Supporting information for

Toward highly transparent and colorless DSSC featuring new thienyl pyrrolopyrrole cyanine dyes

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1. General Methods

^1H and ^{13}C NMR spectra were recorded on an AVANCE 300 MHz BRUKER, AVANCE III 400 MHz BRUKER. Chemical shifts for ^1H NMR spectra are calibrated on residual protons in the deuterated solvent ($CDCl_3$ δ = 7.26 ppm for ^1H and δ = 77.16 ppm for ^{13}C). Spectra were recorded at room temperature, chemical shifts are given in ppm and coupling constants in Hz. High-resolution mass (HRMS) spectra were obtained by electrospray ionization coupled with high resolution ion trap orbitrap (LTQ-Orbitrap, ThermoFisher Scientific,) working in ion-positive or ion-negative mode. Electrochemical measurements were performed with a potentiostat-galvanostat Autolab PGSTAT 302N controlled by resident GPES software (General Purpose Electrochemical System 4.9) or NOVA software using a conventional single-compartment three-electrodes cell. The working electrode was a glassy carbon one. The auxiliary electrode was a stainless wire and the reference one was the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.1 N Bu4NPF6 in DMF and solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the presented experiments the scan rate was 100 mV/s.
UV-Visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer using 1 cm path length cells. Emission spectra were recorded on a SPEX Fluoromax-4 Jobin Yvon fluorimeter (1 cm quartz cells). Emission spectra are corrected in near-infrared part.

2. Experimental Section

Compound **1**, **2** and **4** were prepared according to literature.[1,2]

Compound 3. In a sealable tube, **1** (0.6 g, 0.91 mmol), **2** (0.63 g, 2.00 mmol, 2.2 eq), and K_2CO_3 (0.62 g, 4.56 mmol, 5 eq) were placed under argon atmosphere and dissolved in THF (20 mL) and water (6 mL). The solution was degassed 30 minutes in an ultrasonic bath and $Pd(PPh_3)_4$ (0.094 g, 0.081 mmol, 0.2 eq) was added. The reaction mixture was stirred at 85°C overnight. The reaction was cooled to room temperature, quenched with water, extracted 3 times with ethyl acetate, dried over magnesium sulfate and solvents were removed under reduce pressure. The crude was then heated at 180 °C for 30 minutes in the oven. After cooling to room temperature, the resulting solid was dissolved in THF and filtrated through celite. After solvents removal, the product was taken up in cyclohexane and filtrated through PTFE membrane to afford the desired compound as a violet solid (0.33 g, 54%).

NMR (^{1}H, THF, 400 MHz) δ (ppm): 10.16 (s, 2H), 8.58 (d, ^3J=4.04 Hz, 2H), 7.62 (d, ^4J=1,74 Hz, 4H), 7.69 (d, ^3J=4.03 Hz, 2H), 7.72 (t, ^4J=1.72 Hz, 2H), 1.52 (s, 36H)

NMR (^{13}C, THF, 100 MHz) δ (ppm): 159.5, 149.6, 148.3, 133.9, 133.0, 132.7, 131.1, 131.0, 130.0, 129.9, 129.4, 128.1, 126.5, 126.3, 126.2, 125.8, 122.7, 120.9, 118.4, 107.9, 32.7, 28.8

HRMS (ASAP+) m/z: $[M+H]^+$ calculated for $C_{42}H_{49}N_2O_2S_2$: 677.3235; found: 677.3254. Δ=2.8ppm

Compound 5. **3** (0.150 g, 0.222 mmol) and **4** (0.10 g, 0.055 mmol, 2.5 eq) were heated to reflux in anh. toluene under argon. Phosphoryl chloride (0.17 mL, 1.78 mmol, 8 eq) was then added. The reaction was monitored by thin-layer chromatography. As soon as complete consumption of **3** or the concentration of by-products increased, the reaction was quenched with water and extracted 3 times with ethyl acetate. The organic layer was dried over $MgSO_4$ and solvents were evaporated. The crude product was treated with methanol in an ultrasonic bath. The solid was collected by filtration and washed with methanol until the filtrate was colorless to afford the desired compound as a dark green solid (0.093 g, 43%).

NMR (^{1}H, $CDCl_3$, 300 MHz) δ (ppm): 13.74 (s, 2H), 8.68 (d, ^{3}J=5.22 Hz, 2H), 8.25 (m, 2H), 7.60 (dd, ^{4}J=3.87 Hz, ^{4}J=1.23 Hz, 2H), 7.54 (m, 6H), 7.46 (t, ^{4}J=1.35 Hz, 2H), 7.43 (d, ^{4}J=2.88 Hz, 2H), 3.97 (s, 6H), 1.41 (s, 36H)

NMR (^{13}C, $CDCl_3$, 75 MHz) δ (ppm): 165.3, 156.6, 151.6, 150.0, 148.2, 145.0, 138.4, 136.1, 136.1, 132.6, 128.4, 123.3, 123.2, 120.8, 120.8, 119.7, 118.0, 116.6, 52.7, 34.9, 31.4, 29.7

HRMS (ES+) m/z: $[M+Na]^+$ calculated for $C_{60}H_{60}N_6O_4S_2Na$: 1015.4015; found: 1015.3998. Δ=-1.7ppm.

Compound 6. Under argon atmosphere, **5** (0.035 g, 0.087 mmol) and *N*,*N*-diisopropylethylamine (0.123 mL, 0.705 mmol, 20 eq) were heated to reflux in dry dichloromethane. $BF_3{\cdot}Et_2O$ (0.17 mL, 1.41 mmol, 40 eq) was added dropwise and the mixture was heated to reflux for 1h. The reaction mixture was quenched with water, extracted three times with dichloromethane and dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography using dichloromethane as eluent to afford the desired compound as a purple solid (0.038 g, 100%).

NMR (^{1}H, $CDCl_3$, 300 MHz) δ (ppm): 8.48 (d, ^{3}J=6.59 Hz, 2H), 8.28 (d, ^{4}J=1.03 Hz, 2H), 7.69 (dd, ^{3}J=6.63 Hz, ^{4}J=1.57 Hz, 2H), 7.63 (d, ^{3}J=3.92 Hz, 2H), 7.53 (d, ^{4}J=1.73 Hz, 4H), 7.48 (d, ^{3}J=3.82 Hz, 2H), 7.40 (t, J=1.71 Hz, 2H), 3.97 (s, 6H), 1.37 (s, 36H)

HRMS (ES+) m/z: $[M+Na]^+$ calculated for $C_{60}H_{58}N_6O_4S_2{}^{19}F_4{}^{10}B_2Na$: 1109.4054; found: 1109.4034. Δ=-2.0ppm.

Compound TB179. **6** (0.040, 0.0371 mmol) was stirred at room temperature in EtOH (10 mL) and THF (3.5 mL). A solution of LiOH (0.020 g, 0.743 mmol, 20 eq) in water (5 mL) is added dropwise in the reaction mixture and stirred for 2h. Aqueous HCl (2M) was added slowly until pH = 4. The remaining solution is extracted 3 times with ethyl acetate. After evaporation, the crude product was treated with dichloromethane in an ultrasonic bath. The solid was collected by filtration to afford the desired compound as a purple solid (0.028 g, 72%).

NMR (^{1}H, $CDCl_3/CD_3OD$ 9:1, 300 MHz) δ (ppm): 8.35 (d, ^{3}J=6.6 Hz, 2H), 8.13 (s, 2H), 7.60 (d, ^{3}J=5.58 Hz, 2H), 7.47 (s, 2H), 7.38 (s, 4H), 7.32 (d, ^{4}J=3.27 Hz, 2H), 7.27 (s, 2H), 1.21 (s, 36H)

HRMS (ES-) m/z: $[M]^-$ calculated for $C_{82}H_{72}{}^{10}B_2N_6O_4S_2$: 1056.3686; found: 1056.3730. Δ=4.2ppm.

Compound 7. Under argon atmosphere, **5** (0.040 g, 0.040 mmol) and *N*,*N*-diisopropylethylamine (0.07 mL, 0.40 mmol, 10 eq) were heated to reflux in dry dichloromethane. Chloro(diphenyl)borane (0.1 mL) was added dropwise and the mixture was heated to reflux for 10min. The reaction mixture was quenched with water, extracted three times with dichloromethane and dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography using dichloromethane/petroleum ether : 7/3 as eluent to afford the desired compound as a purple solid (0.014 g, 26%).

NMR (^1H, $CDCl_3$, 300 MHz) δ (ppm): 8.01 (d, ^3J=6.87 Hz, 2H), 7.98 (d, ^4J=1.55 Hz, 2H), 7.34 (t, ^4J=1.65 Hz, 2H), 7.21 (m, 26H), 6.82 (d, ^3J=3.73 Hz, 2H), 6.30 (d, ^3J=3.76 Hz, 2H), 3.82 (s, 6H), 1.35 (s, 36H)

HRMS (ES+) m/z: $[M+Na]^+$ calculated for $C_{84}H_{78}N_6O_4S_2{}^{10}B_2Na$: 1342.5646; found: 1342.5643. Δ=-0.2ppm.

Compound TB202. 7 (0.014, 0.011 mmol) was stirred at room temperature in THF (5 mL). A solution of LiOH (0.005 g, 0.212 mmol, 20 eq) in water (1 mL) is added dropwise to the reaction mixture and stirred for 1h. Aqueous HCl (2M) was added slowly until pH = 4. The remaining solution is extracted three times with ethyl acetate. After evaporation, the crude product was dissolved in dichloromethane and petroleum ether was added. The resulting precipitate was collected by filtration and washed with petroleum ether to afford the desired compound as a dark purple solid (0.012 g, 87%).

NMR (^1H, $CDCl_3/CD_3OD$ 9:1, 300 MHz) δ (ppm): 8.02 (m, 4H), 7.34 (t, ^4J=2.07 Hz, 4Hz), 7.22 (m, 26H), 6.82 (d, ^3J=4.02 Hz, 2H), 6.30 (d, ^3J=3.84 Hz, 2H), 1.34 (s, 36H)

HRMS (ES+) hm/z: $[M]^+$ calculated for $C_{82}H_{72}N_6O_4S_2{}^{10}B_2$: 1288.5315; found: 1288.5350. Δ=2.7ppm.

3. Spectroscopic and Electrochemical Properties

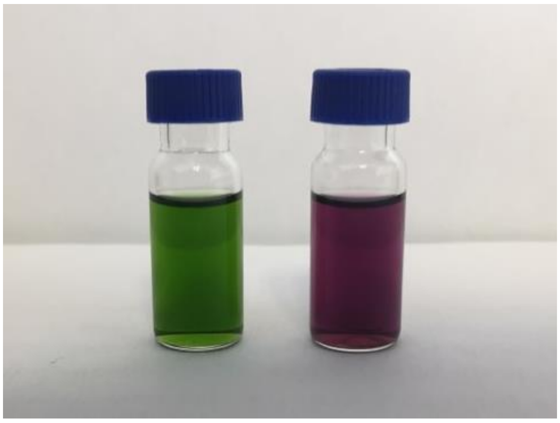

Figure S1. *Pictures of compound **TB207**[3] and **TB202** solubilized in DMF solution at room temperature.*

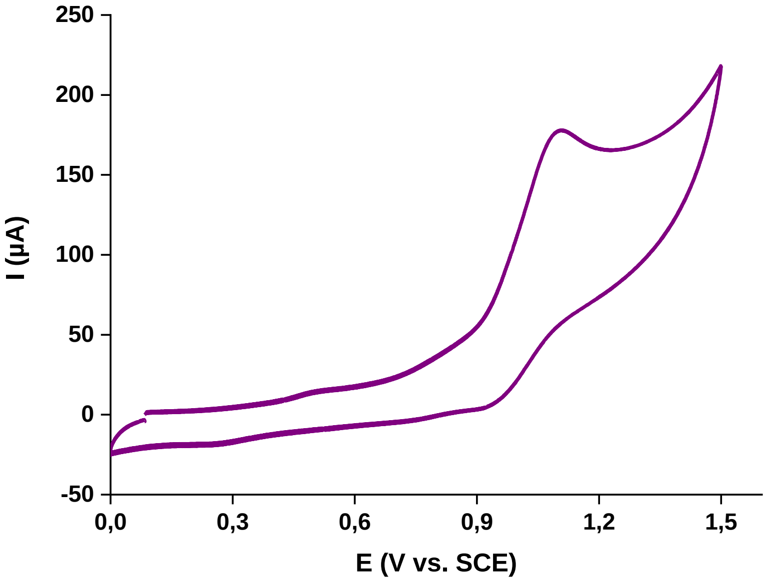

Figure S2. *Electrochemical properties of **TB179** in supporting electrolyte (0.1 N Bu_4NPF_6 in DMF), scan rate = 100 mV/s.*

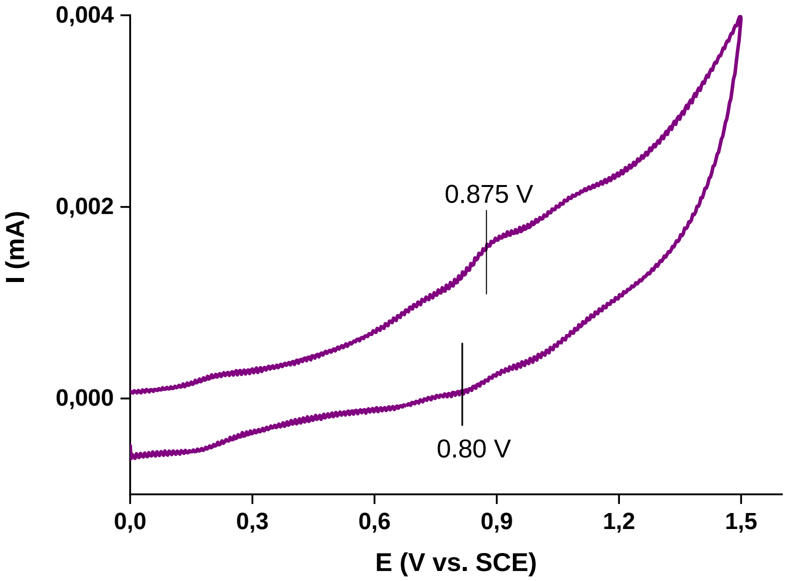

Figure S3. *Electrochemical properties of **TB202** in supporting electrolyte (0.1 N Bu_4NPF_6 in DMF), scan rate = 100 mV/s.*

4. Quantum Chemical Calculations

Methods. The dyes were modelled without any structural simplification using the same protocol as in our previous work.[3] We use a computational strategy relying on TD-DFT combined with the popular Polarizable Continuum Model (PCM)[4] for simulating solvent effects (here DMF).

All calculations were achieved with the Gaussian16.A03 program,[5] with improved self-consistent field (10^{-10} a.u.) and geometry optimization (10^{-5} a.u.) thresholds. During the optimizations and frequency calculations we used the finest DFT integration grid available in Gaussian 16, the so-called *superfinegrid* whereas in the CP-KS procedure the *ultrafine* grid was used. Default grid were used for the SP calculations. Point group symmetry (here C_i) was enforced during the calculation which led to true minima (no imaginary frequency). The DFT and TD-DFT calculations use Truhlar's M06-2X meta-GGA hybrid functional,[6] a choice justified as this functional tends to provide consistent (high correlation) energies with respect to experimental data.[7] Following our approach for computing 0-0 energies,[7] the 6-31G(d) atomic basis set was selected for geometries and vibrations whereas the 6-311+G(d) basis set is chosen for obtaining total and transition energies. We have optimized and computed frequencies on both the ground and excited states, and no imaginary frequencies were found. In combining PCM and TD-DFT, we used the LR model for optimization/frequencies, and the cLR^2 model[8] for energies.

Additional theoretical results.

Table S1. *Summary of the vertical absorption and emission data computed for **TB179** and **TB202:** Symmetry, vertical excitation wavelength and related oscillator strength. Note that the reported absorption values are obtained in non-equilibrium PCM limit, whereas the emission is determined in the equilibrium limit. In both cases, LR-PCM is applied here.*

	TB179			***TB202***		
	Sym	λ^{vert} (nm)	*f*	Sym	λ^{vert} (nm)	*f*
S_0-S_1	A_u	668	0.919	A_u	688	0.935
S_0-S_2	A_g	452	0.000	A_u	465	0.003
S_0-S_3	A_u	445	0.805	A_g	456	0.000
S_0-S_4	A_g	394	0.000	A_g	427	0.000
S_0-S_5	A_u	377	0.111	A_g	413	0.000
S_0-S_6				A_u	387	0.025
S_0-S_7				A_g	353	0.000
S_1-S_0	A_u	749	0.844	A_u	830	1.146

Cartesian coordinates. Below are the Cartesian coordinates (Å) of the different systems, as obtained at the PCM(DMF)-M06-2X/6-31G(d) level of theory, together with the computed Gibbs energies (in Hartree). All systems are true minima (no imaginary frequency).

TB179 – Ground-State – *G*= -4115.723896 au

C	-0.6252670	1.6242930	0.0928680
C	-1.7100040	-0.3602730	0.3383130
C	-0.3247060	-0.6328800	0.0809540
C	0.3247060	0.6328800	-0.0809540
C	0.6252670	-1.6242930	-0.0928680
C	1.7100040	0.3602730	-0.3383130
C	2.8332300	1.1798890	-0.4175470
C	-2.8332300	-1.1798890	0.4175470
C	-0.4974750	3.0469800	-0.1617220
C	0.0959950	3.5595440	-1.2913280
C	0.1046750	4.9741170	-1.3216150
H	0.5035850	2.9278370	-2.0733100
C	-0.4587850	5.5362420	-0.2025770
H	0.5417110	5.5574820	-2.1233590
C	0.4974750	-3.0469800	0.1617220
C	-0.0959950	-3.5595440	1.2913280
C	-0.1046750	-4.9741170	1.3216150
H	-0.5035850	-2.9278370	2.0733100
C	0.4587850	-5.5362420	0.2025770
H	-0.5417110	-5.5574820	2.1233590
N	1.8329690	-1.0122470	-0.4024210
N	-1.8329690	1.0122470	0.4024210
C	2.7559210	2.5580480	-0.0850920
N	2.7703440	3.6795550	0.2142400
C	-2.7559210	-2.5580480	0.0850920
N	-2.7703440	-3.6795550	-0.2142400
C	4.1458260	0.6490680	-0.6814320
C	5.2808010	1.4828860	-0.7803050
N	4.3015880	-0.6862330	-0.8419850
C	6.5133320	0.9311520	-1.0451540
H	5.1679330	2.5520570	-0.6496430
C	5.5176260	-1.2240960	-1.1040420
C	6.6464540	-0.4560280	-1.2158710
H	5.5337120	-2.3014620	-1.2152800
C	-4.1458260	-0.6490680	0.6814320
C	-5.2808010	-1.4828860	0.7803050
N	-4.3015880	0.6862330	0.8419850
C	-6.5133320	-0.9311520	1.0451540
H	-5.1679330	-2.5520570	0.6496430
C	-5.5176260	1.2240960	1.1040420
C	-6.6464540	0.4560280	1.2158710
H	-5.5337120	2.3014620	1.2152800
B	-3.1407020	1.7654310	0.7113230
B	3.1407020	-1.7654310	-0.7113230
H	-7.6104520	0.9006710	1.4258260
H	7.6104520	-0.9006710	-1.4258260
C	-7.7464100	-1.7776730	1.1613720
O	-8.8389220	-1.3213370	1.3943920
O	-7.4955310	-3.0744220	0.9789450
H	-8.3347060	-3.5628050	1.0671640
C	7.7464100	1.7776730	-1.1613720
O	8.8389220	1.3213370	-1.3943920
O	7.4955310	3.0744220	-0.9789450
H	8.3347060	3.5628050	-1.0671640
F	-3.4889760	2.6287240	-0.3046300
F	-3.0546950	2.4241870	1.9247440
F	3.4889760	-2.6287240	0.3046300
F	3.0546950	-2.4241870	-1.9247440

C	0.6059480	-6.9652390	-0.1145290
C	0.6373780	-7.4087560	-1.4458430
C	0.7103700	-7.8939420	0.9201440
C	0.7702180	-8.7604080	-1.7457640
H	0.5344630	-6.6787930	-2.2423050
C	0.8349870	-9.2630600	0.6547140
H	0.7149360	-7.5378590	1.9466920
C	0.8640410	-9.6688530	-0.6786710
H	0.9642390	-10.7243350	-0.9082370
C	-0.6059480	6.9652390	0.1145290
C	-0.7103700	7.8939420	-0.9201440
C	-0.6373780	7.4087560	1.4458430
C	-0.8349870	9.2630600	-0.6547140
H	-0.7149360	7.5378590	-1.9466920
C	-0.7702180	8.7604080	1.7457640
H	-0.5344630	6.6787930	2.2423050
C	-0.8640410	9.6688530	0.6786710
H	-0.9642390	10.7243350	0.9082370
C	0.9451500	-10.2466690	1.8239440
C	2.1904950	-9.9052410	2.6597570
C	-0.3089840	-10.1277310	2.7065670
C	1.0655220	-11.6987370	1.3507420
H	3.0981430	-9.9813750	2.0518670
H	2.1380670	-8.8913950	3.0683290
H	2.2797570	-10.6024330	3.5001130
H	-1.2107440	-10.3672010	2.1332750
H	-0.2415090	-10.8249300	3.5489090
H	-0.4224150	-9.1182650	3.1137510
H	1.1352690	-12.3589120	2.2210500
H	0.1924000	-12.0062930	0.7654610
H	1.9625210	-11.8519520	0.7413810
C	-0.9451500	10.2466690	-1.8239440
C	0.3089840	10.1277310	-2.7065670
C	-2.1904950	9.9052410	-2.6597570
C	-1.0655220	11.6987370	-1.3507420
H	1.2107440	10.3672010	-2.1332750
H	0.4224150	9.1182650	-3.1137510
H	0.2415090	10.8249300	-3.5489090
H	-3.0981430	9.9813750	-2.0518670
H	-2.2797570	10.6024330	-3.5001130
H	-2.1380670	8.8913950	-3.0683290
H	-1.1352690	12.3589120	-2.2210500
H	-1.9625210	11.8519520	-0.7413810
H	-0.1924000	12.0062930	-0.7654610
C	-0.8076630	9.2870000	3.1835510
C	-0.6942370	8.1603330	4.2154070
C	0.3629140	10.2611100	3.4000890
C	-2.1362880	10.0257620	3.4187780
H	-1.5173980	7.4439280	4.1225940
H	0.2513540	7.6165870	4.1173760
H	-0.7323150	8.5858890	5.2231500
H	0.3086110	11.1165500	2.7197840
H	0.3453230	10.6450720	4.4260090
H	1.3214280	9.7569550	3.2380540
H	-2.1743110	10.4092950	4.4442930
H	-2.2538280	10.8742970	2.7378130
H	-2.9861340	9.3508370	3.2723820
C	0.8076630	-9.2870000	-3.1835510
C	-0.3629140	-10.2611100	-3.4000890
C	0.6942370	-8.1603330	-4.2154070
C	2.1362880	-10.0257620	-3.4187780
H	-0.3086110	-11.1165500	-2.7197840
H	-1.3214280	-9.7569550	-3.2380540
H	-0.3453230	-10.6450720	-4.4260090
H	1.5173980	-7.4439280	-4.1225940
H	0.7323150	-8.5858890	-5.2231500
H	-0.2513540	-7.6165870	-4.1173760
H	2.1743110	-10.4092950	-4.4442930

H	2.9861340	-9.3508370	-3.2723820
H	2.2538280	-10.8742970	-2.7378130
S	-1.0442930	4.3192120	0.8841710
S	1.0442930	-4.3192120	-0.8841710

TB179 – Excited-State – *G*= -4115.663740 au

C	-0.6393490	1.6352220	0.2159540
C	-1.6789870	-0.3695000	0.4121860
C	-0.3172840	-0.6247760	0.0651850
C	0.3172840	0.6247760	-0.0651850
C	0.6393490	-1.6352220	-0.2159540
C	1.6789870	0.3695000	-0.4121860
C	2.8136820	1.1965290	-0.4750990
C	-2.8136820	-1.1965290	0.4750990
C	-0.4900680	3.0438710	-0.0223220
C	0.2305100	3.5445400	-1.0931960
C	0.2667290	4.9502800	-1.1361240
H	0.7039110	2.8993770	-1.8258140
C	-0.4135180	5.5378690	-0.0903350
H	0.7946850	5.5161030	-1.8944070
C	0.4900680	-3.0438710	0.0223220
C	-0.2305100	-3.5445400	1.0931960
C	-0.2667290	-4.9502800	1.1361240
H	-0.7039110	-2.8993770	1.8258140
C	0.4135180	-5.5378690	0.0903350
H	-0.7946850	-5.5161030	1.8944070
N	1.8017970	-0.9985770	-0.5662860
N	-1.8017970	0.9985770	0.5662860
C	2.7947620	2.5071980	0.0757540
N	2.8628610	3.5611190	0.5588650
C	-2.7947620	-2.5071980	-0.0757540
N	-2.8628610	-3.5611190	-0.5588650
C	4.0770250	0.7139300	-0.9450980
C	5.1898510	1.5665030	-1.1162590
N	4.2016980	-0.6034970	-1.2669410
C	6.3634450	1.0662420	-1.6322720
H	5.1017150	2.6136390	-0.8526370
C	5.3564750	-1.0848700	-1.7876980
C	6.4556040	-0.2919320	-1.9900330
H	5.3510170	-2.1415330	-2.0269520
C	-4.0770250	-0.7139300	0.9450980
C	-5.1898510	-1.5665030	1.1162590
N	-4.2016980	0.6034970	1.2669410
C	-6.3634450	-1.0662420	1.6322720
H	-5.1017150	-2.6136390	0.8526370
C	-5.3564750	1.0848700	1.7876980
C	-6.4556040	0.2919320	1.9900330
H	-5.3510170	2.1415330	2.0269520
B	-3.1170690	1.7138960	0.9512210
B	3.1170690	-1.7138960	-0.9512210
H	-7.3692480	0.6954460	2.4067010
H	7.3692480	-0.6954460	-2.4067010
C	-7.5644470	-1.9353310	1.8403380
O	-8.6045370	-1.5263860	2.2974350
O	-7.3552800	-3.1991360	1.4659280
H	-8.1737860	-3.7030110	1.6285150
C	7.5644470	1.9353310	-1.8403380
O	8.6045370	1.5263860	-2.2974350
O	7.3552800	3.1991360	-1.4659280
H	8.1737860	3.7030110	-1.6285150
F	-3.5837280	2.4935680	-0.0849860
F	-2.9401420	2.4582010	2.1039480
F	3.5837280	-2.4935680	0.0849860
F	2.9401420	-2.4582010	-2.1039480
C	0.5769120	-6.9699600	-0.1848740
C	0.8268670	-7.4300760	-1.4884260

C	0.4809060	-7.8908350	0.8594920
C	0.9787370	-8.7867290	-1.7510210
H	0.8784340	-6.7085770	-2.2973720
C	0.6206570	-9.2642570	0.6295120
H	0.3175900	-7.5258490	1.8696440
C	0.8688140	-9.6850250	-0.6764940
H	0.9839160	-10.7447620	-0.8776390
C	-0.5769120	6.9699600	0.1848740
C	-0.4809060	7.8908350	-0.8594920
C	-0.8268670	7.4300760	1.4884260
C	-0.6206570	9.2642570	-0.6295120
H	-0.3175900	7.5258490	-1.8696440
C	-0.9787370	8.7867290	1.7510210
H	-0.8784340	6.7085770	2.2973720
C	-0.8688140	9.6850250	0.6764940
H	-0.9839160	10.7447620	0.8776390
C	0.5095450	-10.2375510	1.8073150
C	1.6018730	-9.9115940	2.8400730
C	-0.8736780	-10.0853040	2.4626510
C	0.6782870	-11.6964370	1.3713090
H	2.5976910	-10.0123410	2.3958750
H	1.5025560	-8.8925160	3.2262990
H	1.5321360	-10.6011850	3.6884650
H	-1.6695570	-10.3132060	1.7458670
H	-0.9647300	-10.7751610	3.3087750
H	-1.0339220	-9.0699210	2.8380770
H	0.5849660	-12.3487810	2.2452620
H	-0.0887780	-11.9929460	0.6480090
H	1.6625370	-11.8734420	0.9248730
C	-0.5095450	10.2375510	-1.8073150
C	0.8736780	10.0853040	-2.4626510
C	-1.6018730	9.9115940	-2.8400730
C	-0.6782870	11.6964370	-1.3713090
H	1.6695570	10.3132060	-1.7458670
H	1.0339220	9.0699210	-2.8380770
H	0.9647300	10.7751610	-3.3087750
H	-2.5976910	10.0123410	-2.3958750
H	-1.5321360	10.6011850	-3.6884650
H	-1.5025560	8.8925160	-3.2262990
H	-0.5849660	12.3487810	-2.2452620
H	-1.6625370	11.8734420	-0.9248730
H	0.0887780	11.9929460	-0.6480090
C	-1.2500950	9.3300710	3.1569560
C	-1.3374670	8.2130960	4.2017760
C	-0.1137670	10.2842690	3.5622910
C	-2.5841600	10.0959870	3.1555810
H	-2.1477940	7.5117670	3.9759560
H	-0.4005450	7.6502070	4.2705860
H	-1.5375080	8.6507930	5.1848430
H	-0.0330040	11.1326410	2.8757530
H	-0.2987420	10.6804210	4.5667880
H	0.8476200	9.7600450	3.5710770
H	-2.7883580	10.4923700	4.1562470
H	-2.5670690	10.9383400	2.4572740
H	-3.4100730	9.4350530	2.8723890
C	1.2500950	-9.3300710	-3.1569560
C	0.1137670	-10.2842690	-3.5622910
C	1.3374670	-8.2130960	-4.2017760
C	2.5841600	-10.0959870	-3.1555810
H	0.0330040	-11.1326410	-2.8757530
H	-0.8476200	-9.7600450	-3.5710770
H	0.2987420	-10.6804210	-4.5667880
H	2.1477940	-7.5117670	-3.9759560
H	1.5375080	-8.6507930	-5.1848430
H	0.4005450	-7.6502070	-4.2705860
H	2.7883580	-10.4923700	-4.1562470
H	3.4100730	-9.4350530	-2.8723890
H	2.5670690	-10.9383400	-2.4572740

S	-1.1343640	4.3445620	0.9391320
S	1.1343640	-4.3445620	-0.9391320

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C	-0.4437950	1.6596040	-0.2540930
C	-1.7645250	-0.1219770	0.2007300
C	-0.4025830	-0.5739100	0.1419920
C	0.4025830	0.5739100	-0.1419920
C	0.4437950	-1.6596040	0.2540930
C	1.7645250	0.1219770	-0.2007300
C	2.9614050	0.7826220	-0.4473540
C	-2.9614050	-0.7826220	0.4473540
C	-0.1185010	3.0535870	-0.5698970
C	-0.0977380	3.6466160	-1.8018830
C	0.2415710	5.0252530	-1.7354530
H	-0.3440940	3.1171200	-2.7153030
C	0.4763290	5.4635490	-0.4563480
H	0.2723150	5.6785520	-2.6000030
C	0.1185010	-3.0535870	0.5698970
C	0.0977380	-3.6466160	1.8018830
C	-0.2415710	-5.0252530	1.7354530
H	0.3440940	-3.1171200	2.7153030
C	-0.4763290	-5.4635490	0.4563480
H	-0.2723150	-5.6785520	2.6000030
N	1.7429580	-1.2406350	0.0337080
N	-1.7429580	1.2406350	-0.0337080
C	2.9991170	2.1819900	-0.6932260
N	3.1383380	3.3147520	-0.9068900
C	-2.9991170	-2.1819900	0.6932260
N	-3.1383380	-3.3147520	0.9068900
C	4.2148050	0.0742300	-0.5713920
C	5.3842900	0.7377280	-0.9978160
N	4.2619350	-1.2539210	-0.3033410
C	6.5599230	0.0357960	-1.1447130
H	5.3444920	1.7981770	-1.2126550
C	5.4197670	-1.9348340	-0.4676550
C	6.5858330	-1.3380570	-0.8798000
H	5.3689230	-2.9949610	-0.2574820
C	-4.2148050	-0.0742300	0.5713920
C	-5.3842900	-0.7377280	0.9978160
N	-4.2619350	1.2539210	0.3033410
C	-6.5599230	-0.0357960	1.1447130
H	-5.3444920	-1.7981770	1.2126550
C	-5.4197670	1.9348340	0.4676550
C	-6.5858330	1.3380570	0.8798000
H	-5.3689230	2.9949610	0.2574820
B	-3.0299080	2.0754050	-0.3845130
B	3.0299080	-2.0754050	0.3845130
H	-7.4954460	1.9129210	0.9960830
H	7.4954460	-1.9129210	-0.9960830
C	-7.8273200	-0.6985690	1.5932420
O	-8.8685210	-0.1047750	1.7354860
O	-7.6723090	-2.0051070	1.8130920
H	-8.5303760	-2.3692260	2.0987030
C	7.8273200	0.6985690	-1.5932420
O	8.8685210	0.1047750	-1.7354860
O	7.6723090	2.0051070	-1.8130920
H	8.5303760	2.3692260	-2.0987030
C	-0.8013480	-6.8230690	-0.0010620
C	-0.4895270	-7.2282940	-1.3086050
C	-1.4105420	-7.7279680	0.8670790
C	-0.7795000	-8.5151680	-1.7488860
H	0.0074540	-6.5228120	-1.9668120
C	-1.6962220	-9.0385370	0.4646250
H	-1.6778530	-7.3974050	1.8672350
C	-1.3732980	-9.4070620	-0.8409960

H	-1.5868280	-10.4171740	-1.1738850
C	0.8013480	6.8230690	0.0010620
C	1.4105420	7.7279680	-0.8670790
C	0.4895270	7.2282940	1.3086050
C	1.6962220	9.0385370	-0.4646250
H	1.6778530	7.3974050	-1.8672350
C	0.7795000	8.5151680	1.7488860
H	-0.0074540	6.5228120	1.9668120
C	1.3732980	9.4070620	0.8409960
H	1.5868280	10.4171740	1.1738850
C	-2.3563760	-10.0005950	1.4576200
C	-1.4553070	-10.1509470	2.6951500
C	-3.7195320	-9.4316640	1.8866110
C	-2.5828150	-11.3910890	0.8557030
H	-0.4770100	-10.5558730	2.4153810
H	-1.2956660	-9.1920380	3.1977570
H	-1.9178350	-10.8354570	3.4147560
H	-4.3804430	-9.3154730	1.0212170
H	-4.2014600	-10.1103630	2.5990170
H	-3.6160380	-8.4550990	2.3694100
H	-3.0491840	-12.0389570	1.6047090
H	-3.2476480	-11.3515430	-0.0136750
H	-1.6399680	-11.8567100	0.5494970
C	2.3563760	10.0005950	-1.4576200
C	3.7195320	9.4316640	-1.8866110
C	1.4553070	10.1509470	-2.6951500
C	2.5828150	11.3910890	-0.8557030
H	4.3804430	9.3154730	-1.0212170
H	3.6160380	8.4550990	-2.3694100
H	4.2014600	10.1103630	-2.5990170
H	0.4770100	10.5558730	-2.4153810
H	1.9178350	10.8354570	-3.4147560
H	1.2956660	9.1920380	-3.1977570
H	3.0491840	12.0389570	-1.6047090
H	1.6399680	11.8567100	-0.5494970
H	3.2476480	11.3515430	0.0136750
C	0.4505810	8.9906160	3.1673650
C	-0.0927680	7.8581430	4.0454450
C	1.7214690	9.5421610	3.8359210
C	-0.6094310	10.1023130	3.0903830
H	-1.0302880	7.4505040	3.6526840
H	0.6278710	7.0378890	4.1328910
H	-0.2921530	8.2414910	5.0511920
H	2.1334120	10.3957490	3.2895580
H	1.4920010	9.8760040	4.8537810
H	2.4951200	8.7693220	3.8942790
H	-0.8541520	10.4611060	4.0963270
H	-0.2535130	10.9550800	2.5034620
H	-1.5281560	9.7286840	2.6250830
C	-0.4505810	-8.9906160	-3.1673650
C	-1.7214690	-9.5421610	-3.8359210
C	0.0927680	-7.8581430	-4.0454450
C	0.6094310	-10.1023130	-3.0903830
H	-2.1334120	-10.3957490	-3.2895580
H	-2.4951200	-8.7693220	-3.8942790
H	-1.4920010	-9.8760040	-4.8537810
H	1.0302880	-7.4505040	-3.6526840
H	0.2921530	-8.2414910	-5.0511920
H	-0.6278710	-7.0378890	-4.1328910
H	0.8541520	-10.4611060	-4.0963270
H	1.5281560	-9.7286840	-2.6250830
H	0.2535130	-10.9550800	-2.5034620
S	0.2988860	4.1699830	0.6804080
S	-0.2988860	-4.1699830	-0.6804080
C	-2.9952900	3.5344340	0.3131940
C	-2.9263410	4.7325660	-0.4071150
C	-3.0055050	3.6291880	1.7149700
C	-2.8599980	5.9691060	0.2348940

H	-2.8946180	4.7003860	-1.4930780
C	-2.9494350	4.8571160	2.3691110
H	-3.0541310	2.7175020	2.3101600
C	-2.8768340	6.0355950	1.6255190
H	-2.7891170	6.8809360	-0.3519820
H	-2.9598310	4.8979720	3.4549460
H	-2.8367730	6.9997940	2.1255540
C	2.9952900	-3.5344340	-0.3131940
C	3.0055050	-3.6291880	-1.7149700
C	2.9263410	-4.7325660	0.4071150
C	2.9494350	-4.8571160	-2.3691110
H	3.0541310	-2.7175020	-2.3101600
C	2.8599980	-5.9691060	-0.2348940
H	2.8946180	-4.7003860	1.4930780
C	2.8768340	-6.0355950	-1.6255190
H	2.9598310	-4.8979720	-3.4549460
H	2.7891170	-6.8809360	0.3519820
H	2.8367730	-6.9997940	-2.1255540
C	-3.2893620	2.0236290	-1.9857730
C	-2.5241630	1.2141190	-2.8381270
C	-4.3294710	2.7573650	-2.5802990
C	-2.7709190	1.1452910	-4.2099930
H	-1.7067320	0.6201260	-2.4329230
C	-4.5894050	2.6963840	-3.9471520
H	-4.9495090	3.4077250	-1.9659670
C	-3.8064770	1.8878090	-4.7701740
H	-2.1545330	0.5090270	-4.8386050
H	-5.3995420	3.2826780	-4.3711850
H	-4.0029860	1.8381980	-5.8369660
C	3.2893620	-2.0236290	1.9857730
C	4.3294710	-2.7573650	2.5802990
C	2.5241630	-1.2141190	2.8381270
C	4.5894050	-2.6963840	3.9471520
H	4.9495090	-3.4077250	1.9659670
C	2.7709190	-1.1452910	4.2099930
H	1.7067320	-0.6201260	2.4329230
C	3.8064770	-1.8878090	4.7701740
H	5.3995420	-3.2826780	4.3711850
H	2.1545330	-0.5090270	4.8386050
H	4.0029860	-1.8381980	5.8369660

TB202 – Excited-State – *G*=- -4642.069955 au

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C	0.3965730	0.5675360	-0.1413250
C	0.4692870	-1.6688630	0.3036820
C	1.7555200	0.1237180	-0.1671150
C	2.9603490	0.7865220	-0.4433930
C	-2.9603490	-0.7865220	0.4433930
C	-0.1468740	3.0586540	-0.6253150
C	-0.1637150	3.6735170	-1.8475800
C	0.1899100	5.0479620	-1.7738960
H	-0.4453300	3.1599380	-2.7599330
C	0.4706060	5.4671730	-0.4974380
H	0.1942280	5.7140990	-2.6292900
C	0.1468740	-3.0586540	0.6253150
C	0.1637150	-3.6735170	1.8475800
C	-0.1899100	-5.0479620	1.7738960
H	0.4453300	-3.1599380	2.7599330
C	-0.4706060	-5.4671730	0.4974380
H	-0.1942280	-5.7140990	2.6292900
N	1.7466570	-1.2325630	0.1058540
N	-1.7466570	1.2325630	-0.1058540
C	2.9734080	2.1700430	-0.7707930
N	3.0789970	3.2897140	-1.0601670

C	-2.9734080	-2.1700430	0.7707930
N	-3.0789970	-3.2897140	1.0601670
C	4.2173630	0.1022300	-0.5107460
C	5.3977320	0.7779720	-0.8943670
N	4.2678330	-1.2329160	-0.2305160
C	6.5846430	0.0906380	-1.0011760
H	5.3549540	1.8386280	-1.1092110
C	5.4399860	-1.8971930	-0.3607460
C	6.6115040	-1.2885950	-0.7371490
H	5.3960820	-2.9589470	-0.1551330
C	-4.2173630	-0.1022300	0.5107460
C	-5.3977320	-0.7779720	0.8943670
N	-4.2678330	1.2329160	0.2305160
C	-6.5846430	-0.0906380	1.0011760
H	-5.3549540	-1.8386280	1.1092110
C	-5.4399860	1.8971930	0.3607460
C	-6.6115040	1.2885950	0.7371490
H	-5.3960820	2.9589470	0.1551330
B	-3.0439140	2.0671740	-0.4283410
B	3.0439140	-2.0671740	0.4283410
H	-7.5285200	1.8562330	0.8289910
H	7.5285200	-1.8562330	-0.8289910
C	-7.8564000	-0.7664700	1.4027460
O	-8.9094920	-0.1850060	1.5118940
O	-7.6975010	-2.0737520	1.6239770
H	-8.5621310	-2.4444690	1.8792360
C	7.8564000	0.7664700	-1.4027460
O	8.9094920	0.1850060	-1.5118940
O	7.6975010	2.0737520	-1.6239770
H	8.5621310	2.4444690	-1.8792360
C	-0.8087700	-6.8215560	0.0344850
C	-0.5245770	-7.2152060	-1.2828530
C	-1.3992260	-7.7341600	0.9075240
C	-0.8228890	-8.4985560	-1.7278600
H	-0.0416600	-6.5035420	-1.9448390
C	-1.6931520	-9.0412860	0.4997980
H	-1.6446830	-7.4121990	1.9160890
C	-1.3972130	-9.3985120	-0.8153510
H	-1.6166220	-10.4060750	-1.1520750
C	0.8087700	6.8215560	-0.0344850
C	1.3992260	7.7341600	-0.9075240
C	0.5245770	7.2152060	1.2828530
C	1.6931520	9.0412860	-0.4997980
H	1.6446830	7.4121990	-1.9160890
C	0.8228890	8.4985560	1.7278600
H	0.0416600	6.5035420	1.9448390
C	1.3972130	9.3985120	0.8153510
H	1.6166220	10.4060750	1.1520750
C	-2.3320680	-10.0122410	1.4980190
C	-1.4051520	-10.1731000	2.7149620
C	-3.6859750	-9.4475490	1.9605850
C	-2.5708970	-11.3975110	0.8888910
H	-0.4330040	-10.5755400	2.4111980
H	-1.2348640	-9.2185170	3.2222750
H	-1.8524880	-10.8637840	3.4382650
H	-4.3649860	-9.3239920	1.1103510
H	-4.1527130	-10.1326350	2.6769810
H	-3.5724600	-8.4752210	2.4496530
H	-3.0214030	-12.0520210	1.6418200
H	-3.2537680	-11.3505930	0.0339780
H	-1.6346040	-11.8601550	0.5589910
C	2.3320680	10.0122410	-1.4980190
C	3.6859750	9.4475490	-1.9605850
C	1.4051520	10.1731000	-2.7149620
C	2.5708970	11.3975110	-0.8888910
H	4.3649860	9.3239920	-1.1103510
H	3.5724600	8.4752210	-2.4496530
H	4.1527130	10.1326350	-2.6769810

H	0.4330040	10.5755400	-2.4111980
H	1.8524880	10.8637840	-3.4382650
H	1.2348640	9.2185170	-3.2222750
H	3.0214030	12.0520210	-1.6418200
H	1.6346040	11.8601550	-0.5589910
H	3.2537680	11.3505930	-0.0339780
C	0.5208150	8.9623690	3.1561200
C	0.0042420	7.8202870	4.0378750
C	1.8009600	9.5192670	3.8021300
C	-0.5489510	10.0663370	3.1078840
H	-0.9393080	7.4096000	3.6633530
H	0.7317340	7.0040210	4.1031350
H	-0.1749460	8.1952200	5.0505720
H	2.1948410	10.3801820	3.2539990
H	1.5899670	9.8438710	4.8269430
H	2.5817230	8.7522660	3.8388710
H	-0.7757090	10.4172890	4.1207940
H	-0.2114510	10.9251320	2.5188370
H	-1.4740920	9.6881640	2.6591930
C	-0.5208150	-8.9623690	-3.1561200
C	-1.8009600	-9.5192670	-3.8021300
C	-0.0042420	-7.8202870	-4.0378750
C	0.5489510	-10.0663370	-3.1078840
H	-2.1948410	-10.3801820	-3.2539990
H	-2.5817230	-8.7522660	-3.8388710
H	-1.5899670	-9.8438710	-4.8269430
H	0.9393080	-7.4096000	-3.6633530
H	0.1749460	-8.1952200	-5.0505720
H	-0.7317340	-7.0040210	-4.1031350
H	0.7757090	-10.4172890	-4.1207940
H	1.4740920	-9.6881640	-2.6591930
H	0.2114510	-10.9251320	-2.5188370
S	0.3242290	4.1585400	0.6259380
S	-0.3242290	-4.1585400	-0.6259380
C	-3.0039580	3.5074150	0.3096400
C	-2.9308830	4.7276440	-0.3723400
C	-3.0094080	3.5568660	1.7135690
C	-2.8554190	5.9423050	0.3088660
H	-2.9008820	4.7307230	-1.4586410
C	-2.9418700	4.7628050	2.4066310
H	-3.0630280	2.6267530	2.2790720
C	-2.8648920	5.9640820	1.7011200
H	-2.7821000	6.8720810	-0.2488820
H	-2.9474690	4.7685510	3.4931910
H	-2.8170020	6.9113400	2.2318690
C	3.0039580	-3.5074150	-0.3096400
C	3.0094080	-3.5568660	-1.7135690
C	2.9308830	-4.7276440	0.3723400
C	2.9418700	-4.7628050	-2.4066310
H	3.0630280	-2.6267530	-2.2790720
C	2.8554190	-5.9423050	-0.3088660
H	2.9008820	-4.7307230	1.4586410
C	2.8648920	-5.9640820	-1.7011200
H	2.9474690	-4.7685510	-3.4931910
H	2.7821000	-6.8720810	0.2488820
H	2.8170020	-6.9113400	-2.2318690
C	-3.2918440	2.0535780	-2.0346580
C	-2.5517240	1.2279440	-2.8940480
C	-4.3053300	2.8282730	-2.6221360
C	-2.7955880	1.1849950	-4.2670600
H	-1.7567590	0.6015940	-2.4928760
C	-4.5610990	2.7934940	-3.9911420
H	-4.9066120	3.4907280	-2.0025820
C	-3.8029600	1.9698780	-4.8217250
H	-2.1986910	0.5360060	-4.9014720
H	-5.3492430	3.4125430	-4.4100250
H	-3.9965740	1.9406960	-5.8897780
C	3.2918440	-2.0535780	2.0346580

C	4.3053300	-2.8282730	2.6221360
C	2.5517240	-1.2279440	2.8940480
C	4.5610990	-2.7934940	3.9911420
H	4.9066120	-3.4907280	2.0025820
C	2.7955880	-1.1849950	4.2670600
H	1.7567590	-0.6015940	2.4928760
C	3.8029600	-1.9698780	4.8217250
H	5.3492430	-3.4125430	4.4100250
H	2.1986910	-0.5360060	4.9014720
H	3.9965740	-1.9406960	5.8897780

5. Steady-state and Time-resolved Spectroscopies

5.1-Transient absorption spectra of **TB202** in solution

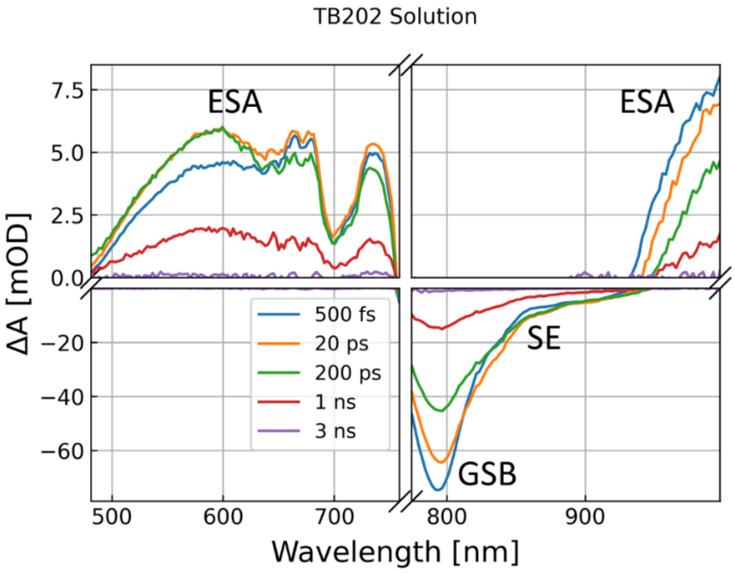


Figure S4. *Transient absorption spectra of* ***TB202*** *solution. Excited state absorption (ESA) can be found between 480 and 760 nm and 740 and 1000 nm. Simulated emission (SE) can be identified between 820 nm and 940 nm respectively partially overlapping with the Ground state bleach (GSB) at 795 nm. As there is no ET or CT in the dye solution the excited state decays without the formation of photoproducts.*

5.2-Global analysis

Global analysis of the transient absorption data was performed under the assumption that the decay times are not dependent on the wavelength. Under this assumption the data was fitted by a 2D function G(λ,t). In the time dimension G(λ,t) is the product of a Heaviside step function and a multi-exponential decay convolved with the Gaussian response function, which is the result of the finite time resolution of the measurement. The fitting function can be expressed by the following way after analytically calculating the convolution:

$$G(\lambda, t) = \frac{A_\sigma(\lambda)k_\sigma}{\sqrt{2\pi}} e^{-\frac{(k_\sigma(t-t_0))^2}{2}} + \sum_s \frac{A_s(\lambda)}{2} e^{\left(\frac{k_s}{\sqrt{2}k_\sigma}\right)^2} e^{-k_s(t-t_0)} \cdot \left(1 + \operatorname{erf}\left(\frac{k_\sigma\left(t - t_0 - \frac{k_s}{k_\sigma^2}\right)}{\sqrt{2}}\right)\right).$$

Here t_0 is the time zero; k_s is the decay rate of the s^{th} component in the multiexponential decay series, k_σ is the inverse of the resolution time and erf is the error function. Fitting was performed with VARPRO algorithm [X4, X5] and the free parameters for the fitting were t_0, k_s, and k_σ and the $A_s(\lambda)$ and $A_\sigma(\lambda)$ functions. After the global fitting is performed the resulting $A_s(\lambda)$ functions are the decay-associated difference spectra and $\tau_s=1/k_s$ are the corresponding decay lifetimes are shown on Fig. SI2. The comparison of the fitting function with the data is displayed on Fig. SI3 for the Al_2O_3 and TiO_2 cell.

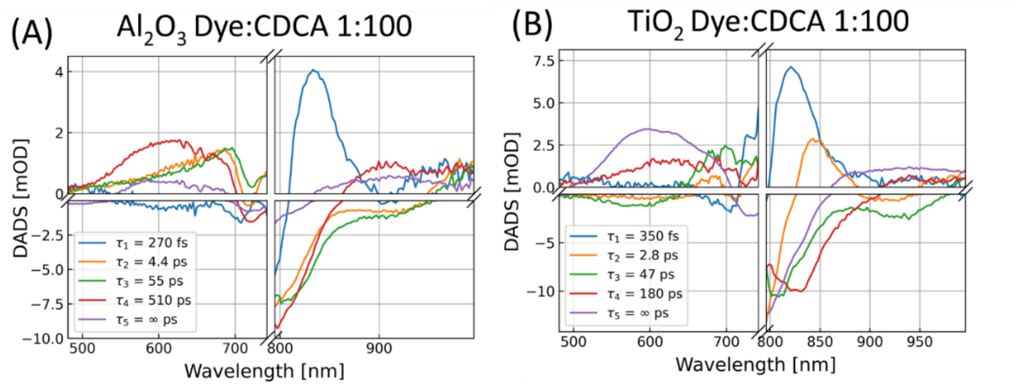


Figure S5. *The DADS resulting from the global analysis of the TA data measured for Al_2O_3 cell (A) and TiO_2 cell (B).*

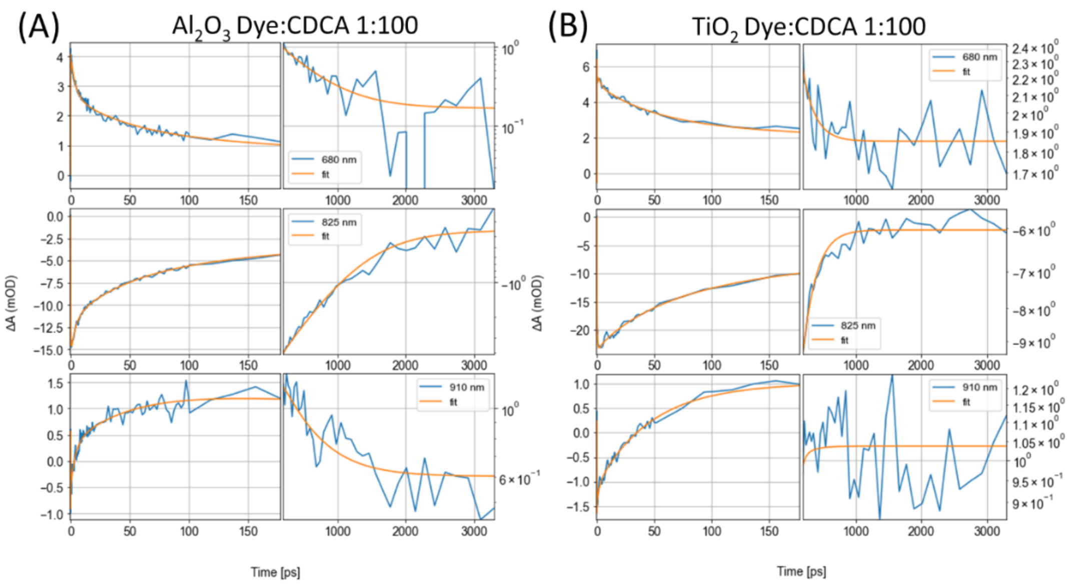


Figure S6. *Comparison of global fitting function compared to the raw datasets are displayed at three selected wavelengths 680 nm, 825 nm and 910 nm for the Al_2O_3 cell (A) and the TiO_2 cell (B). The reduced χ^2 value of the fitting was 1.3E-07 in both cases. The four decay times and the non-decaying component were enough to acquire a good accuracy fit for both the short- and the long-term kinetics.*

Table S2. *Results of single wavelength fits (sum of four exponentials plus "infinity" component) for the stim. emission at 825 nm (figure **S7**) monitoring the excited state decay in **TB202**/Al_2O_3 as a function of the CDCA concentration. The general trend of a slower energy transfer, characterised by the lifetimes t_2 and t_3 is qualitatively obvious from fig. **S7** and consistently reproduced by the fits. Increasing the CDCA concentration from 5 to 10mM (1:50 vs. 1:100) has a minor effect on the ET times. Note that the fit values are not exactly the same as for the global fit (CDCA concentration 10 mM), since the fits are performed on a single wavelength here.*

	λ (nm)	τ_2 [ps]	Amplitude	τ_3 [ps]	Amplitude
Dye:CDCA 1:0	825	1.6±0.07	70 %	16.0±1.1	30%
Dye:CDCA 1:10	825	2.2±0.1	51 %	17.0±0.8	49 %
Dye:CDCA 1:50	825	9.7±0.6	46 %	110.0±11	54 %
Dye:CDCA 1:100	825	13±1	52 %	150±4.3	48 %

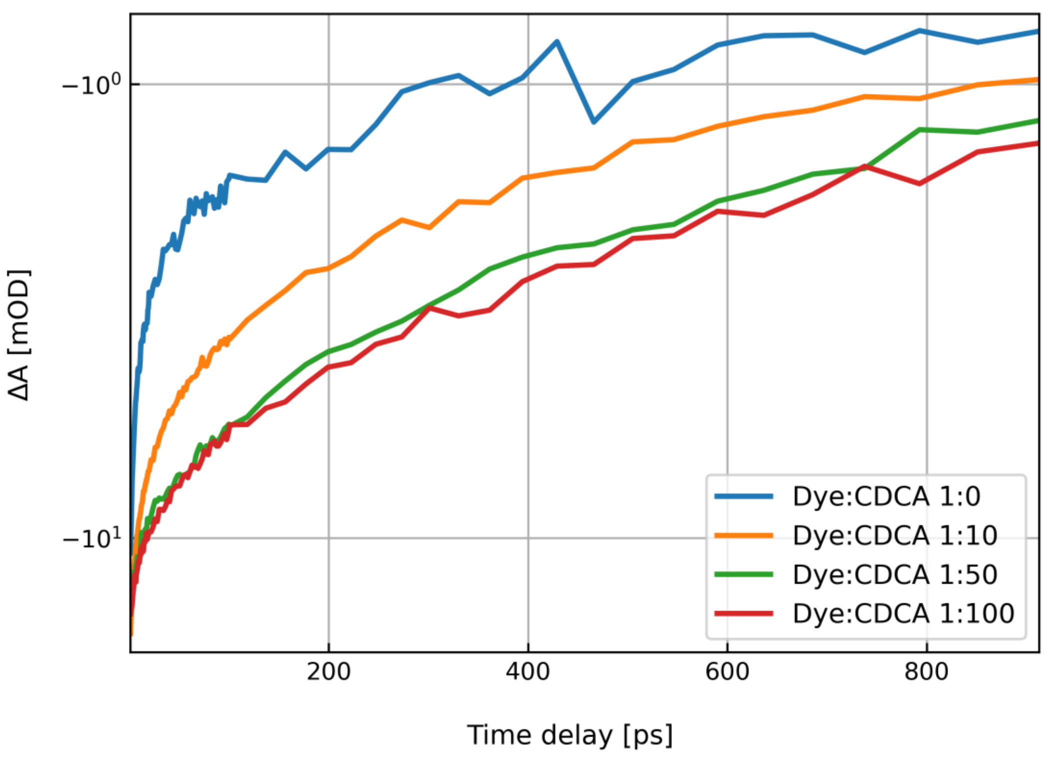


Figure S7. *Decay kinetics of the stim. emission at 825 nm for **TB202**/Al_2O_3 as a function of the CDCA concentration. Y-axis is in log. scale.*

6. Photovoltaic Cells

Fabrication of Solar Cells

The mesoporous TiO_2 electrodes are prepared as previously described yielding 8 µm thick transparent electrode.[4] For the device performance it was sheltered with a 5 µm thick 400 nm-based TiO2 scattering layer. The fluorine-doped SnO_2 (FTO) conducting glass (NSG-10, Nippon Sheet Glass) was thoroughly cleaned with a detergent solution, acetone, and ethanol solvents. Then the substrates were treated with 40 mM $TiCl_4$ aqueous solution at 70 °C for 45 min in order to make a thin and compact TiO_2 underlayer. The colloidal TiO_2 paste of Dyenamo DNEP03 was used. The layers were sequentially deposited on the $TiCl_4$ -treated FTO glass via screen printing technology, which results in a different thickness of TiO_2. The printed TiO_2 was sintered at 500 °C under dry air flow and cooled down to room temperature to obtain a mesoporous, electronic conductive film. The mesoporous TiO_2 film was treated in $TiCl_4$ (40 mmol/L) and kept at 70 °C in an oven for 30 min. After sintering at 500 °C in air and cooled down to 80 °C, the mesoporous TiO_2 electrodes were stained by immersing them into the dye solution at room temperature 12 h. The dye solution is composed of **TB202** or **TB179** (100 µmol/L) and CDCA (50 mmol/L) in $CHCl_3$/EtOH (1:9, v/v). The dye-coated TiO_2 film working electrode and thermally low-concentrated platinized conducting glass counter electrode were assembled using a 25 µm thick Surlyn hot-melt ring (DuPont, USA) heated at 125 °C. The internal space was filled with electrolyte using a vacuum pump through a predrilled hole on the counter electrode. The hole was sealed with a Bynel sheet and a thin glass cover by heating. All PCE values have been reproduced. The reproducibility over cells is in the range of 0.1% in power conversion efficiencies.

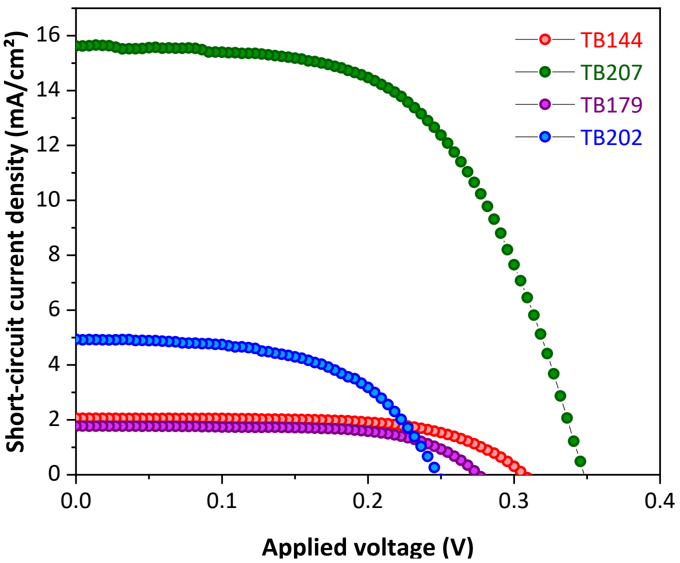


Figure S8. *Evolution of J-V curves as a function of the dyes with no de-aggregating agent in the sensitizing solution.*

Table S2. *Photovoltaic parameters of the different PPcy (**TB144** and **TB207**) and thienyl-PPcy (**TB179** and **TB202**) dyes with no de-aggregating agent in the sensitizing solution.*

Dye	J_{sc}(mA/cm^2)	V_{oc} (mV)	FF	PCE (%)
TB144	2.1	307	0.63	0.4
TB207	15.6	348	0.57	3.1
TB179	1.8	276	0.65	0.3
TB202	4.9	248	0.55	0.7

AVT is defined as the weight of the integration of the transmission spectrum of the PV device against the photopic response of the Human eye. AVT is calculated from the following equation:

$$\text{AVT} = \frac{\int T(\lambda)V(\lambda)S(\lambda)d(\lambda)}{\int V(\lambda)S(\lambda)d(\lambda)} \qquad \text{eq. 1}$$

Where T is the transmission, V is the photopic response and S is the solar photon flux at A.M.1.5G condition.
In addition, CRI value has been calculated from the following equation:

$$CRI = \frac{1}{8}\ \sum_{i=1}^{8}[100 - 4.6\sqrt{(\Delta u_i^*)^2 + (\Delta v_i^*)^2 + (\Delta W_i^*)^2}$$

7. NMR and HRMS Spectra

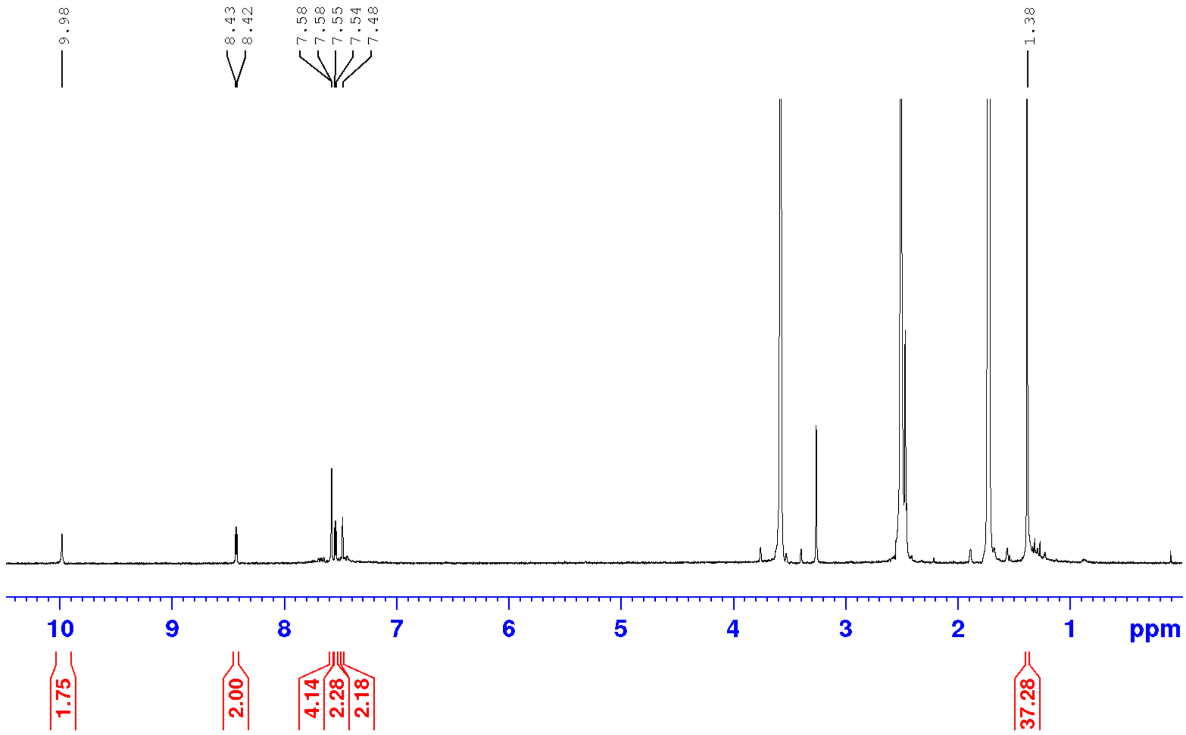


Figure S9. *[1]H NMR of compound **3** recorded in $CDCl_3$.*

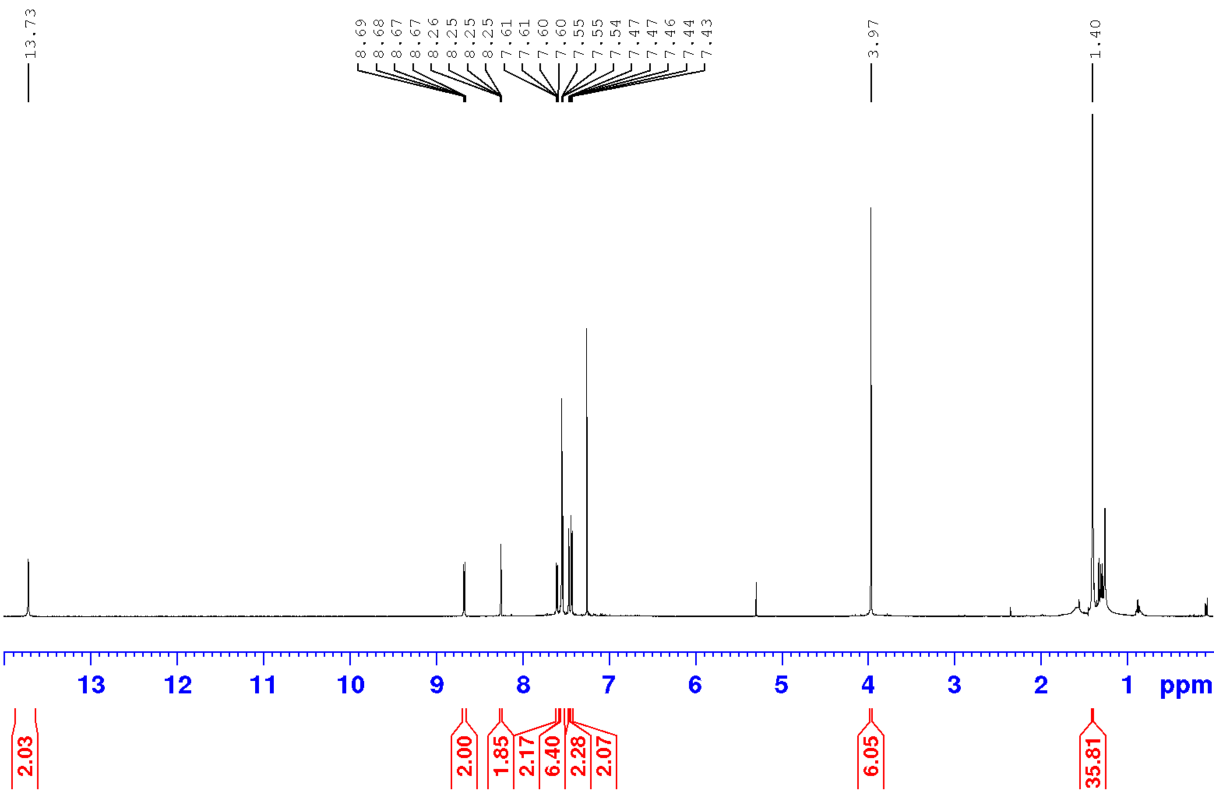


Figure S10. *[1]H NMR of compound **5** recorded in $CDCl_3$.*

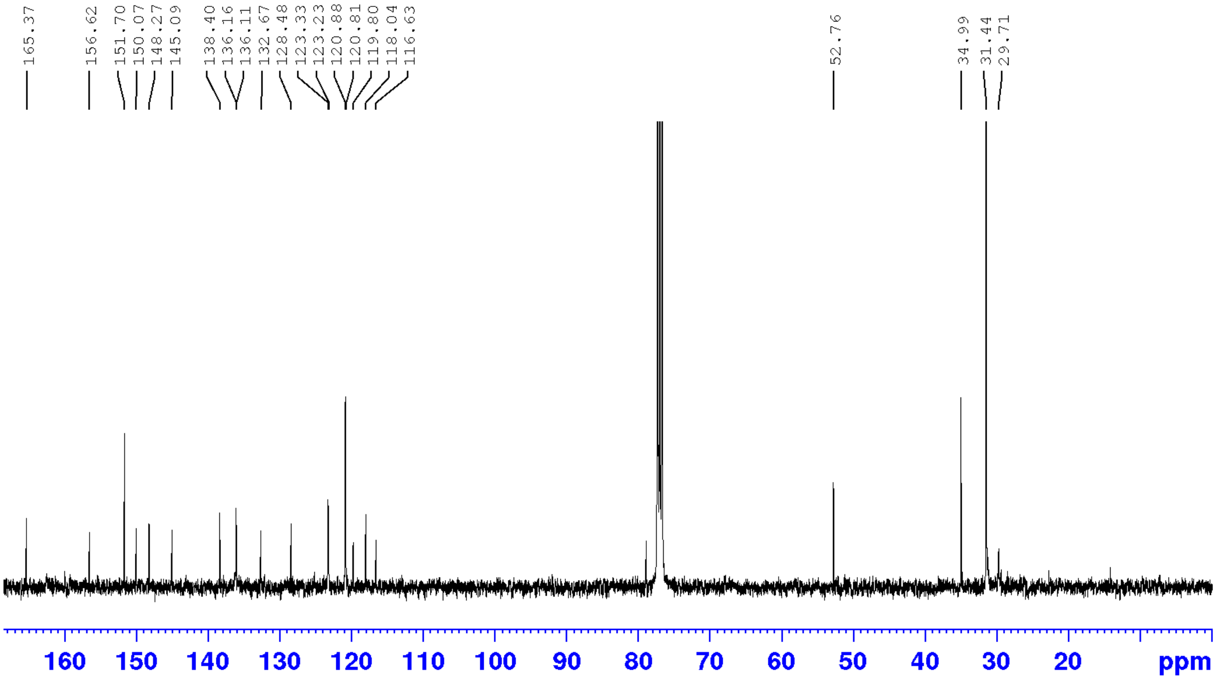


Figure S11. *^{13}C NMR of compound **5** recorded in $CDCl_3$.*

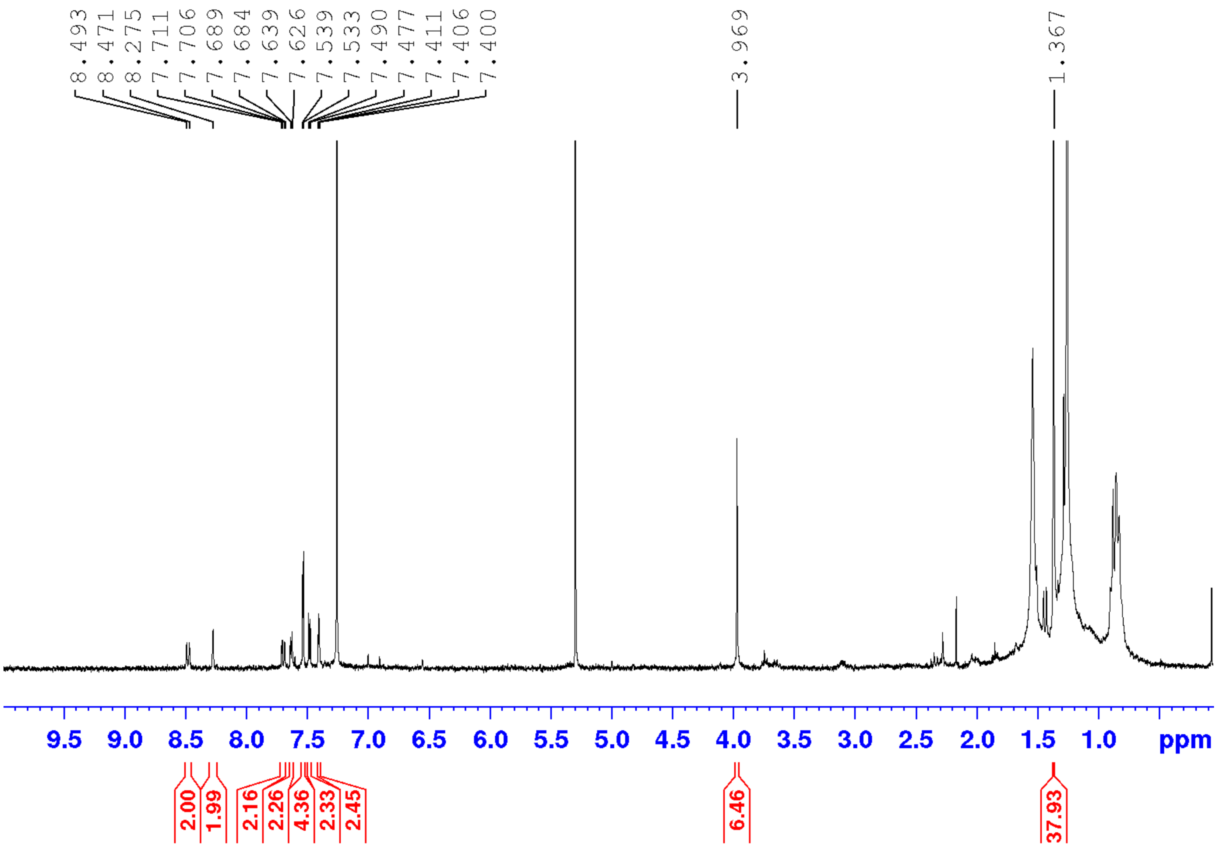


Figure S12. *^{1}H NMR of compound **6** recorded in $CDCl_3$.*

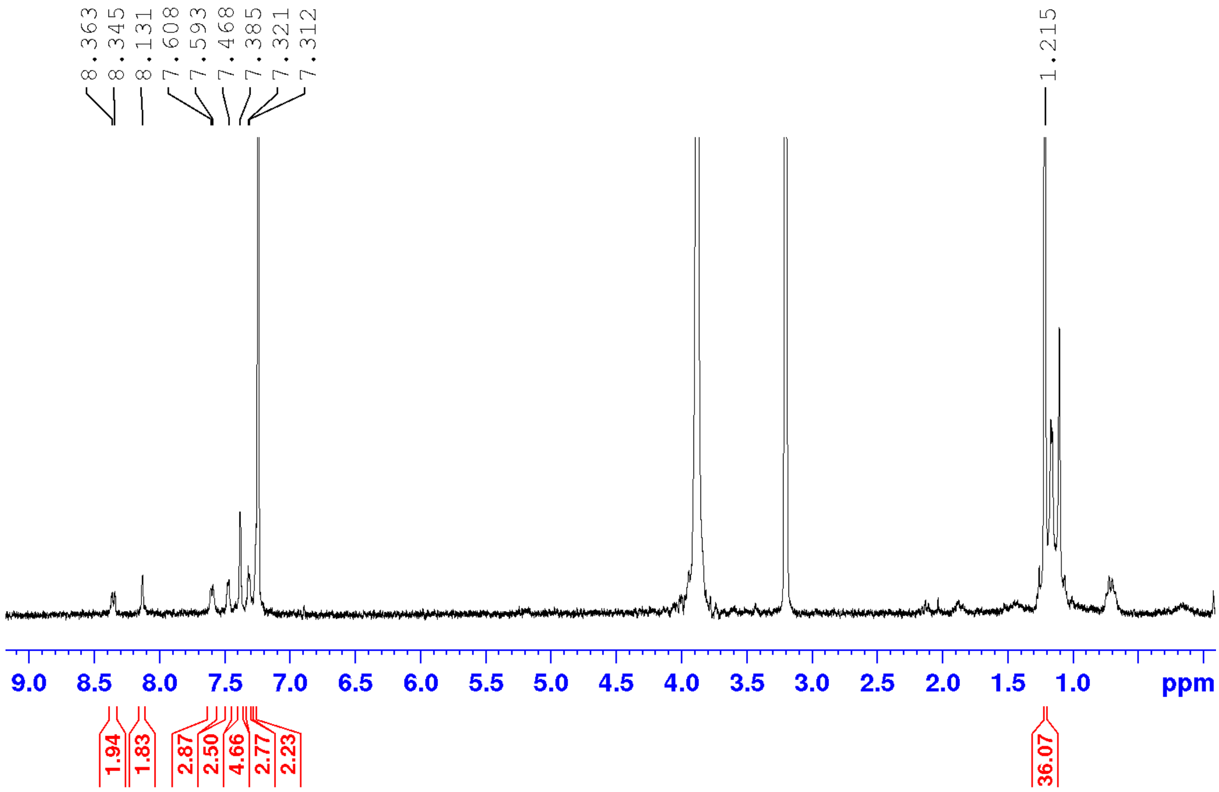


Figure S7. *[1]H NMR of compound* ***TB179*** *recorded in $CDCl_3/CD_3OD$: 9/1.*

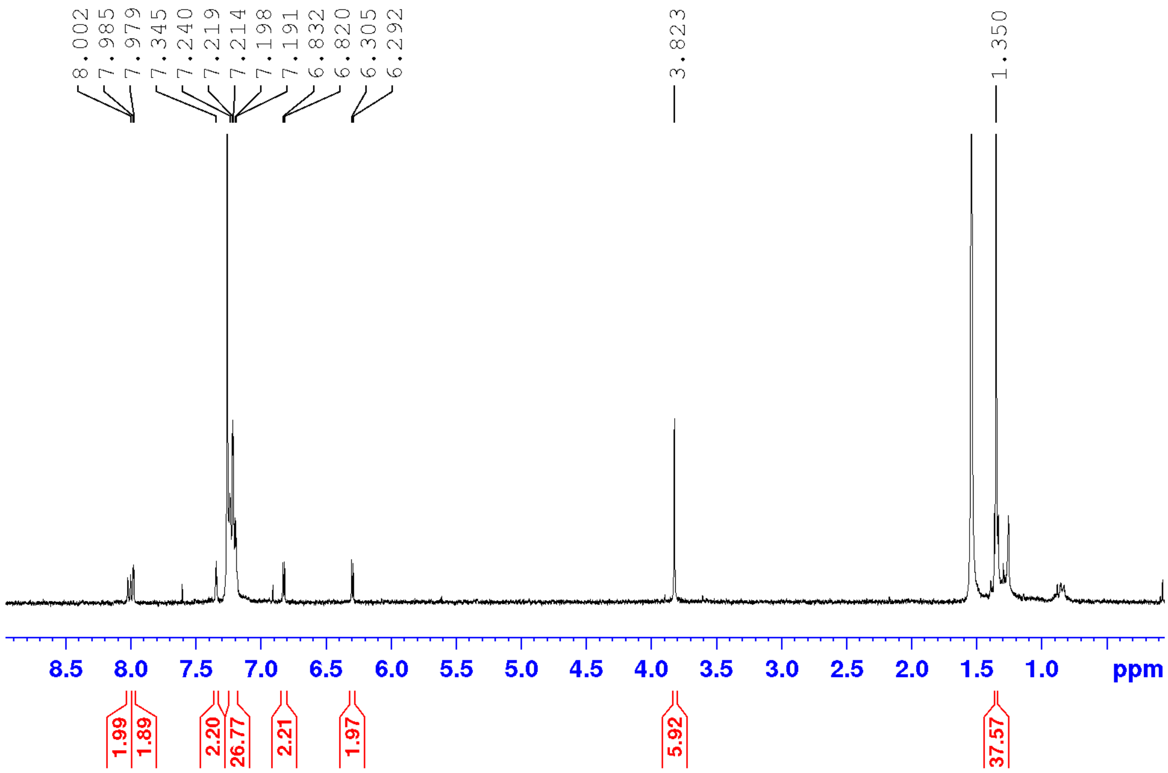


Figure 8*. [1]H NMR of compound* ***7*** *recorded in $CDCl_3$.*

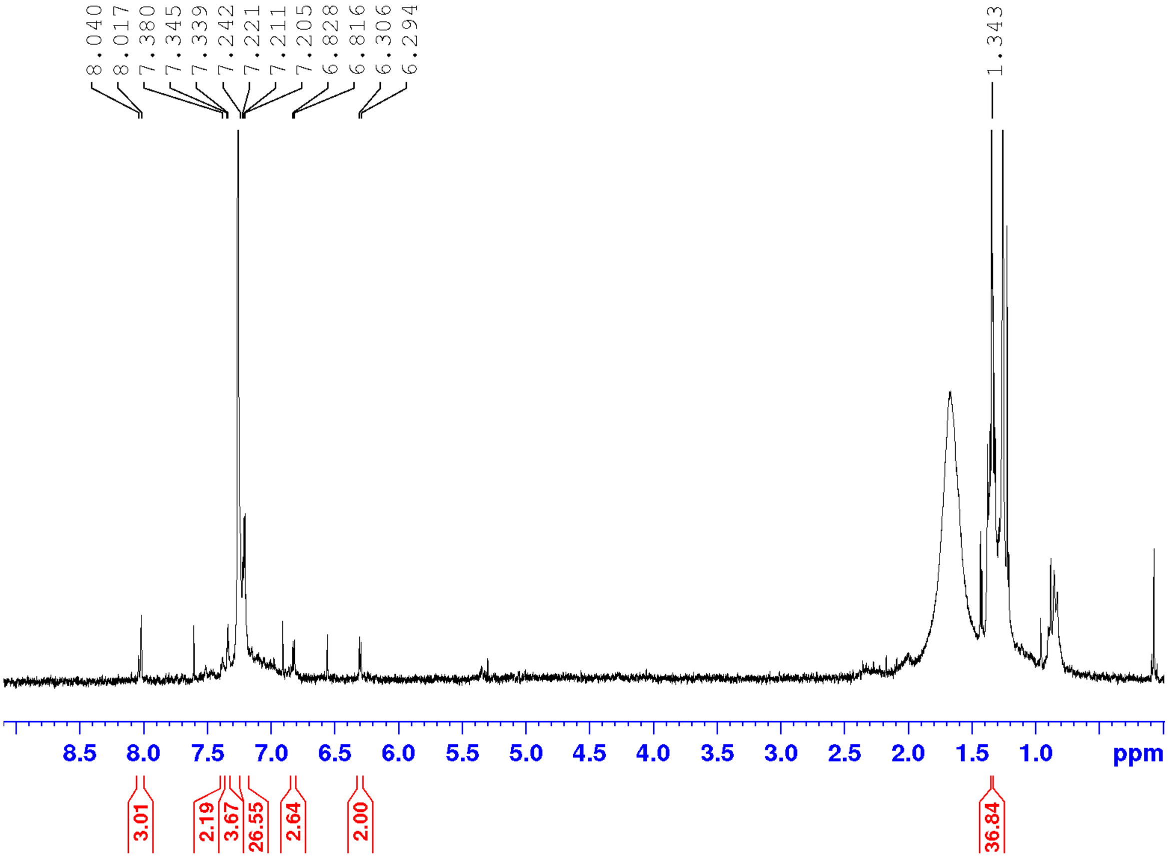
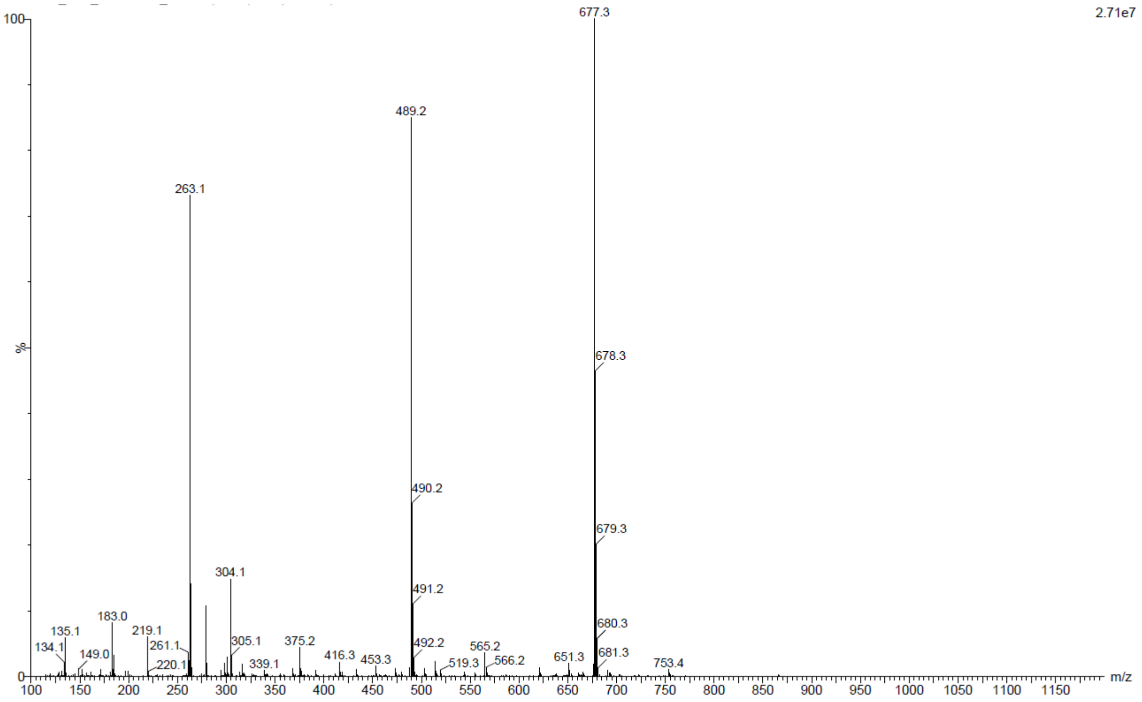


Figure S9. *[1]H NMR of compound **TB202** recorded in $CDCl_3/CD_3OD$: 9/1.*



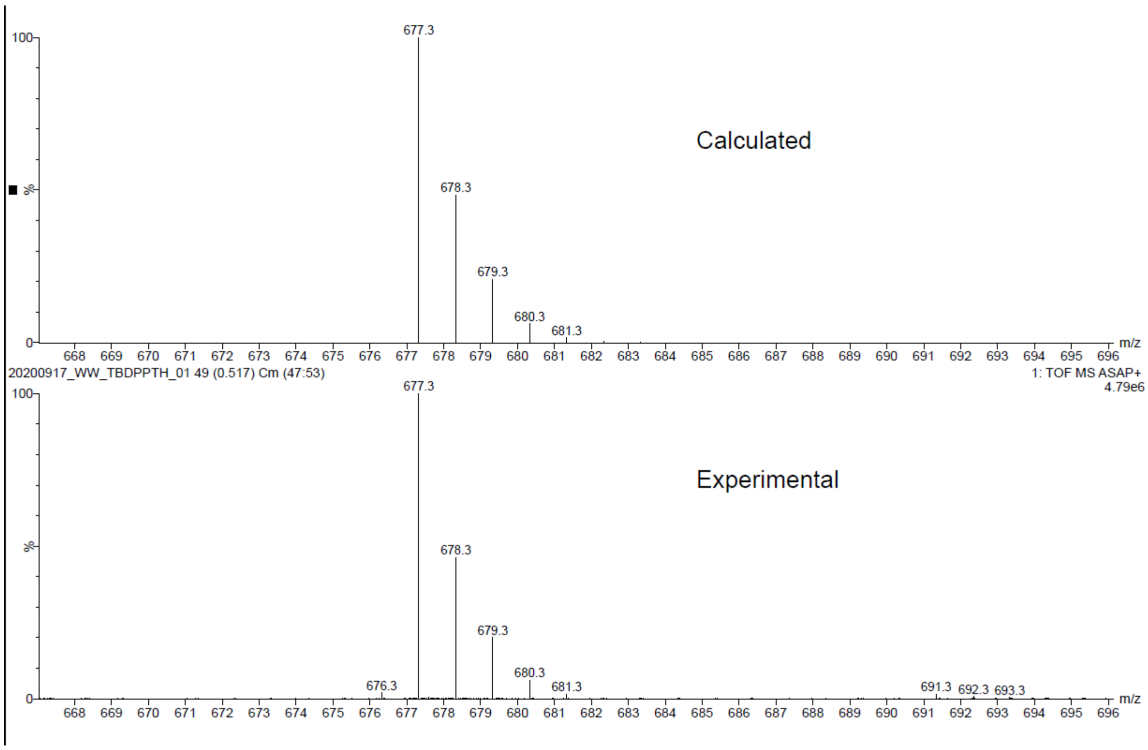
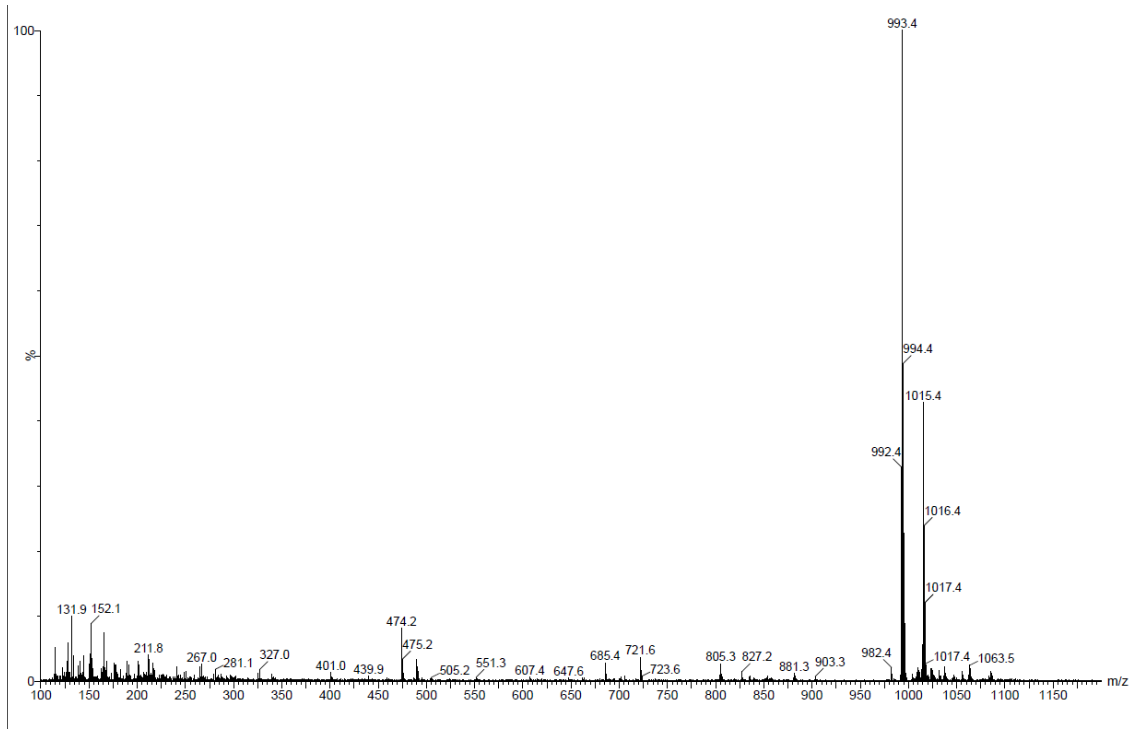


Figure S16. *MALDI-TOF spectrum of compound **3**. Entire experimental spectrum (up) and superimposition of the simulated and experimental molecular fragment (down).*



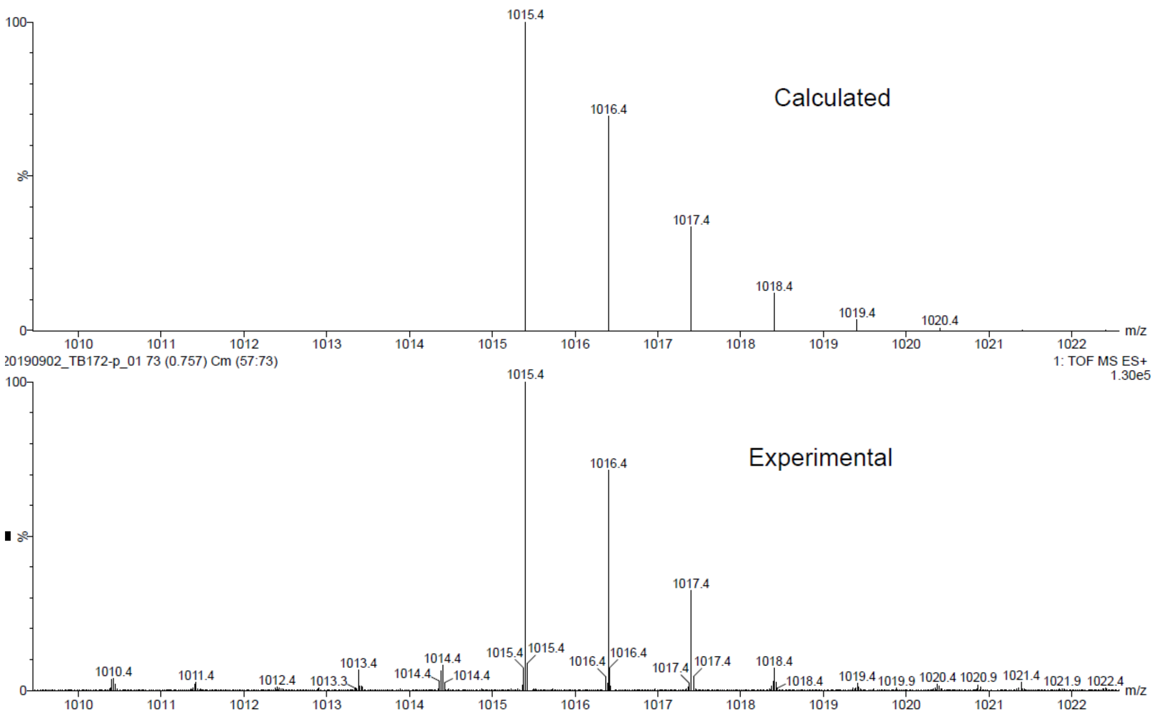
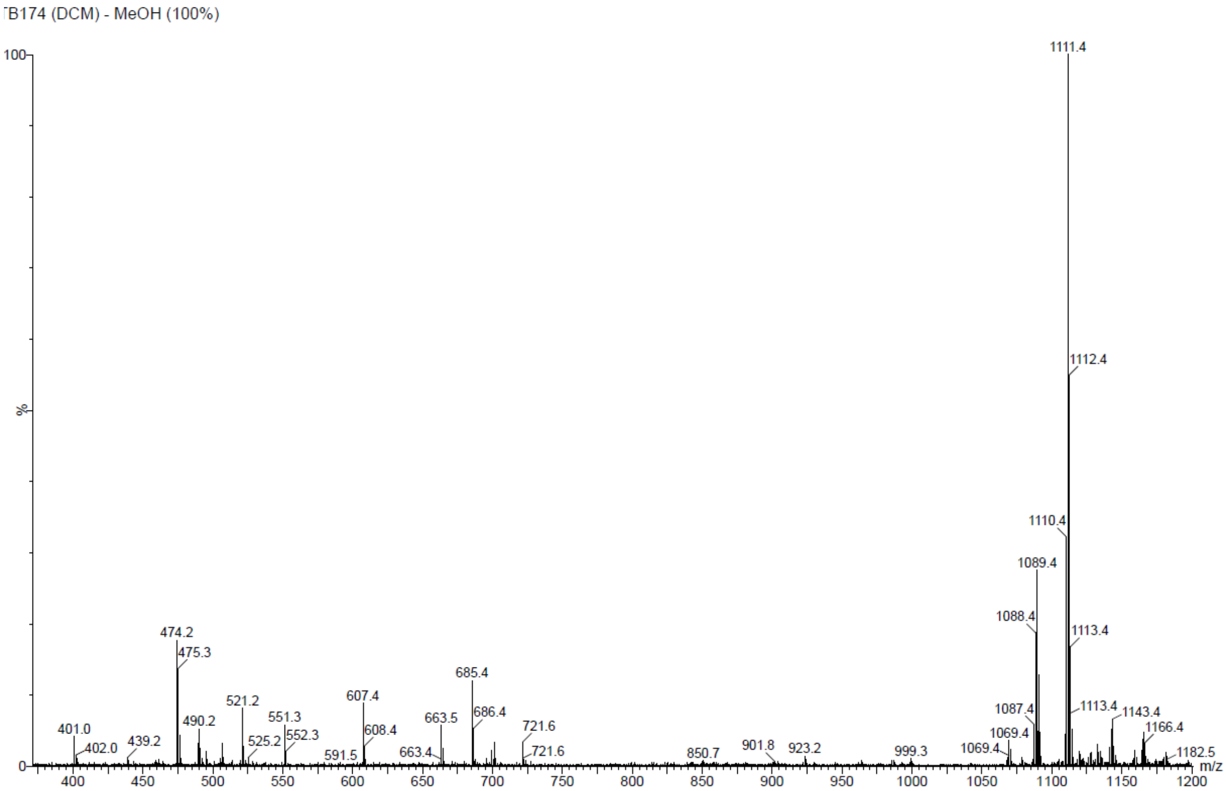


Figure S17. *MALDI-TOF spectrum of compound* ***5****. Entire experimental spectrum (up) and superimposition of the simulated and experimental molecular fragment (down).*



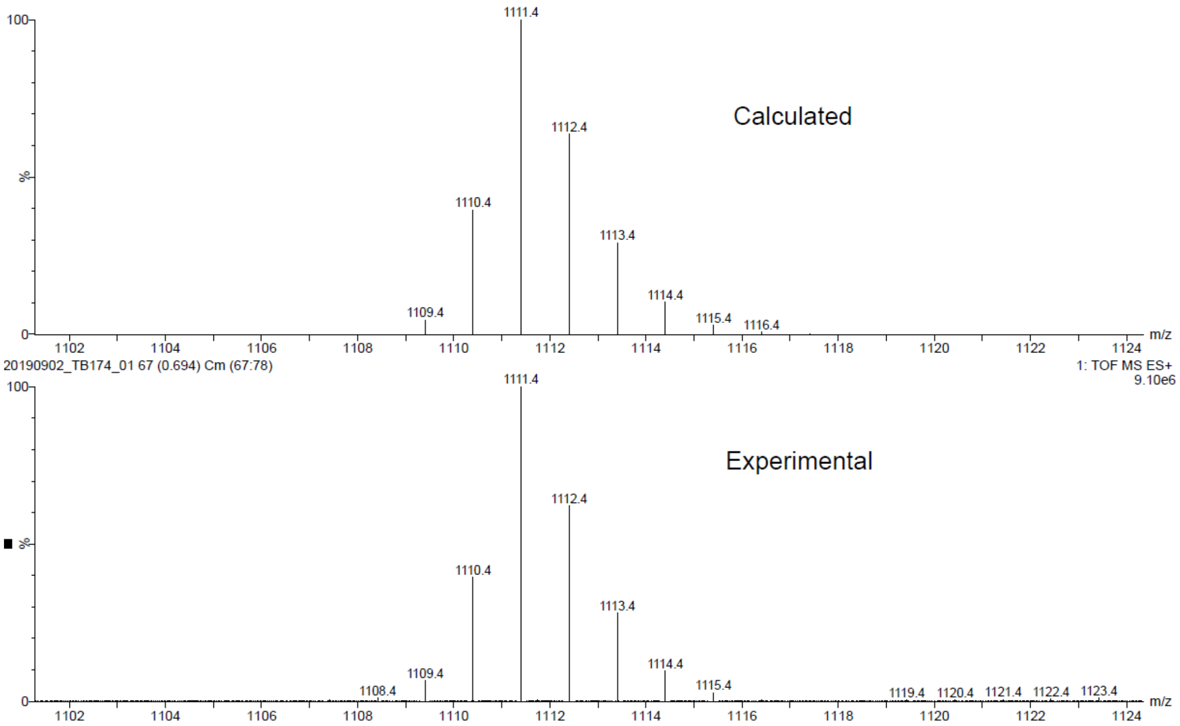
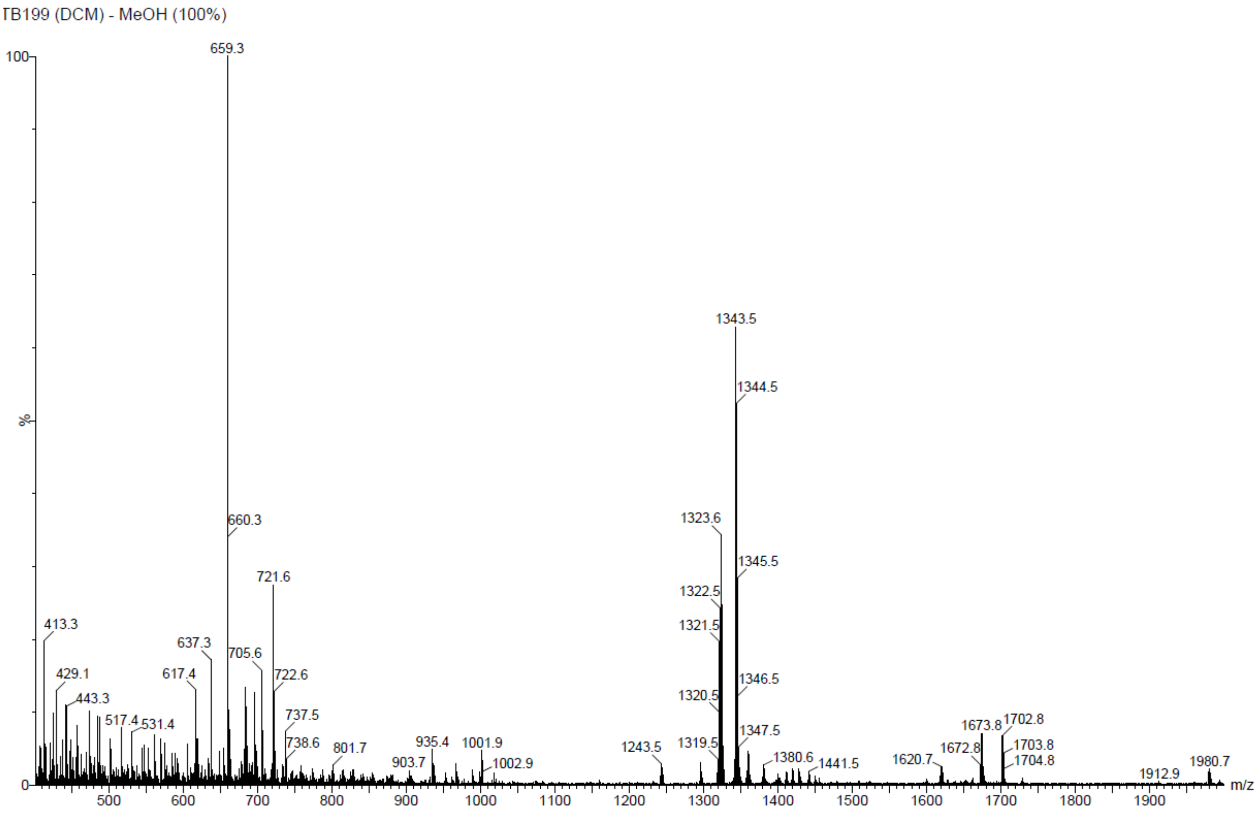


Figure S18. *MALDI-TOF spectrum of compound **6**. Entire experimental spectrum (up) and superimposition of the simulated and experimental molecular fragment (down).*



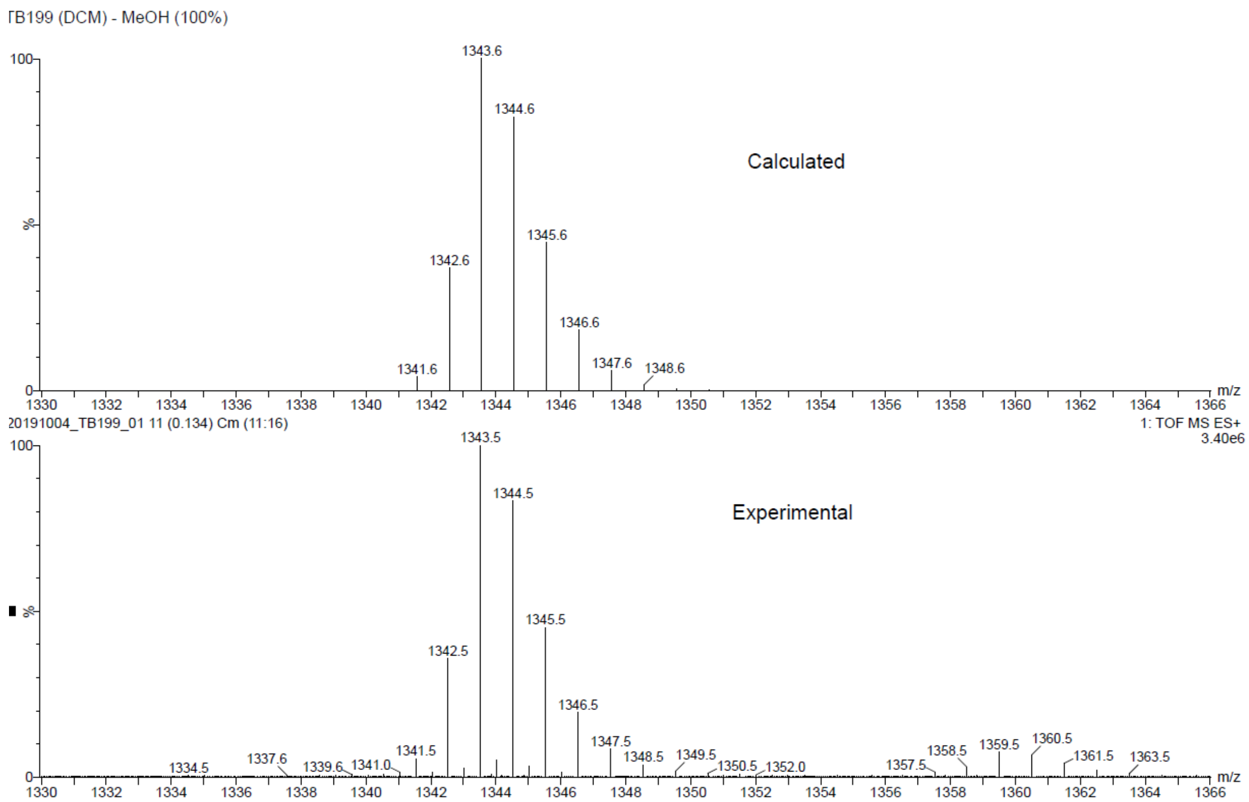


Figure S19. *MALDI-TOF spectrum of compound **7**. Entire experimental spectrum (up) and superimposition of the simulated and experimental molecular fragment (down).*

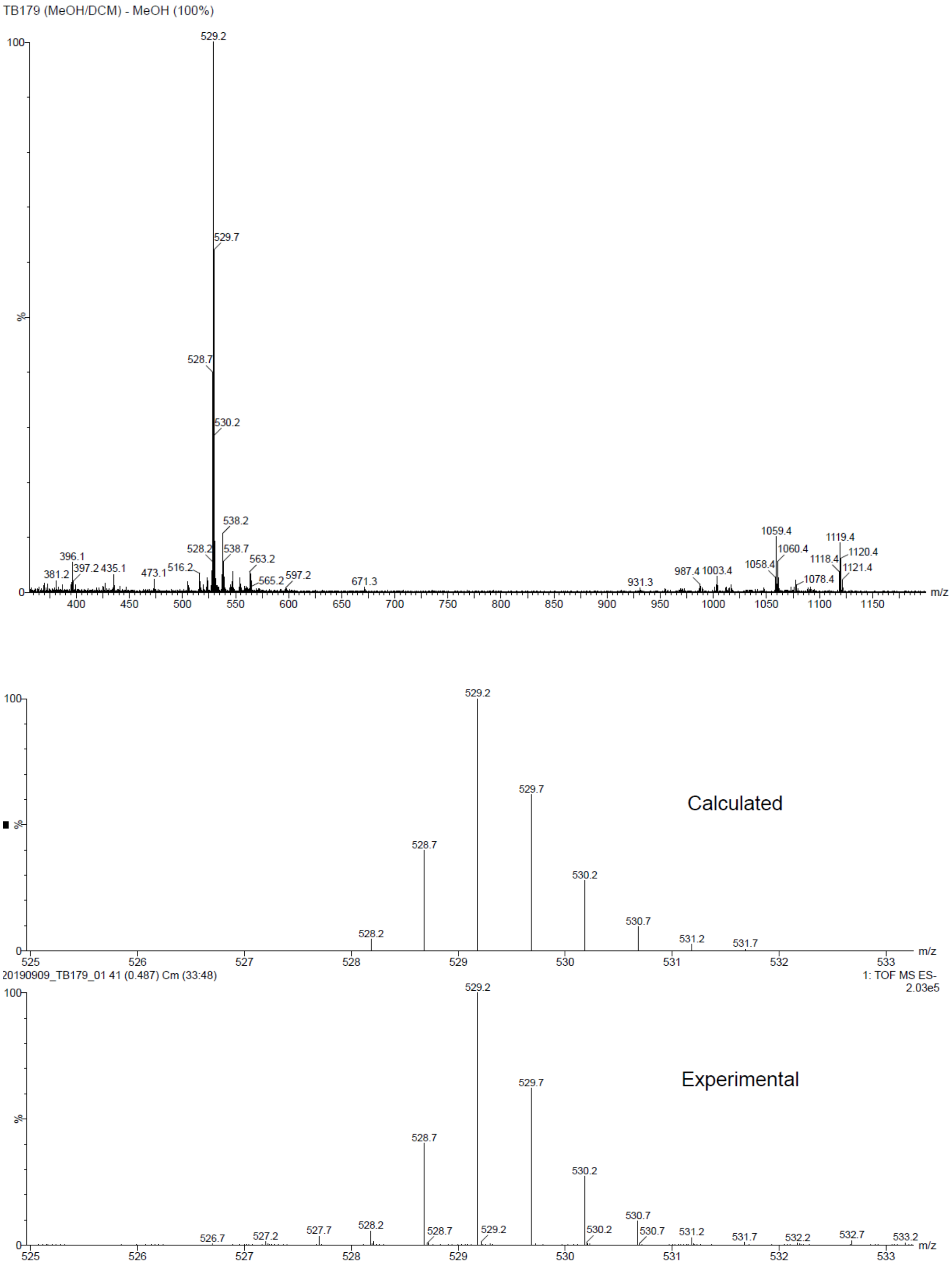


Figure S20. *MALDI-TOF spectrum of compound **TB179**. Entire experimental spectrum (up) and superimposition of the simulated and experimental molecular fragment (down).*

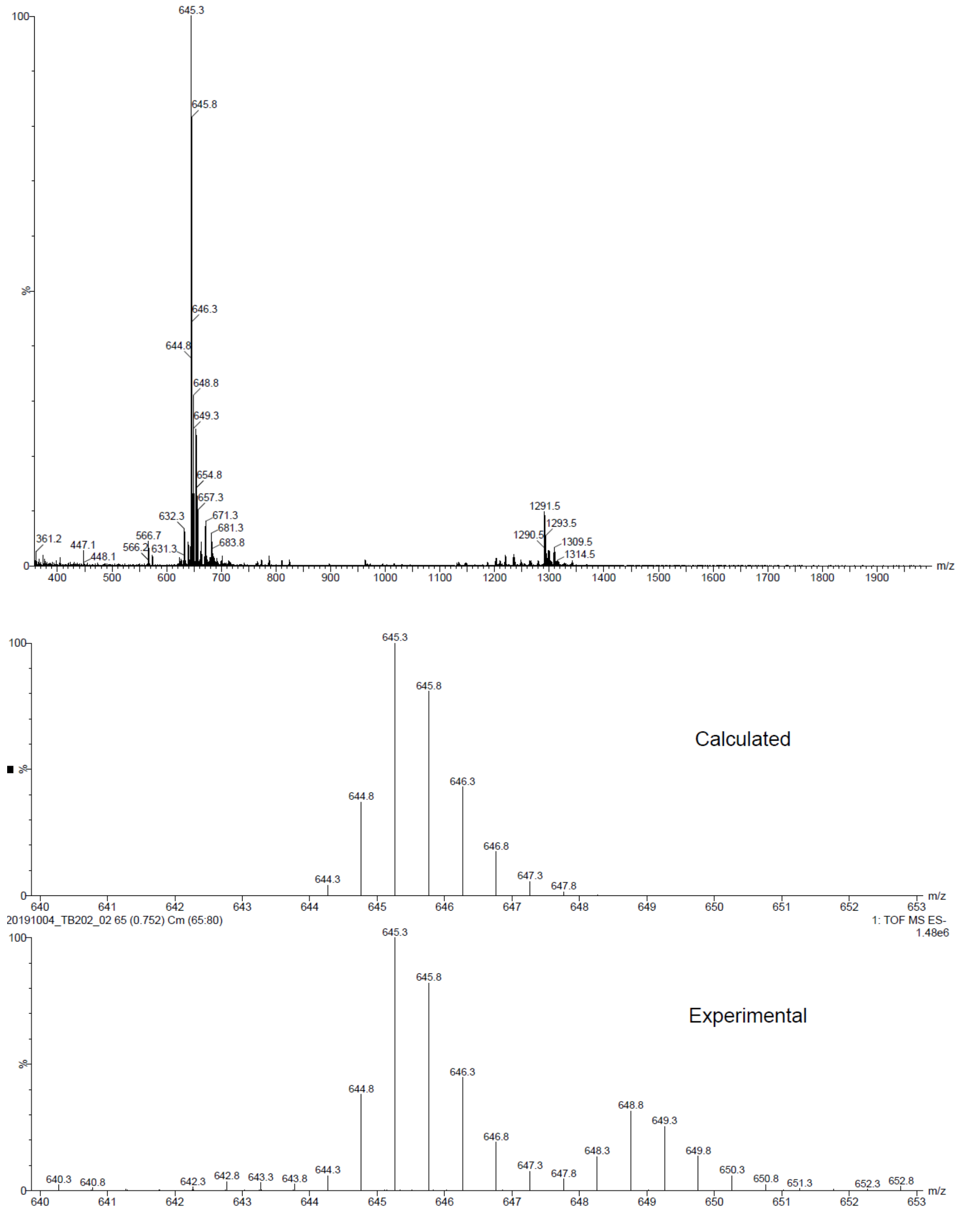


Figure S21. *MALDI-TOF spectrum of compound* ***TB202****. Entire experimental spectrum (up) and superimposition of the simulated and experimental molecular fragment (down).*

10. References

[1] K. Yang, T. He, X. Chen, S. Z. D. Cheng, Y. Zhu, *Macromolecules* **2014**, *47*, 8479–8486.

[2] J. Ranta, T. Kumpulainen, H. Lemmetyinen, A. Efimov, *J. Org. Chem.* **2010**, *75*, 5178–5194.

[3] T. Baron, W. Naim, I. Nikolinakos, B. Andrin, Y. Pellegrin, D. Jacquemin, S. Haacke, F. Sauvage, F. Odobel, *Angew. Chem. Int. Ed.* **2022**, *61*, e202207459.

[4] S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin, M. Grätzel, *Thin Solid Films* **2008**, *516*, 4613–4619.

[4] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, **2005**, *105*, 2999-3094.

[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Rev. B.01*, Wallingford, CT, 2016.

[6] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, **2008**, *120*, 215-241.

[7] D. Jacquemin, A. Planchat, C. Adamo and B. Mennucci, *J. Chem. Theory Comput.*, **2012**, *8*, 2359–2372.

[8] C.A. Guido, A. Chrayteh, G. Sclamani, B. Mennucci, D. Jacquemin, *J. Chem. Theory Comput.*, **2021**, *17*, 5155–5164.