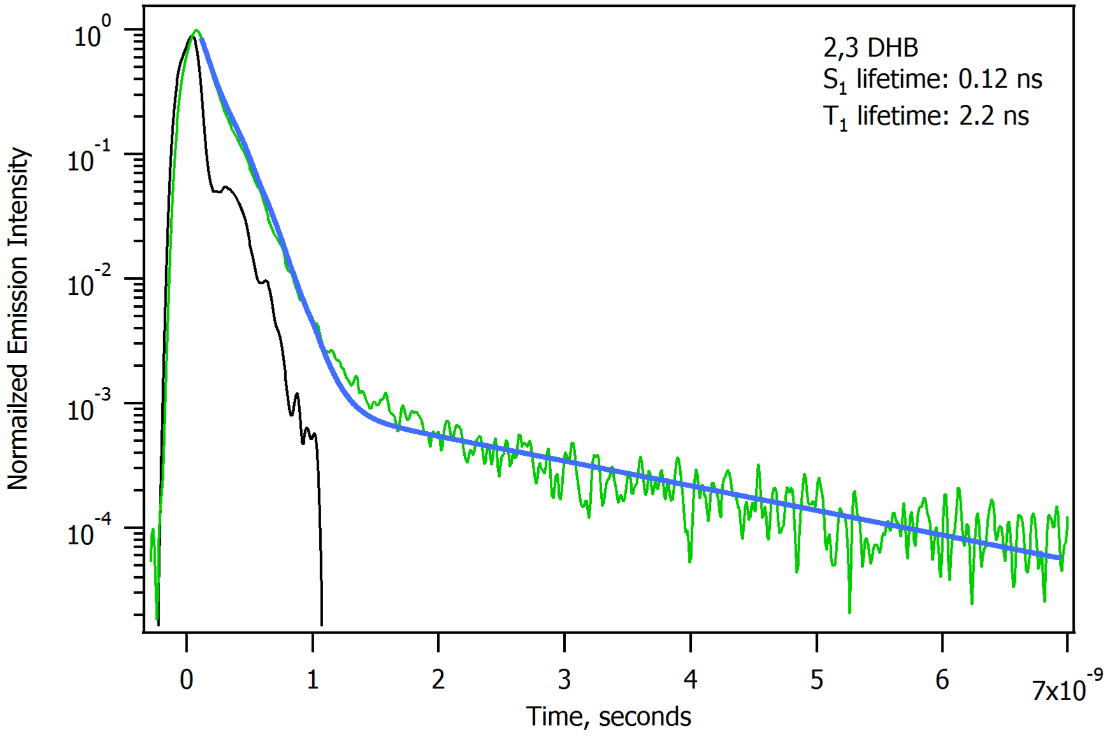
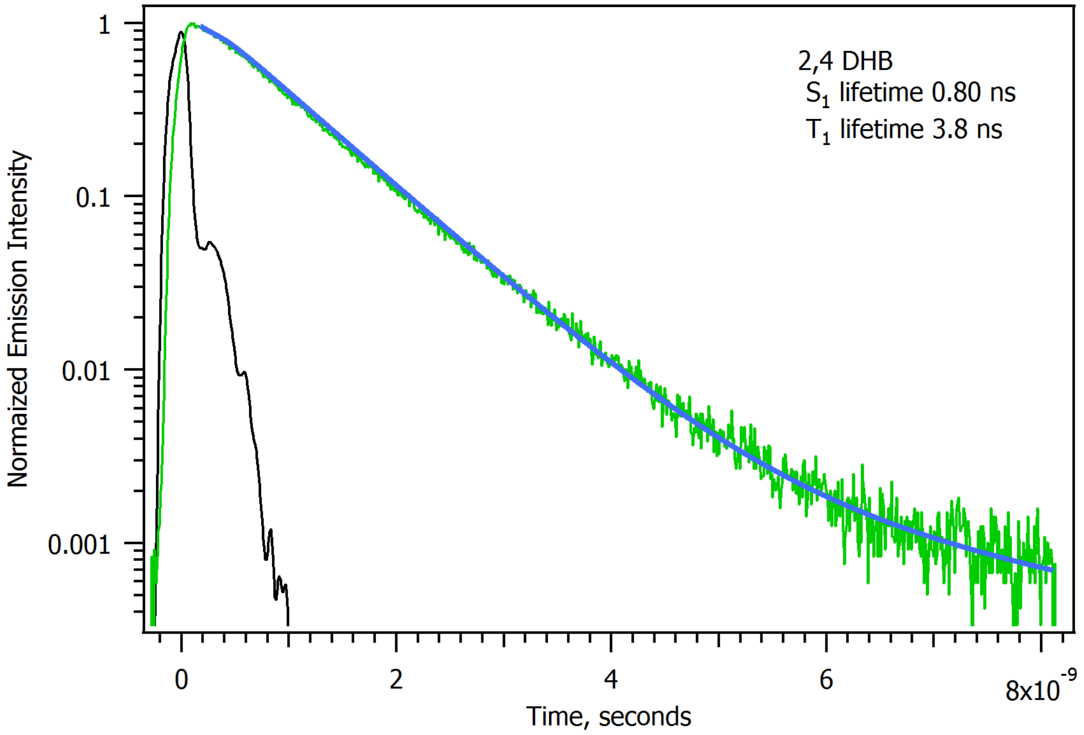
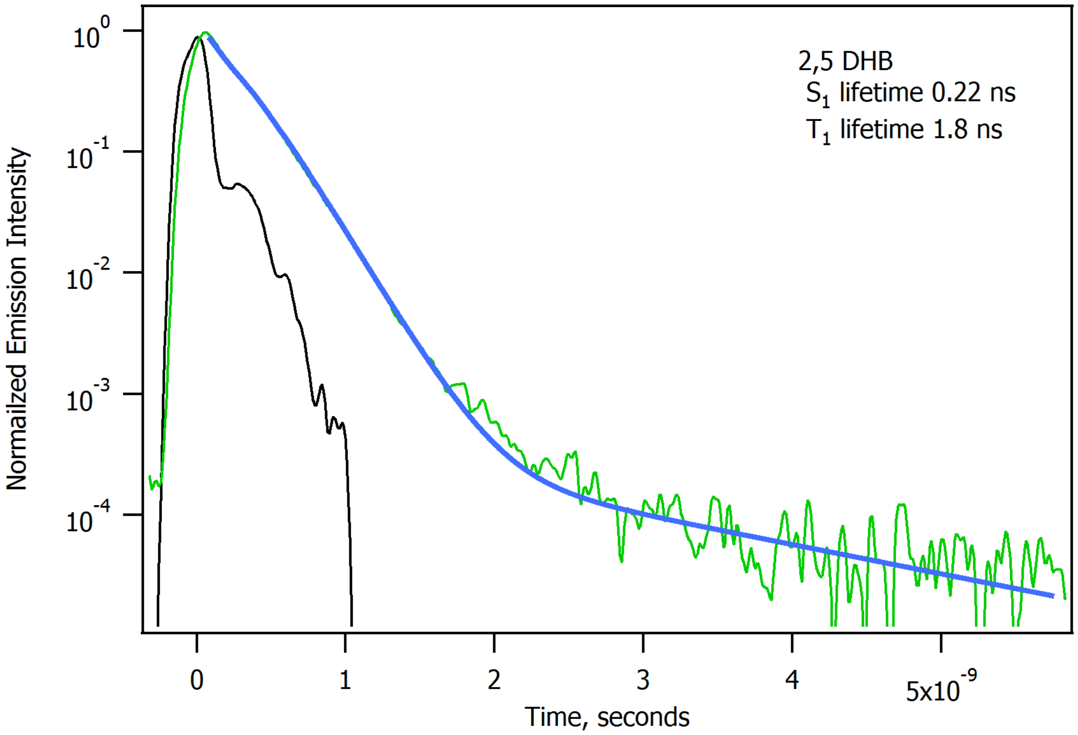
Supplementary material

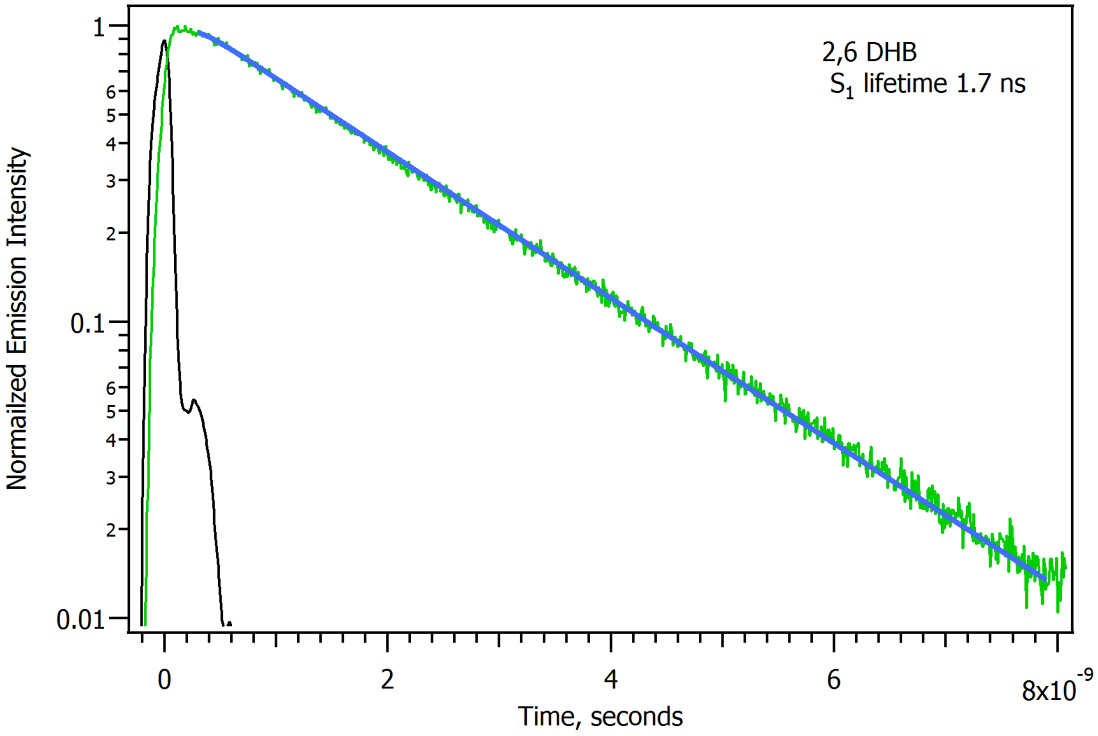
Time resolved luminescence and CPCD model fits.

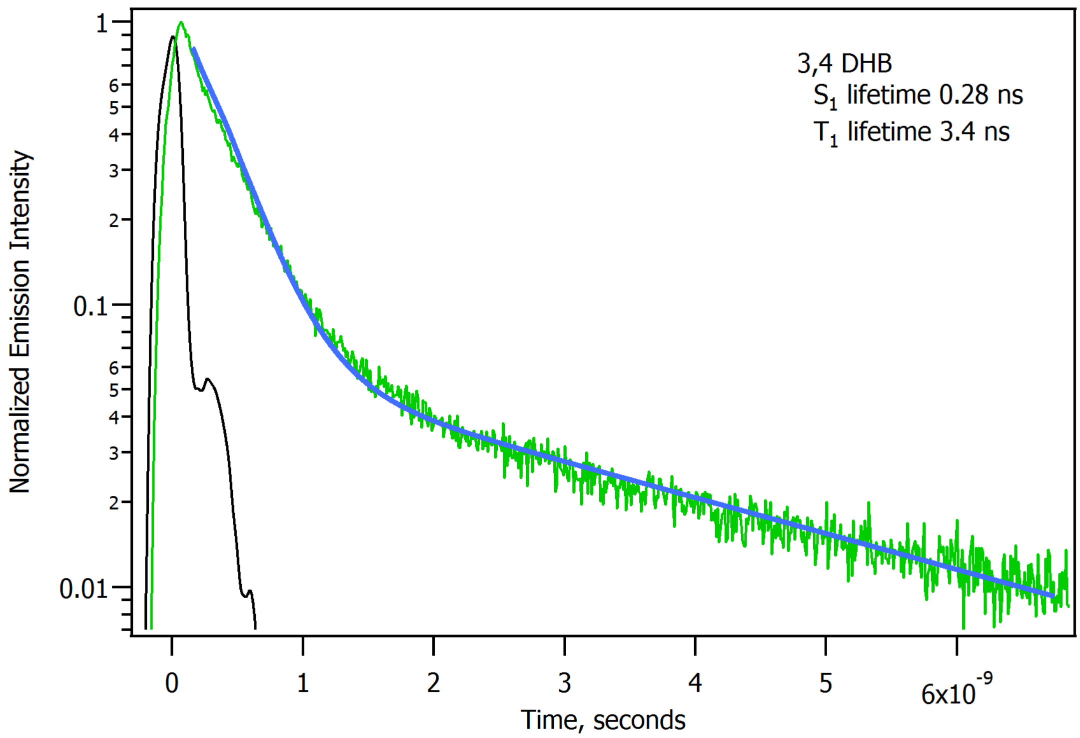
The measured instrument function is shown in black, the data in green and the fit in blue.






2,5 DHB
S_1 lifetime 0.22 ns
T_1 lifetime 1.8 ns
Normailzed Emission Intensity
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0
1
2
3
4
$5x10^{-9}$
Time, seconds


2,6 DHB
S_1 lifetime 1.7 ns
Normailzed Emission Intensity
1
6
5
4
3
2
0.1
6
5
4
3
2
0.01
0
2
4
6
$8x10^{-9}$
Time, seconds


3,4 DHB
S1 lifetime 0.28 ns
T1 lifetime 3.4 ns
Normalized Emission Intensity
1
6
5
4
3
2
0.1
6
5
4
3
2
0.01
0
1
2
3
4
5
6x10-9
Time, seconds

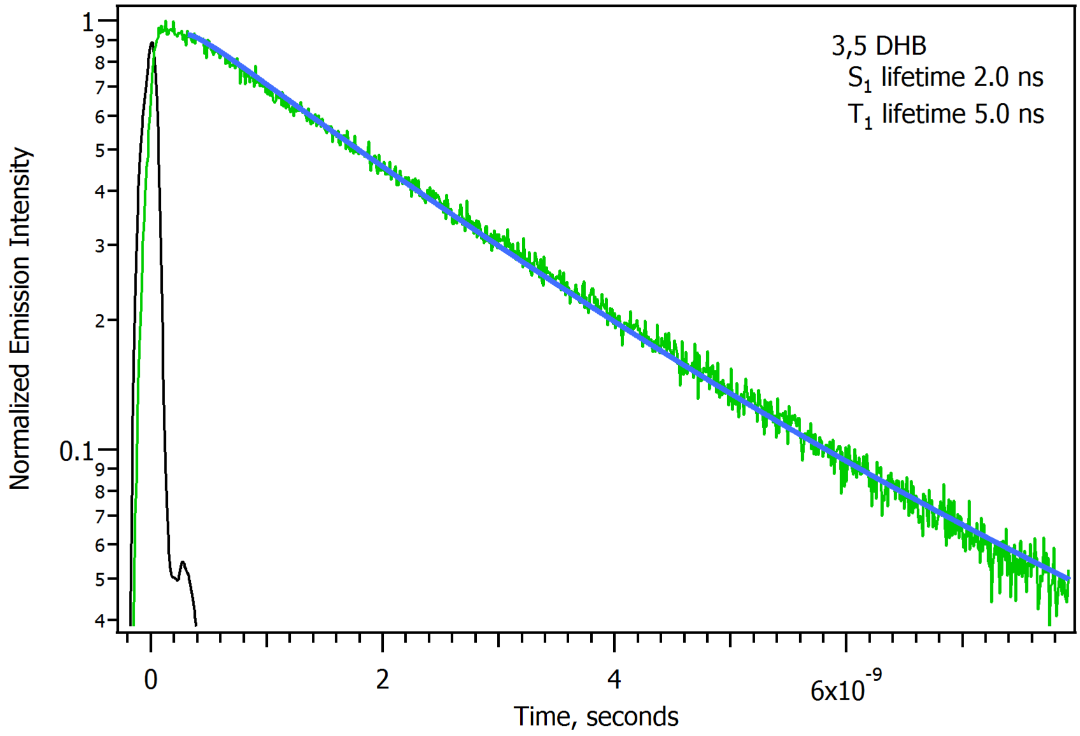

3,5 DHB
S1 lifetime 2.0 ns
T1 lifetime 5.0 ns
Normalized Emission Intensity
1
9
8
7
6
5
4
3
2
0.1
9
8
7
6
5
4
0
2
4
6x10-9
Time, seconds

Table S1. Proton transfer thermodynamics of DHB isomers, kJ/mol. GB stands for gas phase basicitiy.

Isomer	GB(M) G3MP2*	GB(M) Experiment†	GB(M) Yassin & Marynick‡‡	GB(M-H) G3MP2	GB(M-H) Experiment	ΔG Autoprotolysis G3MP2‡
2,3	816	818±7	819	1318		502
2,4	826	831±6	831	1348		522
2,5	816	819±8	819	1340	1329 **	524
2,6	826	830±6	824	1291		465
3,4	813	815±6	821	1391		578
3,5	792	814±6	804	1379		587

* G3(MP2,CCSD(T)) as implemententеd in GAMESS. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery. GAMESS. *J. Comput. Chem.* **1993;** L.A. Curtiss, K. Ragavachari, P.C. Redfern, A.G. Baboul, J.A.Pople, *Chem.Phys.Lett.* 1999, *314*, 101.

† M. Mormann, S. M. Bashir, P. J. Derrick, D. Kuck. Gas-phase Basicities of the Isomeric Dihydroxybenzoic Acids and Gas-phase Acidities of their Radical Cations. *J. Am. Soc. Mass Spectrom.* **2000,** *11,* 544.

‡‡ At the B3LYP/6-31+G** level. F. Yassin, D. S. Marynick. Computational estimates of the gas-phase acidities of dihydroxybenzoic acid radical cations and their corresponding neutral species. *J. Mol. Struct.* **2003,** *629,* 223.

‡ For the reaction: $M + M \rightarrow (M\text{-}H)^- + MH^+$

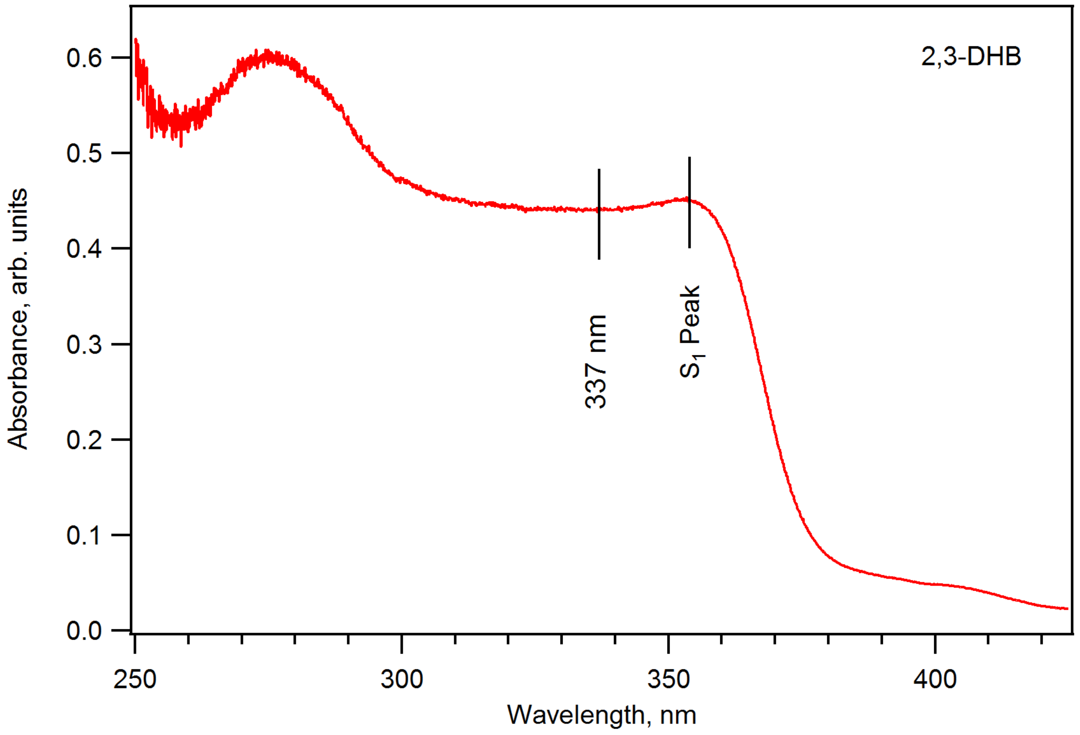
** K. Breuker, R. Knochenmuss, R. Zenobi. The gas-phase basicities of deprotonated MALDI matrix molecules. *Int. J. Mass Spectrom.* **1999,** *184,* 25.

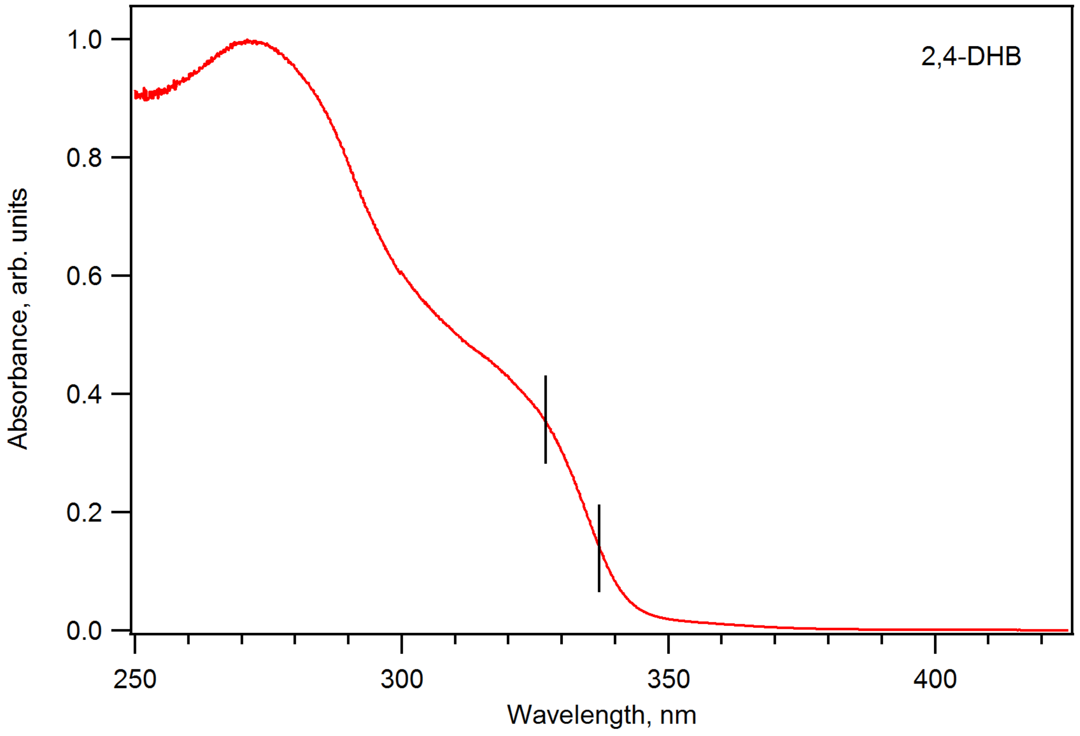
Table S2. Dielectric constants (relative permittivities) of DHB isomers determined by the method of Chu et al.*. The GAMESS TDHFX module was used with a 6-31G(d,p)++ basis to calculate the dipole moment and static polarizability. The density was taken to be 5.59×10^{21} molec/cm^3 at room temperature.

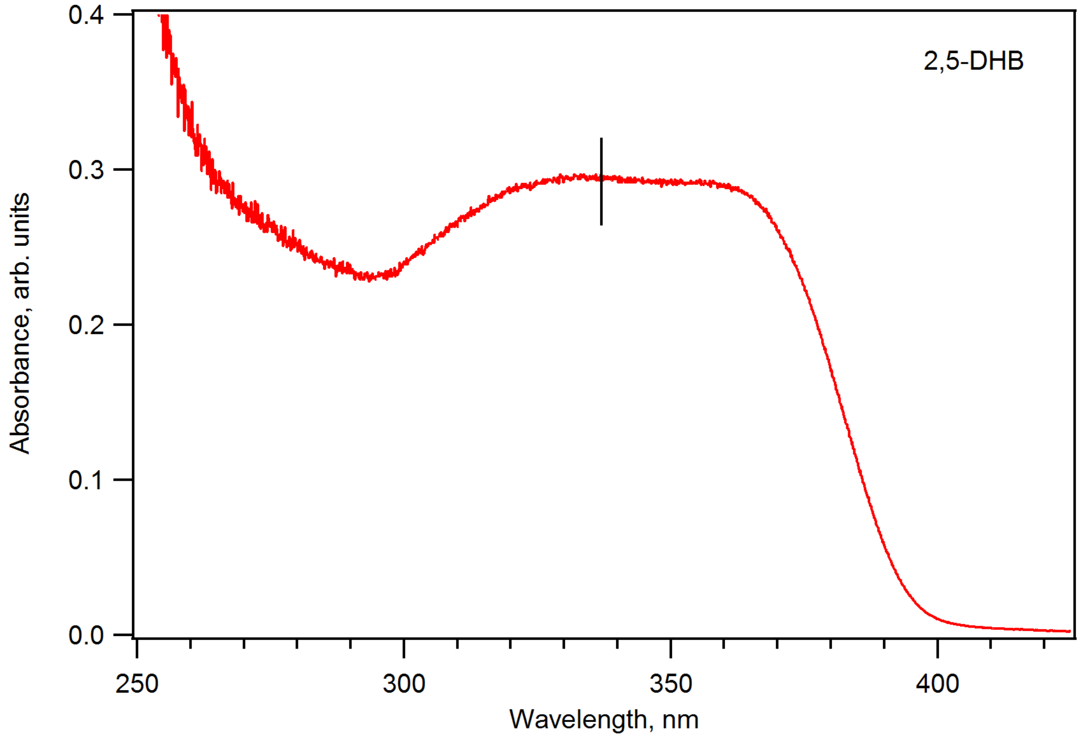
	μ, D	α, 10^{-23} cm^3	ε, 300 K	ε, 1000K
2,3 DHB:	2.3	1.28	10.3	4.4
2,4 DHB:	1.2	1.28	4.3	2.8
2,5 DHB:	2.2	1.28	9.6	4.2
2,6 DHB:	1.9	1.29	7.6	3.7
3,4 DHB:	0.57	1.28	2.8	2.4
3,5 DHB:	2.0	1.27	8.1	4.2

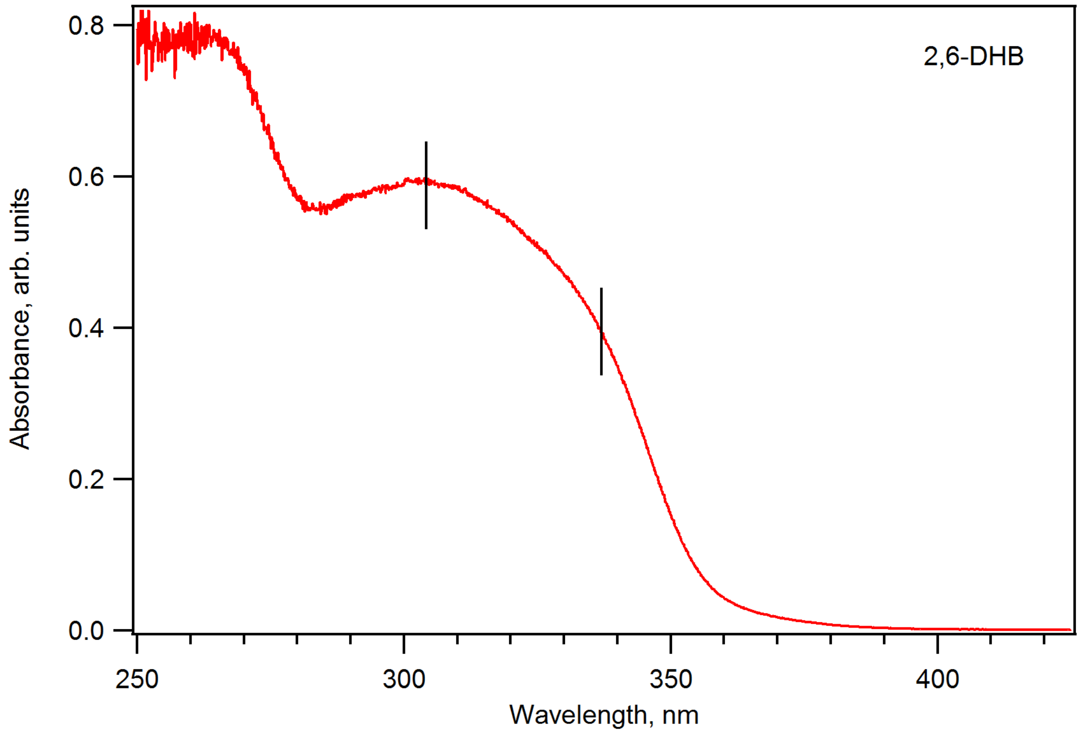
* K. Y. Chu, S. Lee, M.-T. Tsai, I.-C. Lu, Y. A. Dyakov, Y. H. Lai, Y.-T. Lee, C.-K. Ni. Thermal Proton Transfer Reactions in Ultraviolet Matrix-Assisted Laser Desorption/Ionization. *J. Am. Soc. Mass Spectrom.* **2014,** *25*, 310.

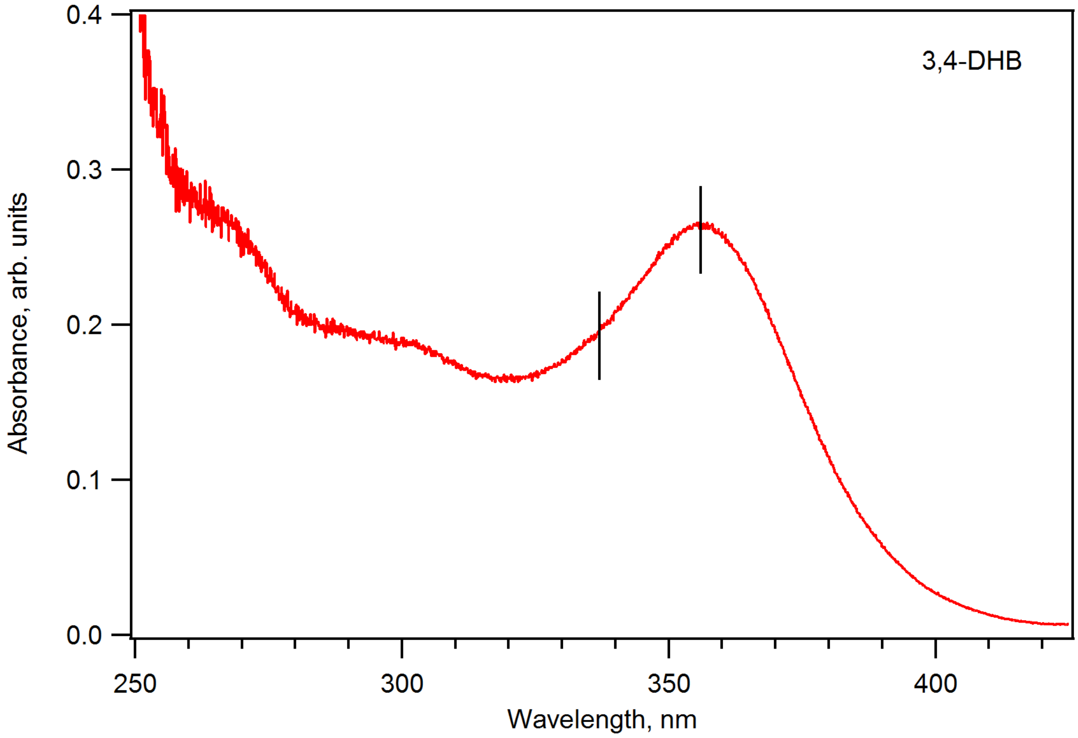
Solid state thin film absorption spectra.
In each case the estimated S_1 peak position and 337 nm are marked by vertical lines. The absorption cross sections reported in Table 2 were estimated as follows: the peak of the S_1 absorption was assumed to correspond to the same cross section in every isomer. From the 2,5 isomer, this was taken to be 2×10^{-17} cm^2. The relative absorbance at 337 nm was determined for each isomer, as a fraction of the absorption at the S_1 peak. This fraction multiplies the peak value of 2×10^{-17} cm^2, as shown in Table 2. Note that the absorbance of 2,5 DHB at 337 nm is the same as at the S_1 peak.

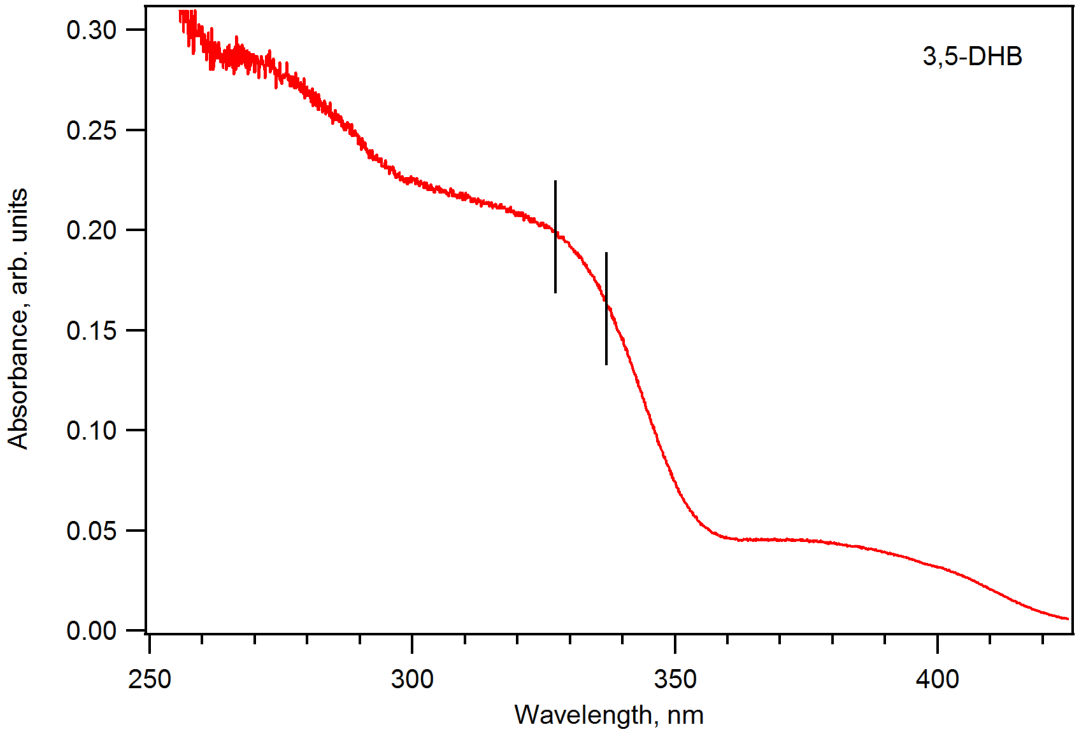





2,5-DHB
Absorbance, arb. units
0.4
0.3
0.2
0.1
0.0
250
300
350
400
Wavelength, nm


2,6-DHB
Absorbance, arb. units
0.8
0.6
0.4
0.2
0.0
250
300
350
400
Wavelength, nm


3,4-DHB
Absorbance, arb. units
0.4
0.3
0.2
0.1
0.0
250
300
350
400
Wavelength, nm


3,5-DHB
Absorbance, arb. units
0.30
0.25
0.20
0.15
0.10
0.05
0.00
250
300
350
400
Wavelength, nm