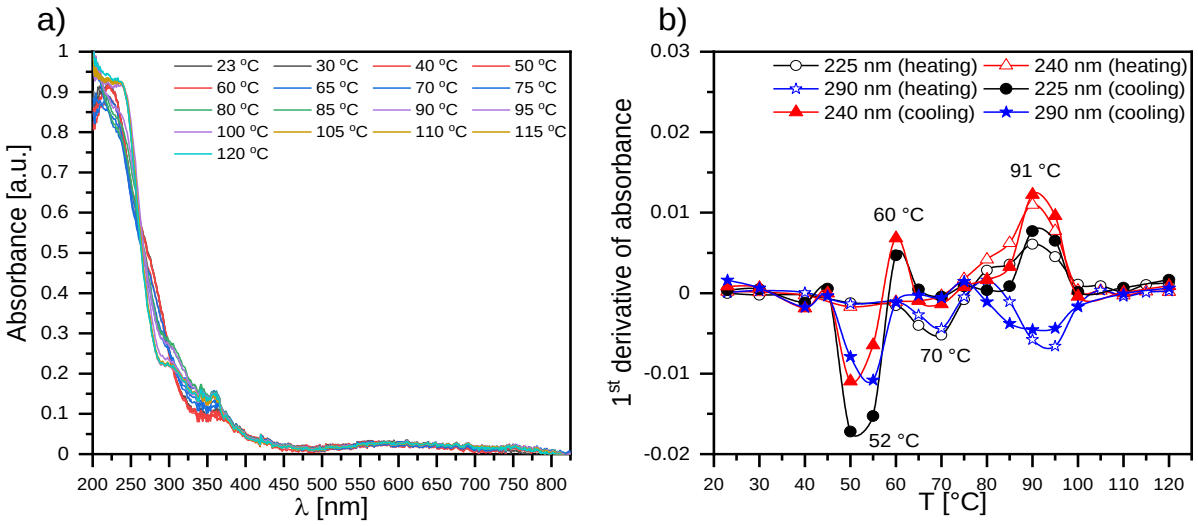

Figure S1. Solid state UV-Vis absorption spectra of Composite 1 (pure EHPDB) at several chosen temperatures in the 200–850 nm range during heating (**a**) and temperature dependence of the first derivative of the absorbance for selected wavelengths 225, 240 and 290 nm during heating and cooling (**b**).

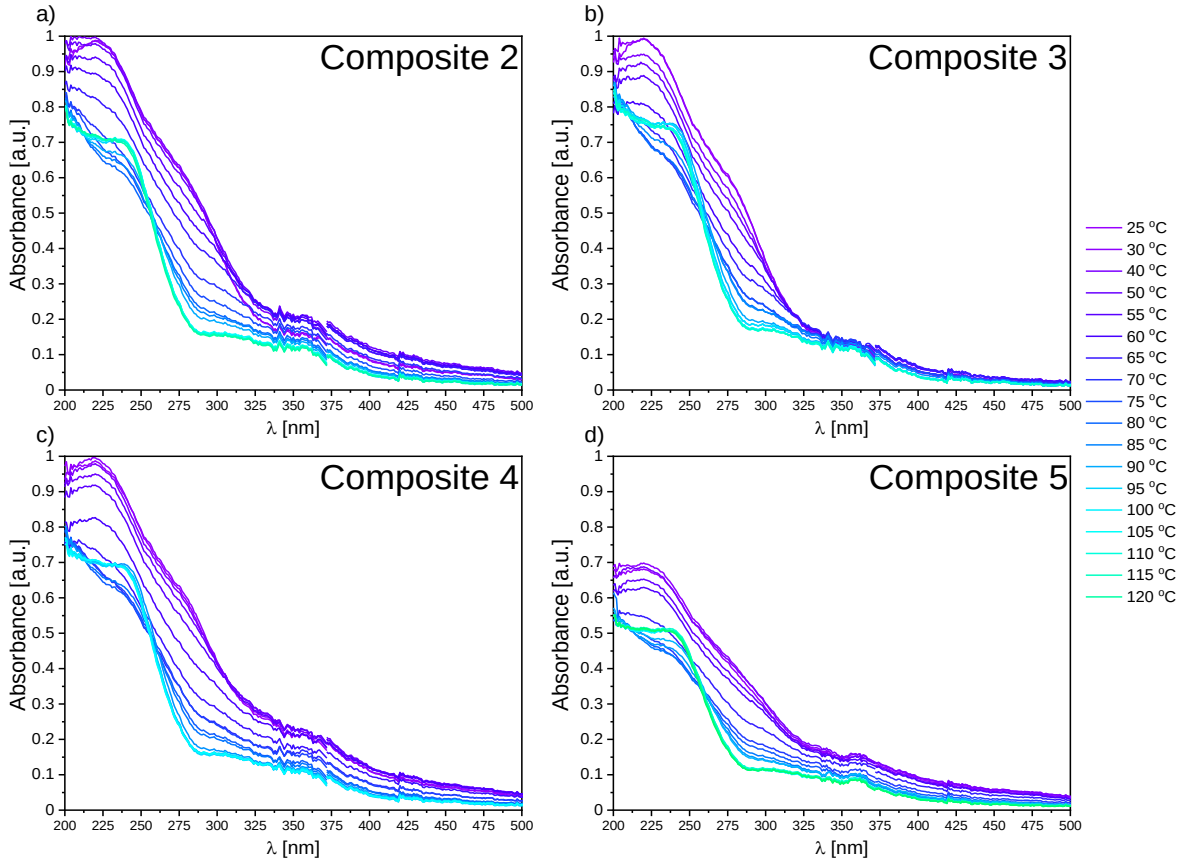

Figure S2. Solid state UV-Vis absorption spectra of Composites 2–5 at several chosen temperatures in the 200–500 nm range during heating. The legend from the right side is for all graphs.

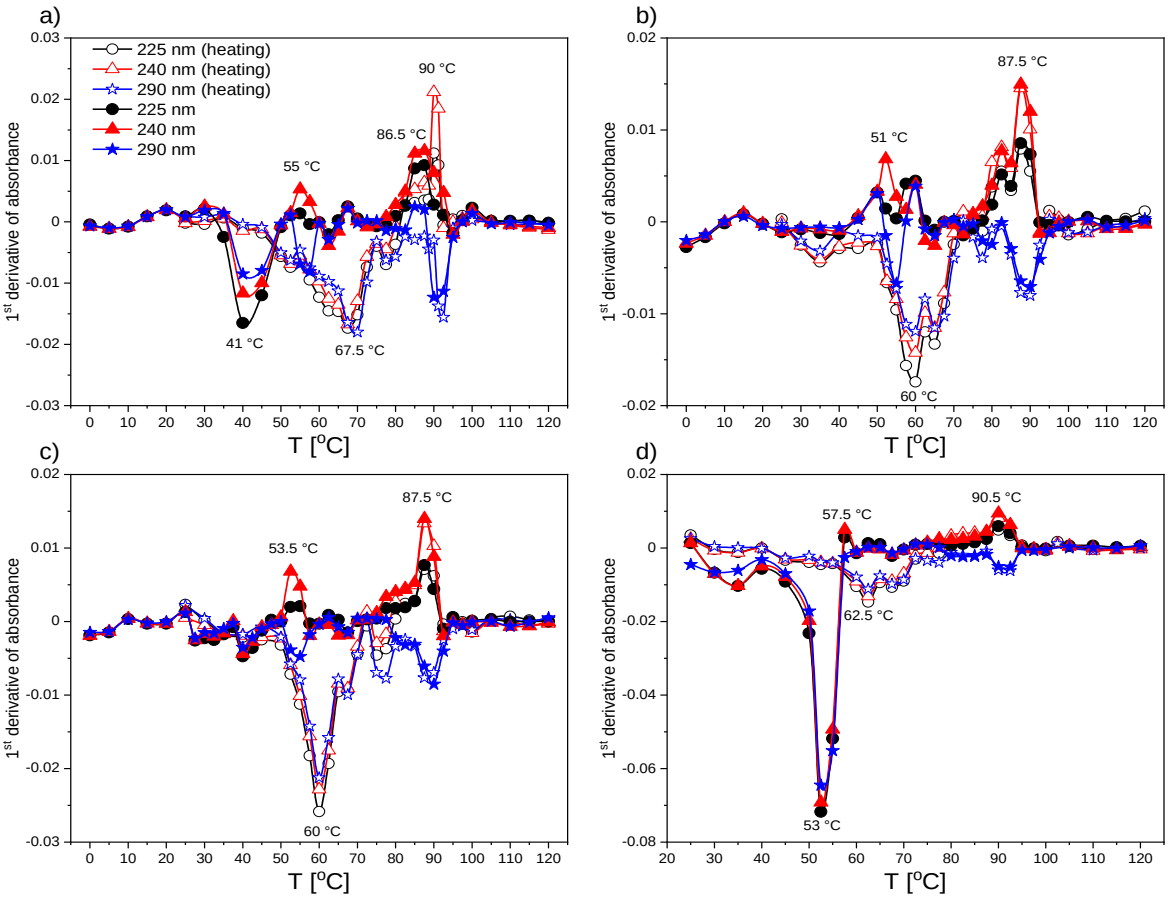

Figure S3. Temperature dependence of the first absorbance derivative for selected wavelengths (225, 240, 290 nm) for Composites 2–4 during heating and cooling. The given temperatures correspond to the phase transitions temperatures.

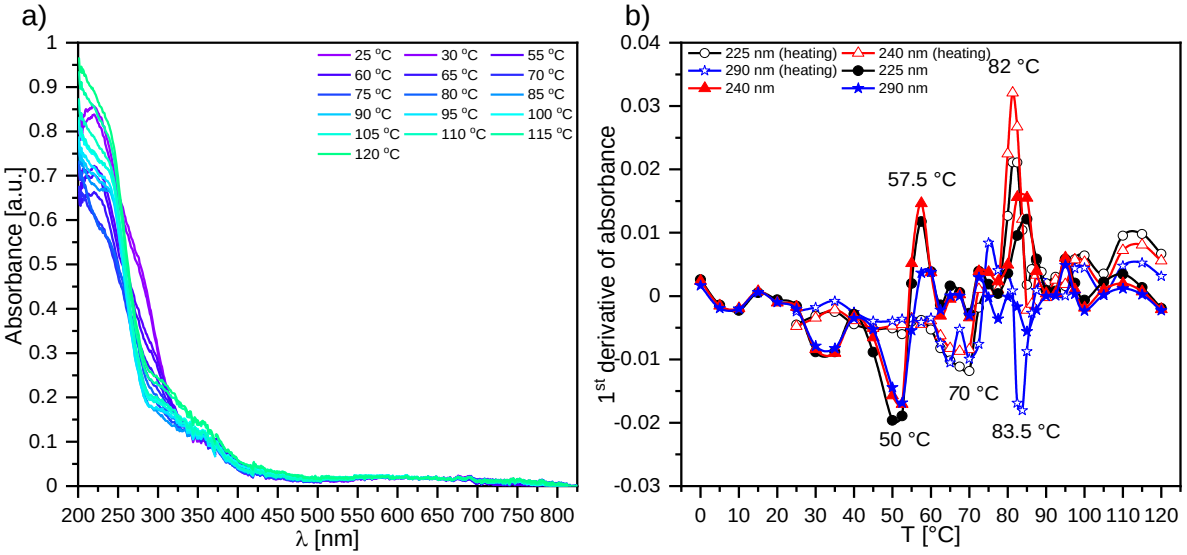

Figure S4. Solid state UV-Vis absorption spectra of Composite 6 at several chosen temperatures in the 200–850 nm range during heating (**a**) and temperature dependence of the first derivative of absorbance for selected wavelengths 225, 240 and 290 nm during heating and cooling (**b**).

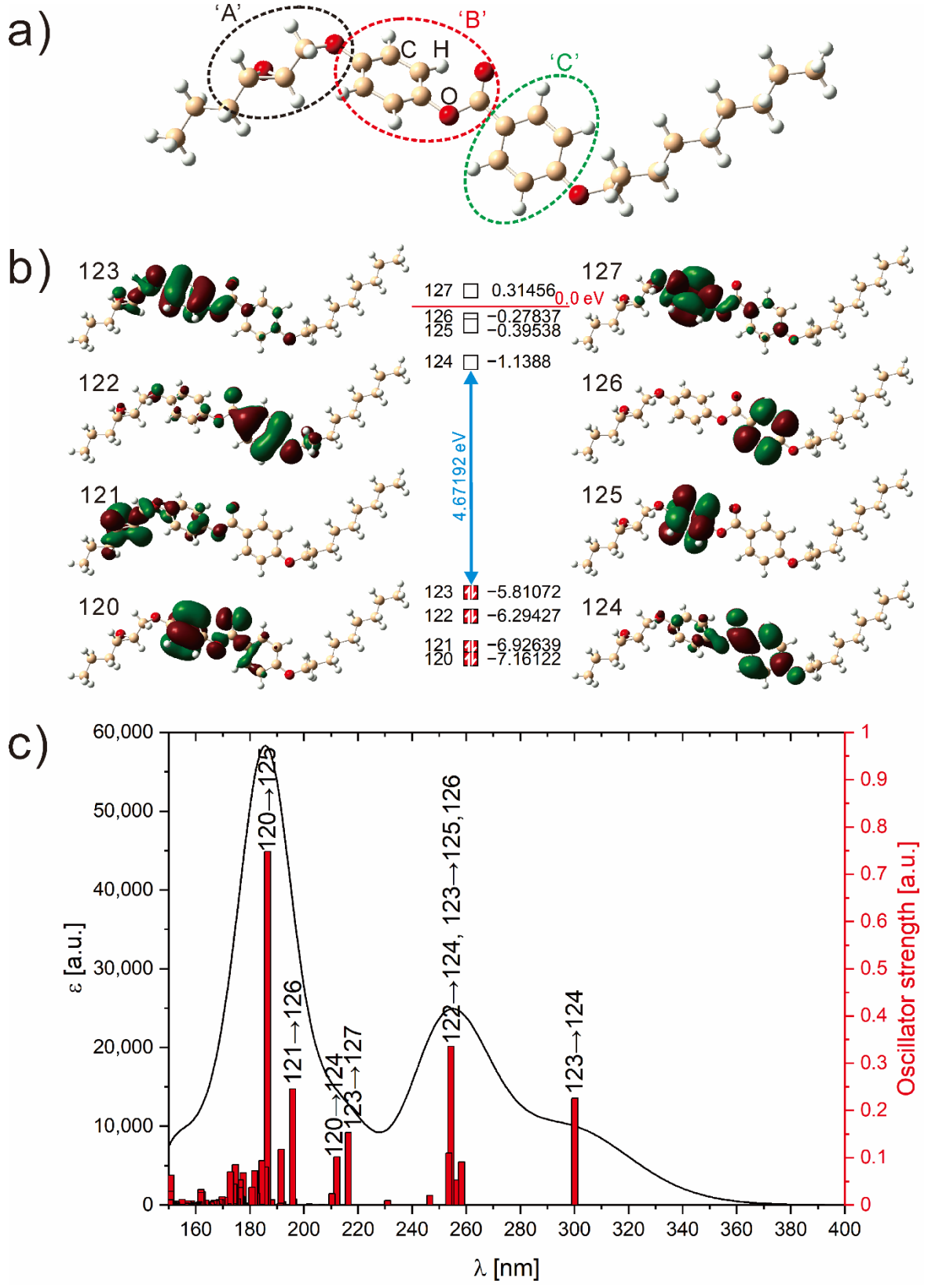

Figure S5. Model for optimized structure of EHPDB molecule used for calculation (**a**). Energy level diagram in eVs with calculated frontier molecular orbitals (**b**). Blue arrow and number correspond to the HOMO-LUMO gap. Calculated UV-Vis spectrum for optimized structure of EHPDB molecule (**c**). Red bars indicate electronic transitions with the largest contributions while legend above bars indicate electronic states involved in transition.

Table S1. List of atomic coordinates for optimized structure of EHPDB molecule.

Atom	X	Y	Z	Atom	X	Y	Z
C	2.1355	−1.7731	1.7295	H	18.7163	−6.4138	3.3196
C	16.9662	−6.67	1.4823	H	19.5618	−7.2845	0.4477
O	17.5989	−7.9895	1.7894	H	19.3947	−5.4226	0.8071
C	18.3242	−6.7769	2.2839	H	15.8922	−7.0283	3.4813
C	19.539	−6.4753	1.2862	H	15.6587	−5.2811	2.7627
C	15.7528	−6.413	2.5014	H	20.8657	−5.7703	2.9961
C	20.9204	−6.5073	2.0949	H	21.1219	−7.5865	2.4865
C	22.0976	−6.0631	1.1035	H	21.7464	−6.1956	0
O	14.479	−6.8472	1.8596	H	22.3645	−4.9446	1.2944
C	13.2898	−6.0524	1.8825	H	23.0369	−6.7264	1.2944
C	11.9971	−6.7122	1.9612	H	11.9392	−7.8749	2.019
C	13.3565	-4.5992	1.8143	H	14.3911	−4.0658	1.7538
C	10.7765	−5.9258	1.9678	H	9.7435	−6.4618	2.0306
C	12.1328	−3.8114	1.8217	H	12.1885	−2.6484	1.7677
C	10.8396	−4.4732	1.8963	H	5.7912	−5.2256	2.37
O	9.6371	−3.6925	1.8897	H	8.1924	−1.381	2.2373
C	8.4122	−4.1925	2.4323	H	3.578	−3.8497	2.1924
O	8.393	−5.3253	3.007	H	5.9759	0	2.0545
C	7.1139	−3.3776	2.3165	H	2.3423	−2.4405	3.8919
C	5.8328	−4.0628	2.3017	H	0.7655	−1.4437	3.5125
C	7.1637	-1.9288	2.2274	H	0	−3.822	3.8548
C	4.6036	−3.2961	2.2017	H	4E-4	−3.5521	1.9704
C	5.9322	−1.1625	2.1258	H	2.2389	−4.7767	1.7185
C	4.6462	−1.8431	2.1131	H	2.4766	−4.8496	3.6058
O	3.4319	-1.0871	2.0103	H	0.1743	−6.2538	3.722
C	1.4898	−2.2664	3.1164	H	0.2418	−6.361	1.8226
C	0.6709	−3.6365	2.92	H	2.5102	−7.5705	1.9061
C	1.6923	−4.868	2.7438	H	2.6407	−7.2993	3.7857
C	0.878	−6.251	2.7929	H	0.4021	−8.6975	4.0916
C	1.9063	−7.4789	2.8987	H	0.4111	−9.0525	2.2214
C	1.0777	−8.8291	3.151	H	2.7229	−10.226	2.4276
C	2.0861	−10.0534	3.3884	H	2.7911	−9.81	4.284
C	1.2389	−11.3758	3.7158	H	0.913	−11.8846	2.719
H	1.435	−1.0144	1.189	H	1.8962	−12.115	4.3324
H	2.3498	−2.6756	1.0239	H	0.2926	−11.0877	4.3324
H	16.6109	−6.1354	0.5095				

Table S2. List of calculated the first 25 excited states with oscillator strengths (f) for optimized structure of EHPDB molecule.

The Excited State	Transition		ΔE [eV], λ [nm], Oscillator Strength [a.u.]
1	123 -> 124	0.70335	Singlet-A, 4.1305 eV 300.17 nm f = 0.2260 <S**2≥0.000
2	118 -> 124 121 -> 124 121 -> 127 122 -> 124 123 -> 126	−0.27413 −0.36861 0.15271 0.23654 0.44480	Singlet-A, 4.8001 eV 258.30 nm f = 0.0911 <S**2≥0.000
3	120 -> 124 122 -> 124 122 -> 125 123 -> 125	−0.34653 −0.25683 0.32247 0.43452	Singlet-A, 4.8415 eV 256.09 nm f = 0.0528 <S**2≥0.000
4	118 -> 124 120 -> 124 121 -> 127 122 -> 124 122 -> 125 123 -> 125 123 -> 126	−0.15895 −0.15580 −0.12444 0.50773 0.16938 0.10294 −0.34003	Singlet-A, 4.8737 eV 254.39 nm f = 0.3359 <S**2≥0.000
5	118 -> 124 121 -> 124 121 -> 127 122 -> 124 123 -> 126	0.45562 0.24850 0.10203 0.29195 0.30331	Singlet-A, 4.8894 eV 253.58 nm f = 0.1100 <S**2≥0.000
6	120 -> 124 122 -> 125 123 -> 125	0.25940 −0.37178 0.53377	Singlet-A, 5.0289 eV 246.54 nm f = 0.0202 <S**2≥ 0.000
7	118 -> 124 121 -> 124 123 -> 126	−0.40403 0.53980 0.16477	Singlet-A, 5.3687 eV 230.94 nm f = 0.0098 <S**2≥0.000
8	122 -> 126	0.70133	Singlet-A 5.5626 eV 222.89 nm f = 0.0002 <S**2≥0.000
9	121 -> 126 123 -> 127	−0.28317 0.62473	Singlet-A, 5.7308 eV 216.35 nm f = 0.1536 <S**2≥0.000
10	119 -> 124 120 -> 124 122 -> 125	0.24260 0.48546 0.40384	Singlet-A, 5.8430 eV 212.19 nm f = 0.1021 <S**2≥0.000
11	119 -> 124 120 -> 124 122 -> 125	0.65286 −0.15430 −0.17068	Singlet-A, 5.8942 eV 210.35 nm f = 0.0240 <S**2≥0.000
12	118 ->125 121 ->125	0.27758 0.64849	Singlet-A, 6.0051 eV 206.46 nm f = 0.0013 <S**2≥0.000
13	120 -> 125 122 -> 127	0.11877 0.68693	Singlet-A 6.1379 eV 202.00 nm f = 0.0024 <S**2≥0.000
14	118 ->125 121 ->125	0.62777 −0.27155	Singlet-A, 6.3183 eV 196.23 nm f = 0.0122 < S**2≥0.000
15	118 -> 125 118 -> 126	−0.12436 0.55308	Singlet-A, 6.3308 eV 195.84 nm f = 0.2456 <S**2≥0.000

	121 -> 126	0.31534	
	123 -> 127	0.13476	
16	119 -> 126	0.37406	Singlet-A, 6.4302 eV 192.81 nm f = 0.0009 <S**2≥0.000
	120 -> 126	0.56814	
	121 -> 127	−0.11596	
17	119 -> 126	0.41361	Singlet-A, 6.4543 eV 192.09 nm f = 0.0068 <S**2≥0.000
	120 -> 126	−0.38587	
	121 -> 127	−0.16811	
	123 -> 129	0.31762	
	123 -> 131	0.12462	
18	116 -> 124	0.23025	Singlet-A, 6.4716 eV 191.58 nm f = 0.1179 <S**2≥0.000
	117 -> 124	0.59557	
	121 -> 126	0.14132	
	123 -> 129	−0.15735	
19	117 -> 124	0.13988	Singlet-A, 6.4811 eV 191.30 nm f = 0.0034 <S**2≥0.000
	118 -> 126	−0.13327	
	119 -> 126	−0.34348	
	120 -> 126	0.12315	
	123 -> 129	0.49678	
	123 -> 131	0.19739	
	123 -> 133	0.10558	
20	122 -> 128	0.37823	Singlet-A, 6.5932 eV 188.05 nm f = 0.0112 <S** 2≥0.000
	123 -> 128	0.55861	
21	116 -> 124	0.20560	Singlet-A, 6.6481 eV 186.50 nm f = 0.7486 <S**2≥0.000
	117 -> 124	−0.21538	
	118 -> 126	−0.23947	
	119 -> 125	0.21078	
	120 -> 125	0.43376	
	121 -> 126	0.22520	
22	116 -> 124	−0.11393	Singlet-A, 6.6743 eV 185.76 nm f = 0.0803 <S**2≥0.000
	119 -> 125	0.65434	
	121 -> 126	−0.10887	
23	112 -> 124	0.19937	Singlet-A, 6.7207 eV 184.48 nm f = 0.0936 <S**2≥0.000
	116 -> 124	0.46500	
	117 -> 124	−0.17961	
	118 -> 127	−0.15722	
	120 -> 125	−0.23204	
	121 -> 127	−0.16804	
	122 -> 128	0.13126	
	123 -> 133	−0.13578	
24	107 -> 124	0.15305	Singlet-A, 6.7372 eV 184.03 nm f = 0.0015 <S**2≥0.000
	109 -> 124	0.26722	
	110 -> 124	−0.11988	
	111 -> 124	0.19258	
	112 -> 124	0.37539	
	115 -> 124	−0.33331	
	116 -> 124	−0.15318	
	117 -> 124	0.10588	
	120 -> 125	0.10294	
25	118 -> 127	0.19228	Singlet-A, 6.7947 eV 182.47 nm f = 0.0245 <S**2≥0.000
	121 -> 127	0.21709	
	122 -> 128	0.48744	

	123 -> 128	−0.34414

Table S3. List of atomic coordinates for 'planar' EHPDB molecule.

Atom	X	Y	Z	Atom	X	Y	Z
C	5.47221	−2.5107	−0.60355	H	−10.23004	1.17922	1.29781
C	−8.36095	0.6968	0.22883	H	−9.8744	−1.50468	−0.21298
O	−9.40905	1.10694	−0.66462	H	−10.40326	−1.35721	1.47605
C	−9.77589	0.48124	0.57779	H	−8.21632	2.67209	1.02497
C	−10.44645	−0.8687	0.48434	H	−7.16712	1.48542	1.85367
C	−7.5601	1.80383	0.87121	H	−12.47003	−0.12974	0.71867
C	−11.9042	−0.76885	0.01581	H	−11.92316	−0.24832	−0.9574
C	−12.58935	−2.13099	−0.10555	H	−12.06563	−2.77879	−0.82896
O	−6.50586	2.28139	0.03726	H	−12.60462	−2.66137	0.86213
C	−5.30563	1.62408	0.01339	H	−13.63213	−2.02738	-0.44545
C	−4.32343	2.20238	−0.80822	H	−4.58109	3.10741	−1.36065
C	−4.99838	0.45943	0.73022	H	−5.73375	−0.02747	1.36993
C	−3.05488	1.64129	−0.91316	H	−2.30108	2.10473	−1.54657
C	−3.71964	−0.10115	0.62848	H	−3.46885	−1.00818	1.181
C	−2.75459	0.48314	−0.18589	H	2.19216	1.1939	−0.12605
O	−1.53805	−0.19479	−0.29163	H	−0.32046	−2.2673	−0.55797
C	−0.34738	0.48732	−0.21758	H	4.21594	−0.22473	−0.28934
O	−0.26804	1.68749	−0.07975	H	1.71232	−3.71281	−0.73686
C	0.80844	−0.43497	−0.33055	H	5.42346	−1.59827	1.36278
C	2.09576	0.11564	−0.26092	H	5.76511	−3.33185	1.34584
C	0.67427	−1.82605	−0.50097	H	7.8058	−2.19416	1.97041
C	3.2316	−0.68624	−0.35595	H	8.05161	−2.86737	0.36064
C	1.79831	−2.63362	−0.6002	H	7.65893	−0.59086	−0.65686
C	3.08899	−2.0743	−0.53074	H	7.32997	0.0699	0.94753
O	4.111	−2.96026	−0.65428	H	9.67135	−0.5212	1.66507
C	5.98795	−2.383	0.8297	H	9.99448	−1.19774	0.06735
C	7.4936	−2.09	0.91643	H	9.5793	1.06237	−0.97497
C	7.91473	−0.7027	0.41286	H	9.25435	1.73951	0.62222
C	9.41002	−0.42028	0.59476	H	11.59711	1.14814	1.34974
C	9.84067	0.96285	0.09565	H	11.92195	0.46959	-0.24711
C	11.33503	1.24648	0.27903	H	11.50415	2.72691	−1.29083
C	11.76613	2.6294	−0.22093	H	11.17939	3.40508	0.30521
C	13.26003	2.90345	−0.03344	H	13.87388	2.16538	−0.57767
H	6.03464	−3.29306	−1.13621	H	13.5376	3.90409	−0.40215
H	5.58344	−1.57559	−1.17684	H	13.54658	2.84885	1.0308
H	−7.78272	−0.16538	−0.12775				

Table S4. List of calculated the first 25 excited states with oscillator strengths (f) for 'planar' EHPDB molecule.

The Excited State	Transition		ΔE [eV], λ [nm], Oscillator Strength [a.u.]
1	123 -> 124	0.70328	Singlet-A, 3.7065 eV 334.50 nm f = 0.2535 <S**2≥0.000
2	117 -> 124	−0.15514	Singlet-A, 4.1199 eV 300.94 nm f = 0.0739 <S**2≥0.000
	118 -> 124	0.15592	
	119 -> 124	−0.35303	
	120 -> 124	0.12629	
	121 -> 124	−0.35605	
	122 -> 124	0.39191	
3	120 -> 124	−0.31977	Singlet-A, 4.4230 eV 280.31 nm f = 0.0097 <S**2≥0.000
	122 -> 125	0.28814	

	123 -> 125	0.54506	
4	121 -> 124 121 -> 127 122 -> 124 123 -> 126	−0.39317 0.16869 −0.28707 0.46020	Singlet-A, 4.4371 eV 279.42 nm f = 0.1201 <S**2≥0.000
5	120 -> 124 122 -> 124 122 -> 125 123 -> 125 123 -> 126	0.33583 −0.24274 −0.35422 0.39292 −0.14252	Singlet-A, 4.5315 eV 273.60 nm f = 0.0463 <S**2≥0.000
6	118 -> 124 119 -> 124 120 -> 124 121 -> 124 121 -> 127 122 -> 124 122 -> 125 123 -> 125 123 -> 126	−0.11928 0.30990 0.11627 0.12768 0.10476 0.40008 −0.20588 0.20816 0.26267	Singlet-A, 4.5857 eV 270.37 nm f = 0.2036 <S**2≥0.000
7	117 -> 124 118 -> 124 119 -> 124 121 -> 124 121 -> 127 123 -> 126	−0.12542 0.12843 −0.32172 0.43825 0.16494 0.33756	Singlet-A, 4.7730 eV 259.76 nm f = 0.0305 <S**2≥0.000
8	121 -> 126 122 -> 126 123 -> 127	−0.23526 0.11869 0.62160	Singlet-A, 5.2327 eV 236.94 nm f = 0.1533 <S**2≥0.000
9	119 -> 125 120 -> 124 121 -> 125 122 -> 125 123 -> 127	0.13200 −0.35113 0.40235 −0.37373 0.11784	Singlet-A, 5.2791 eV 234.86 nm f = 0.0591 <S**2≥0.000
10	120 -> 124 121 -> 125 122 -> 125	0.30226 0.54606 0.25095	Singlet-A, 5.3602 eV 231.30 nm f = 0.0563 <S**2≥0.000
11	119 -> 126 122 -> 126 123 -> 127	−0.11192 0.66766 −0.12259	Singlet-A, 5.3940 eV 229.86 nm f = 0.0277 <S**2≥0.000
12	117 -> 124 118 -> 124 119 -> 124	−0.19378 0.58031 0.32559	Singlet-A, 5.4341 eV 228.16 nm f = 0.0031 <S**2≥0.000
13	115 -> 124 117 -> 124 118 -> 124 119 -> 124	0.12820 0.60097 0.30094 −0.12426	Singlet-A, 5.5323 eV 224.11 nm f = 0.0036 <S**2≥0.000
14	117 -> 125 118 -> 125 119 -> 125 120 -> 125 121 -> 125 122 -> 127	0.15184 −0.19546 0.50366 −0.27682 −0.16855 −0.25127	Singlet-A, 5.6847 eV 218.10 nm f = 0.0237 <S**2≥0.000

15	118 -> 125 119 -> 125 120 -> 125 122 -> 127	−0.10816 0.29022 0.11133 0.59092	Singlet-A, 5.7222 eV 216.67 nm f = 0.0032 <S**2≥0.000
16	116 -> 124 118 -> 126 119 -> 126 120 -> 126 121 -> 126 122 -> 127 123 -> 127 123 ->128	0.13723 −0.10566 0.42070 −0.17106 0.39124 −0.11257 0.10427 −0.17375	Singlet-A, 5.8422 eV 212.22 nm f = 0.2235 <S**2≥0.000
17	114 -> 124 116 -> 124	0.10177 0.66601	Singlet-A, 5.8828 eV 210.76 nm f = 0.0065 <S**2≥0.000
18	119 -> 126 120 -> 125 120 -> 126 121 -> 126 123 -> 128 123 -> 130	0.25900 −0.11406 −0.11429 −0.10412 0.57129 0.11413	Singlet-A, 5.9471 eV 208.48 nm f = 0.0369 <S**2≥0.000
19	119 -> 126 120 -> 126 121 -> 127 123 -> 130 123 -> 131 123 -> 138	−0.15914 0.10989 0.11700 0.59928 −0.16079 −0.12987	Singlet-A, 6.0095 eV 206.31 nm f = 0.0038 <S **2≥0.000
20	115 -> 124 117 -> 124 117 -> 126 118 -> 126 119 -> 127 120 -> 125 121 -> 127 123 -> 126 123 -> 130	0.34686 −0.11531 −0.22305 0.10840 0.19956 0.10035 0.38777 −0.13044 −0.15059	Singlet-A, 6.0471 eV 205.03 nm f = 0.0229 <S**2≥0.000
21	115 -> 124 117 -> 126 119 -> 125 119 -> 126 120 -> 125 121 -> 126 121 -> 127 122 -> 127 122 -> 128 123 -> 128	0.39247 0.22897 0.10519 −0.13490 0.24255 0.15604 −0.23771 −0.13954 −0.11262 0.17716	Singlet-A, 6.1044 eV 203.11 nm f = 0.4016 <S**2≥0.000
22	112 -> 124 113 -> 124 114 -> 124 115 -> 124 116 -> 124 119 -> 126 120 -> 125	0.10525 −0.10746 0.31542 0.26422 −0.11814 0.10383 −0.29128	Singlet-A, 6.1447 eV 201.77 nm f = 0.0063 <S**2≥0.000

	120 -> 126	0.34837	
	121 -> 126	0.12390	
23	114 -> 124	−0.18238	Singlet-A, 6.1484 eV 201.65 nm f = 0.0947 <S**2≥0.000
	115 -> 124	−0.14505	
	119 -> 126	0.17306	
	120 -> 125	0.22991	
	120 -> 126	0.55219	
24	117 -> 125	−0.13124	Singlet-A, 6.1771 eV 200.72 nm f = 0.0022 <S**2≥0.000
	118 -> 125	0.62448	
	119 -> 125	0.28416	
25	112 -> 124	0.17334	Singlet-A, 6.2169 eV 199.43 nm f = 0.1866 <S**2≥0.000
	113 -> 124	−0.11065	
	114 ->124	0.45043	
	115 -> 124	−0.19646	
	120 -> 125	0.26942	
	122 -> 127	−0.11567	
	122 -> 128	−0.14503	
	123 -> 128	0.14629	

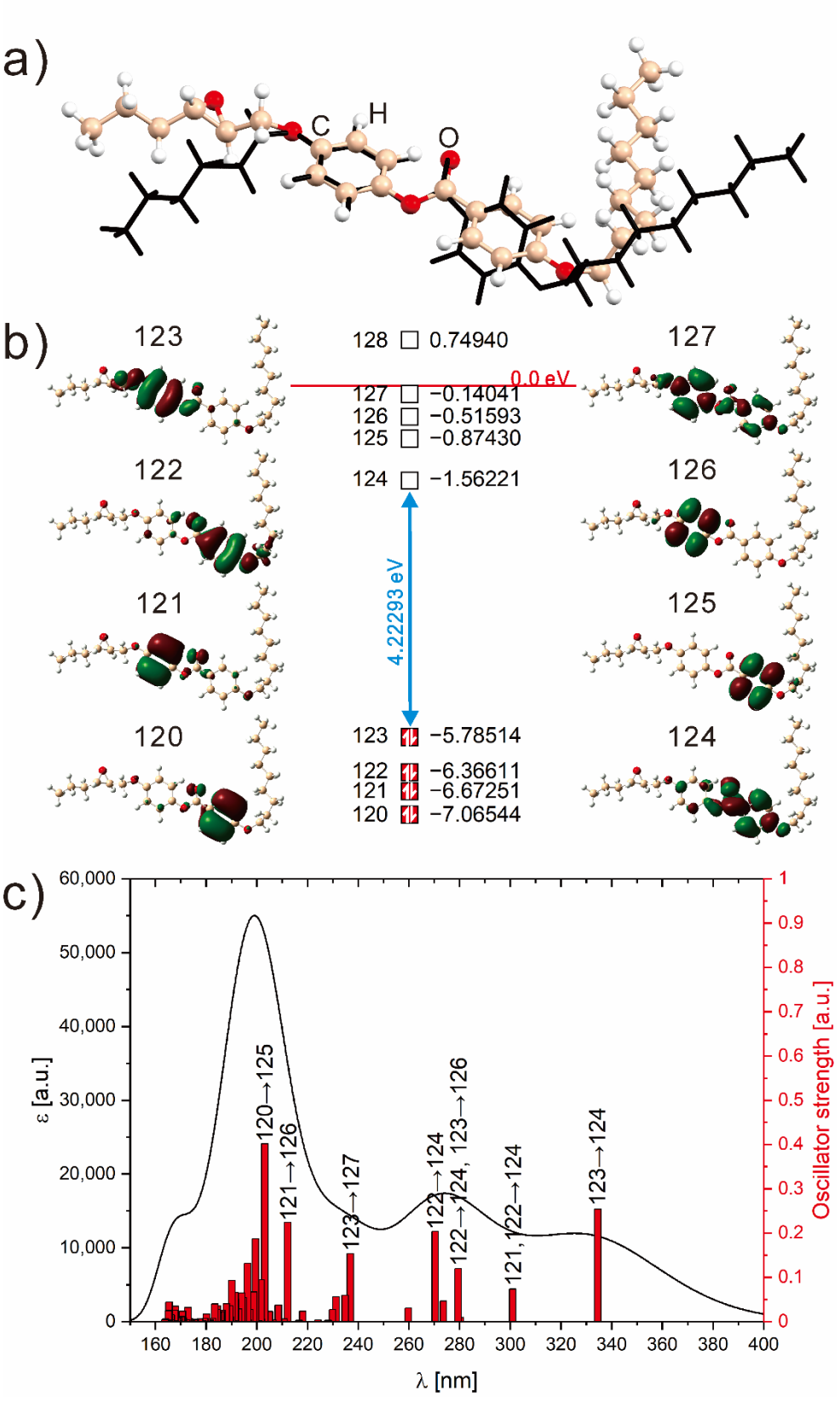

Figure S6. Model of 'planar' EHPDB molecule used for calculation (**a**). Black sticks indicate an overlapped optimized structure of EHPDB. Energy level diagram in eVs with calculated frontier molecular orbitals (**b**). Blue arrow and number correspond to the HOMO-LUMO gap. Calculated UV-Vis spectrum for 'planar' EHPDB molecule (**c**). Red bars indicate electronic transitions with the largest contributions while legend above bars indicate electronic states involved in transition.