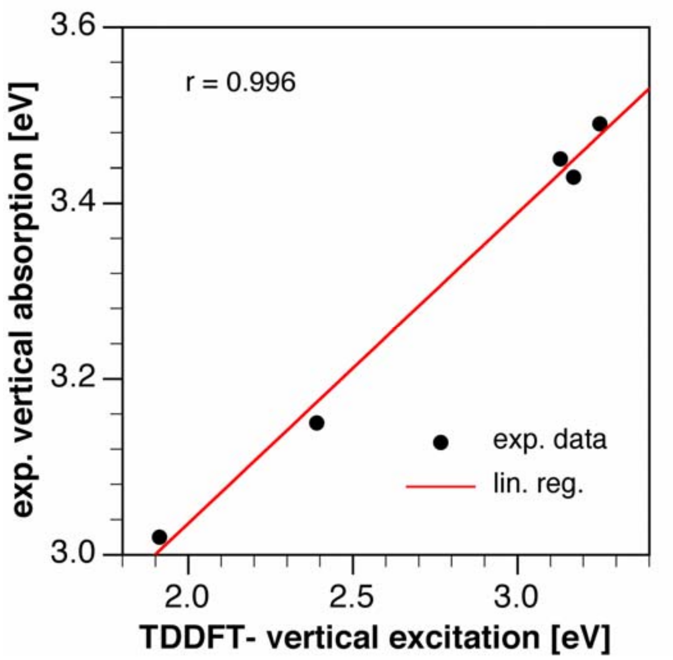


Figure S5. Plot of the computed excitation energies (TDDFT) vs. the experimentally measured absorption energies of **1,3** and their two anions. Note, that the lowest lying absorption is the only weakly allowed π−π* transition of the bisdeprotonated derivative of **3**.

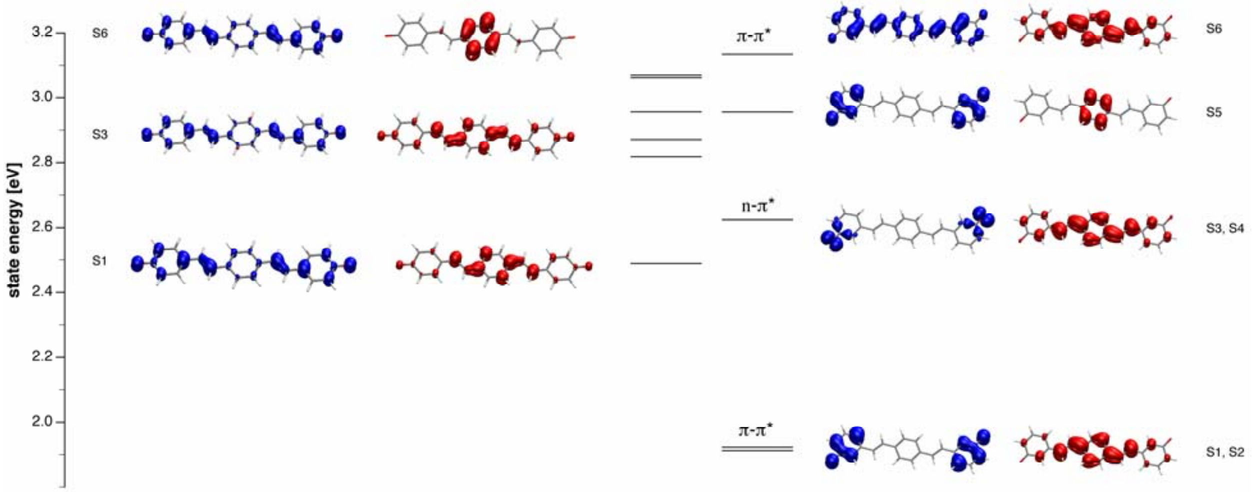


Figure S6. Left: Excited state manifold for dianion **1**$^{=}$ based on TD-DFT calculations (B3LYP/6-311+G(2d,2p)//B3LYP/6-311+G(2d,2p)). The π−π* transition to S1 is symmetry allowed, and contrary to **3** there are no n-π* states involved. **Right:** Excited state manifold for dianion **3**$^{=}$ based on TD-DFT calculations (B3LYP/6-311+G(2d,2p)//B3LYP/6-311+G(2d,2p)). Upon excitation into S6, nonradiative deactivation may occur through rapid intersystem crossing (ISC) to the 3(n-π*) states T3 and T4. The surface plots to the right illustrate the π−π* and n-π* nature of S1, S3 and S6 with the corresponding electron detachment (blue) and attachment (red) densities.e

Table S1: Spectral, Kinetic, and Thermodynamic Properties of 1 and 3 in Neutral and Basic 2:1 v/v MeOH/H_2O Solutions

	1	***$1^{=}$***	***3***	***$3^{=}$***
Absorption (nm)	362	393	355	363
Emission (nm)	428	533	412	quenched
Φ_{fl}	0.34	0.26	0.46	<0.005
τ (ns)	0.91	1.0	1.41	
pK_a	10.10 (±0.03) 11.97 (±0.09)		10.61 (±0.13) 11.16 (±0.3)	
HOMO (eV) ($7B_g$)	-5.22	0.73	-5.50	0.44
LUMO (eV) ($7A_u$) calcd ^{a}	-1.96	3.21	-2.18	2.69
HOMO-LUMO Gap calcd (eV) ^{a}	3.27	2.48	3.32	2.26

Computational Methods for 1 and 3: Quantum chemical calculations were performed using the Q-Chem computational package.[3] Ground state (S_0) equilibrium geometries for each compound were optimized using density functional theory with the B3LYP functional and the triple split valence polarized basis set 6-311+G(2d,2p) with added diffuse functions for improved accuracy of the di-anion structures.

Table S2: Cartesian atomic coordinates for neutral **1** (S_0, B3LYP/6-311+G(2d,2p), C_{2h}, E = –999.91745779 a.u.)

Atom	X (Å)	Y (Å)	Z (Å)
H	8.190388	-2.027408	0.000000
C	7.537830	-1.162661	0.000000
C	5.852421	1.039759	0.000000
C	6.159437	-1.334101	0.000000
C	8.075818	0.120288	0.000000
C	7.222379	1.224806	0.000000
C	5.278915	-0.243655	0.000000
H	5.755633	-2.338069	0.000000
O	9.421003	0.366356	0.000000
H	7.649409	2.217519	0.000000
C	3.839281	-0.491297	0.000000
H	5.216231	1.912979	0.000000
C	2.853885	0.424400	0.000000
H	3.571002	-1.542231	0.000000
H	3.120898	1.475555	0.000000
C	1.415964	0.175381	0.000000
C	-1.415964	-0.175381	0.000000
C	0.838568	-1.103817	0.000000
C	0.534075	1.270723	0.000000
C	-0.838568	1.103817	0.000000

C	-0.534075	-1.270723	0.000000
H	1.469432	-1.981180	0.000000
H	0.944386	2.272408	0.000000
H	-1.469432	1.981180	0.000000
H	-0.944386	-2.272408	0.000000
C	-2.853885	-0.424400	0.000000
C	-3.839281	0.491297	0.000000
H	-3.120898	-1.475555	0.000000
H	-3.571002	1.542231	0.000000
C	-5.278915	0.243655	0.000000
C	-8.075818	-0.120288	0.000000
C	-5.852421	-1.039759	0.000000
C	-6.159437	1.334101	0.000000
C	-7.537830	1.162661	0.000000
C	-7.222379	-1.224806	0.000000
H	-5.216231	-1.912979	0.000000
H	-5.755633	2.338069	0.000000
H	-8.190388	2.027408	0.000000
H	-7.649409	-2.217519	0.000000
O	-9.421003	-0.366356	0.000000
H	-9.907432	0.463425	0.000000
H	9.907432	-0.463425	0.000000

Table S3: Cartesian atomic coordinates for bis-deprotonated **1** (S_0, B3LYP/6-311+G(2d,2p), C_{2h}, E = –998.77466211 a.u.)

Atom	X (Å)	Y (Å)	Z (Å)
H	8.202461	-2.053109	0.000000
C	7.558534	-1.181180	0.000000
C	5.912279	1.057413	0.000000
C	6.187937	-1.321974	0.000000
C	8.202498	0.110293	0.000000
C	7.277020	1.224496	0.000000
C	5.300876	-0.219936	0.000000
H	5.760865	-2.321038	0.000000
O	9.458358	0.262081	0.000000
H	7.707866	2.219344	0.000000
C	3.874781	-0.442546	0.000000
H	5.281360	1.939095	0.000000
C	2.862560	0.464247	0.000000
H	3.598983	-1.494805	0.000000
H	3.117790	1.519514	0.000000
C	1.432478	0.197043	0.000000
C	-1.432478	-0.197043	0.000000
C	0.853651	-1.087804	0.000000
C	0.518261	1.272336	0.000000
C	-0.853651	1.087804	0.000000
C	-0.518261	-1.272336	0.000000
H	1.494125	-1.959865	0.000000
H	0.912553	2.282531	0.000000
H	-1.494125	1.959865	0.000000
H	-0.912553	-2.282531	0.000000
C	-2.862560	-0.464247	0.000000

C	-3.874781	0.442546	0.000000
H	-3.117790	-1.519514	0.000000
H	-3.598983	1.494805	0.000000
C	-5.300876	0.219936	0.000000
C	-8.202498	-0.110293	0.000000
C	-5.912279	-1.057413	0.000000
C	-6.187937	1.321974	0.000000
C	-7.558534	1.181180	0.000000
C	-7.277020	-1.224496	0.000000
H	-5.281360	-1.939095	0.000000
H	-5.760865	2.321038	0.000000
H	-8.202461	2.053109	0.000000
H	-7.707866	-2.219344	0.000000
O	-9.458358	-0.262081	0.000000

Table S4: Cartesian atomic coordinates for neutral **3** (S_0, B3LYP/6-311+G(2d,2p), C_{2h}, E = –999.91750715 a.u.)

Atom	X (Å)	Y (Å)	Z (Å)
H	-1.604277	-1.876594	0.000000
C	-0.913069	-1.045581	0.000000
C	0.913069	1.045581	0.000000
C	0.444978	-1.305180	0.000000
C	-1.397647	0.271181	0.000000
C	-0.444978	1.305180	0.000000
C	1.397647	-0.271181	0.000000
H	0.790118	-2.331721	0.000000
H	-0.790118	2.331721	0.000000
H	1.604277	1.876594	0.000000
C	-2.815610	0.615632	0.000000
C	-3.857395	-0.234014	0.000000
H	-3.014612	1.680827	0.000000
H	-3.663218	-1.300048	0.000000
C	2.815610	-0.615632	0.000000
C	3.857395	0.234014	0.000000
H	3.014612	-1.680827	0.000000
H	3.663218	1.300048	0.000000
C	5.276894	-0.121179	0.000000
C	8.034079	-0.677247	0.000000
C	5.740870	-1.447650	0.000000
C	6.220172	0.912961	0.000000
C	7.584061	0.639344	0.000000
C	7.099788	-1.711613	0.000000
H	5.042114	-2.270996	0.000000
H	5.896697	1.945374	0.000000
H	7.446984	-2.735884	0.000000
H	9.094634	-0.895843	0.000000
C	-5.276894	0.121179	0.000000
C	-8.034079	0.677247	0.000000
C	-5.740870	1.447650	0.000000
C	-6.220172	-0.912961	0.000000
C	-7.584061	-0.639344	0.000000
C	-7.099788	1.711613	0.000000

H	-5.042114	2.270996	0.000000
H	-5.896697	-1.945374	0.000000
H	-7.446984	2.735884	0.000000
H	-9.094634	0.895843	0.000000
O	-8.434834	-1.713118	0.000000
O	8.434834	1.713118	0.000000
H	-9.346301	-1.406724	0.000000
H	9.346301	1.406724	0.000000

Table S5: Cartesian atomic coordinates for bis-deprotonated **3** (S_0, B3LYP/6-311+G(2d,2p), C_{2h}, E = –998.75867344 a.u.)

Atom	X (Å)	Y (Å)	Z (Å)
H	-1.593934	-1.882857	0.000000
C	-0.907323	-1.047007	0.000000
C	0.907323	1.047007	0.000000
C	0.454670	-1.297360	0.000000
C	-1.411849	0.264387	0.000000
C	-0.454670	1.297360	0.000000
C	1.411849	-0.264387	0.000000
H	0.804517	-2.323551	0.000000
H	-0.804517	2.323551	0.000000
H	1.593934	1.882857	0.000000
C	-2.832891	0.602387	0.000000
C	-3.882571	-0.243920	0.000000
H	-3.035988	1.667582	0.000000
H	-3.685018	-1.311460	0.000000
C	2.832891	-0.602387	0.000000
C	3.882571	0.243920	0.000000
H	3.035988	-1.667582	0.000000
H	3.685018	1.311460	0.000000
C	5.306983	-0.099107	0.000000
C	8.064326	-0.633663	0.000000
C	5.763484	-1.433798	0.000000
C	6.235826	0.944660	0.000000
C	7.665446	0.749973	0.000000
C	7.137377	-1.666594	0.000000
H	5.069243	-2.262166	0.000000
H	5.882261	1.970686	0.000000
H	7.494337	-2.692940	0.000000
H	9.127716	-0.845638	0.000000
C	-5.306983	0.099107	0.000000
C	-8.064326	0.633663	0.000000
C	-5.763484	1.433798	0.000000
C	-6.235826	-0.944660	0.000000
C	-7.665446	-0.749973	0.000000
C	-7.137377	1.666594	0.000000
H	-5.069243	2.262166	0.000000
H	-5.882261	-1.970686	0.000000
H	-7.494337	2.692940	0.000000
H	-9.127716	0.845638	0.000000
O	-8.492208	-1.713939	0.000000
O	8.492208	1.713939	0.000000

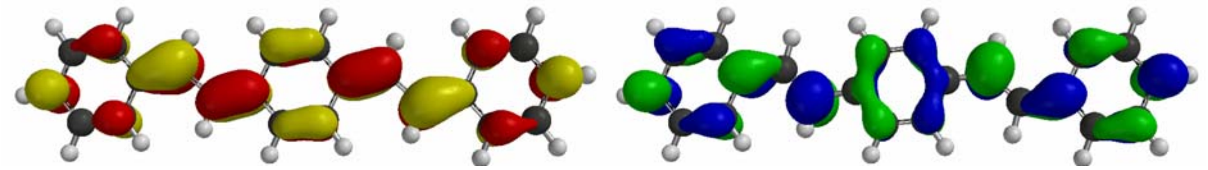


Figure S4. HOMO (left) and LUMO (right) of Distyrylbenzene

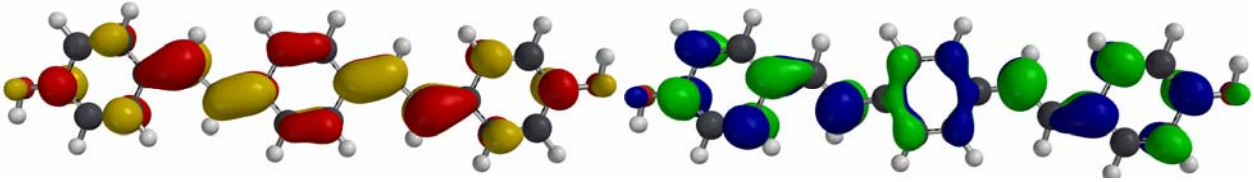


Figure S5. HOMO (left) and LUMO (right) of **1**

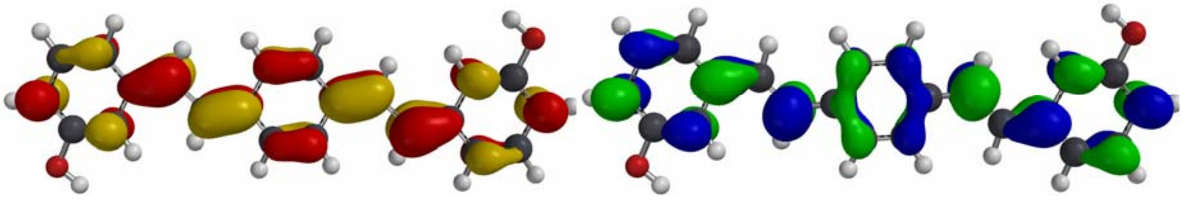


Figure S6. HOMO (left) and LUMO (right) of **3**

Table S6: Cartesian atomic coordinates for 1,4-distyrylbenzene (S_0, B3LYP/6-31G**// B3LYP/6-31G**, C_{2h}, E = –849.200878 a.u.)

Atom	X (Å)	Y (Å)	Z (Å)
H	10.90760707830000	-4.33157870623000	0
C	11.67345021230000	-2.42508833042000	0
C	13.64695020630000	2.44233902502000	0
C	9.99498555383000	-0.36197147354900	0
C	14.28169349670000	-2.06919718090000	0
C	15.28415247840000	0.36860155215900	0
C	11.04359994970000	2.08524080681000	0
H	15.53125577280000	-3.69791290620000	0
H	17.31632689660000	0.65430872682200	0
H	9.81126663566000	3.72476865916000	0
H	14.40684940840000	4.34960007595000	0
C	7.27201492864000	-0.85990991968100	0
C	5.39189748024000	0.86426073014500	0
H	6.77877431811000	-2.85757424191000	0
H	5.88268477943000	2.86241376473000	0
C	2.67554460823000	0.36452798024700	0
C	-2.67554460823000	-0.36452798024700	0
C	1.61428290106000	-2.07585590769000	0
C	0.98298950580400	2.42213352784000	0
C	-1.61428290106000	2.07585590769000	0
C	-0.98298950580400	-2.42213352784000	0
H	2.83514482956000	-3.72387679038000	0
H	1.74165306595000	4.33155689016000	0
H	-2.83514482956000	3.72387679038000	0

H	-1.74165306595000	-4.33155689016000	0
C	-5.39189748024000	-0.86426073014500	0
C	-7.27201492864000	0.85990991968100	0
H	-5.88268477943000	-2.86241376473000	0
H	-6.77877431811000	2.85757424191000	0
C	-9.99498555383000	0.36197147354900	0
C	-15.28415247840000	-0.36860155215900	0
C	-11.04359994970000	-2.08524080681000	0
C	-11.67345021230000	2.42508833042000	0
C	-14.28169349670000	2.06919718090000	0
C	-13.64695020630000	-2.44233902502000	0
H	-9.81126663566000	-3.72476865916000	0
H	-10.90760707830000	4.33157870623000	0
H	-15.53125577280000	3.69791290620000	0
H	-14.40684940840000	-4.34960007595000	0
H	-17.31632689660000	-0.65430872682200	0

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