

Electronic Supplementary Information

Gas-phase action and fluorescence spectroscopy of mass-selected fluorescein monoanions and two derivatives

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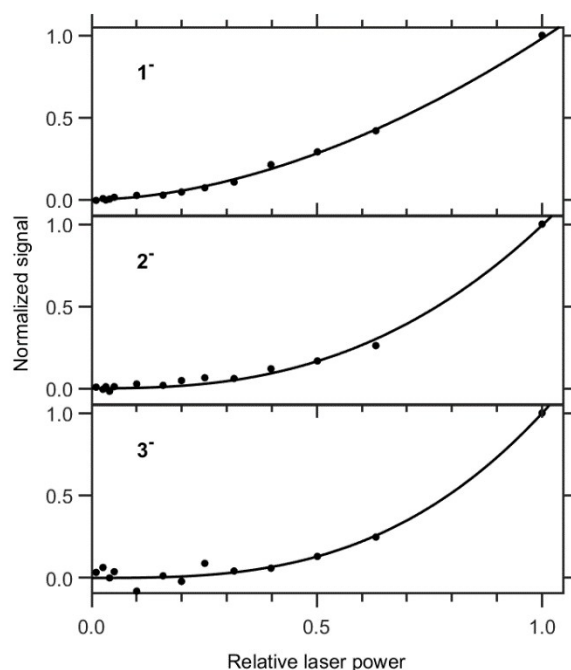


Figure 1. Yield of fragment ion (m/z 287 (1^-), m/z 286 (2^- and 3^-)) as a function of relative laser power for 1^- (top), 2^- (middle), and 1^- (bottom). The laser power was attenuated with neutral density filters. A power fit to $f(x) = \beta x^\alpha$ gives $\alpha = 1.8, 2.6$ and 3.0 , respectively. The excitation wavelength was 525 nm in all cases.

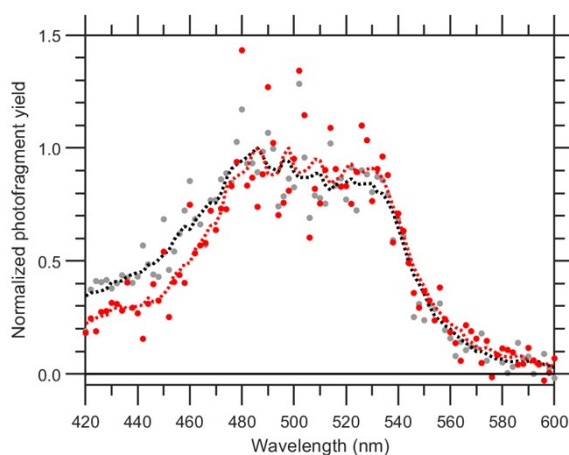


Figure 2. Gas-phase action spectra of 1^- measured using full laser power (grey dots, black dotted line) and laser power reduced to 63 % (red dots and dotted line). Action spectra were obtained as the photoinduced yield of m/z -287 fragment ions. Dotted lines are 8-point moving averages.

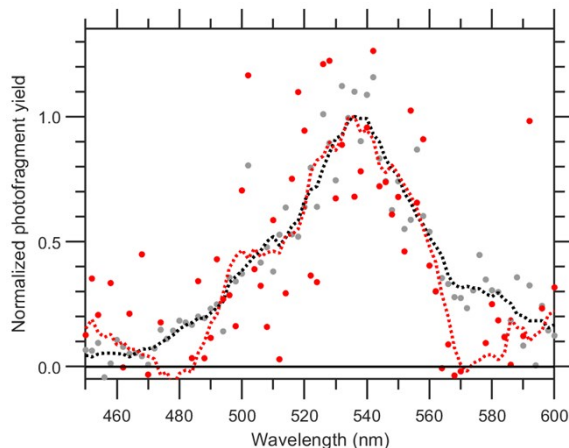
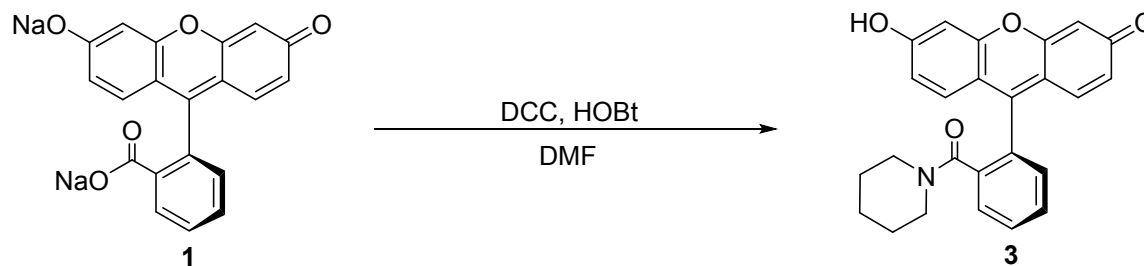


Figure 2. Gas-phase action spectra of **3** obtained as the photoinduced yield of two different fragment ions. m/z -287 fragment ion yield is shown by the black dotted line (grey dots) and m/z 315 is shown by the red dotted line (red dots). Dotted lines are 8-point moving averages of the data points.

Synthesis of (6-hydroxy-9-(2-(piperidine-1-carbonyl)phenyl)-3H-xanthen-3-one)



To a solution of piperidine (0.25 mL, 2.51 mmol, 0.9 eq.) and DMF (50 mL), fluorescein sodium salt (**1**, 1.027 g, 2.73 mmol, 1 eq.), Et₃N (2.9 mL, 21.1 mmol, 7.7 eq.), hydroxybenzotriazole (HOBt) monohydrate (458 mg, 3.39 mmol, 1.2 eq.) and dicyclohexylcarbodiimide (DCC) (660 mg, 3.20 mmol, 1.2 eq.) were added at 0 °C. The resulting mixture was stirred at rt for 23 h. before it was concentrated in vacuo. Crystallisation from absolute EtOH resulted in removal of formed dicyclohexylurea. The filtrate was concentrated and dissolved in MeOH, which was left at room temperature overnight to yield a brown-red powder. This was filtered and further purified by flash column chromatography (1:3 pentane/EtOAc→10% MeOH in EtOAc) to give the product (**3**) as an orange powder (76 mg, 19 μmol, 6%).

R_f (8% MeOH in EtOAc) 0.48.

^1H NMR (400 MHz, CDCl_3): δ_{H} (ppm) 7.69-7.63 (m, 2H, ArH), 7.57-7.53 (m, 1H, ArH), 7.49-7.44 (m, 1H, ArH), 6.93 (d, 2H, ArH), 6.61-6.48 (m, 4H, ArH), 3.27-3.14 (m, 4H, CH_2NCO), 1.46 (qu, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.33-1.19 (m, 4H, $\text{CH}_2\text{CH}_2\text{N}$).

^{13}C NMR (100 MHz, CDCl_3): δ_{C} (ppm) 193.2 (ArC=O), 166.4 (ArCH), 155.3 ($\text{CON}(\text{CH}_2)_2$), 148.3 (ArC), 136.2 (ArC), 130.8-127.0 (ArCH), 125.5-110.2 (ArC), 103.2 (ArCH), 47.8 (C1/C5), 41.8 (C1/C5), 25.5 (C2/C4), 25.1 (C2/C4), 23.7 (C3).

HRMS (ESI): Calcd. for $\text{C}_{25}\text{H}_{21}\text{NO}_4\text{H}^+$: m/z 400.1543; found m/z 400.1550.

Coordinates

Theoretical method: WB97X-D/AUG-PCSEG-1

Fluorescein monoanion (1^-), ground state

C,0,2.6567239738,-3.2622448439,-0.0486063576
C,0,3.0568467823,-1.8756425938,0.0772634644
C,0,2.1493894774,-0.8637812164,-0.0309536623
C,0,0.7542129029,-1.0957422799,-0.2622056815
C,0,0.3439680122,-2.4635142458,-0.3922710173
C,0,1.2266234944,-3.4866401434,-0.2870916784
C,0,-0.1034287133,0.009584422,-0.3681980663
C,0,0.3856674393,1.305824203,-0.2502046494
C,0,1.789792252,1.4965263581,-0.0280343439
C,0,2.3587520143,2.7295216513,0.0822447446
H,0,3.4276349673,2.8237431217,0.2492146343
C,0,1.5619191264,3.935698127,-0.0197465643
C,0,0.1230510764,3.7276801082,-0.2248192337
C,0,-0.417197295,2.4909135198,-0.3327039036
H,0,4.1048430217,-1.6502182313,0.2514141489
H,0,-0.7093645573,-2.6675691502,-0.5770265124
H,0,0.9041753508,-4.5207922477,-0.3847262458
H,0,-0.4945183983,4.6207892068,-0.2880033054
H,0,-1.488466379,2.3745573767,-0.485910319
O,0,2.6129046832,0.4135893441,0.0849885314
O,0,2.0486531396,5.0737437109,0.060840838
O,0,3.4581688495,-4.2061486922,0.0341243896
C,0,-1.5567087156,-0.2170187368,-0.6189844666
C,0,-1.9834491894,-0.2144554985,-1.9488786075
C,0,-2.5003334942,-0.4066540797,0.4017291712
C,0,-3.3186252622,-0.4041377862,-2.2738509863
H,0,-1.2429982883,-0.0556353876,-2.728793831
C,0,-3.8457080493,-0.5824076487,0.0620143644
C,0,-4.2563645672,-0.5900039735,-1.261713689

H,0,-3.6267574108,-0.4026087246,-3.316978926
H,0,-4.560156344,-0.7078017027,0.8703421955
H,0,-5.306211204,-0.7366533596,-1.503516043
C,0,-2.2042046099,-0.4153936725,1.8853178623
O,0,-3.0785068038,-0.2071993822,2.6918677621
O,0,-0.9694679687,-0.6933128323,2.3024851749
H,0,-0.3547793132,-0.8637547199,1.5676108087

Fluorescein monoanion (1⁻), excited state

C,0,2.5925104444,-3.256985049,0.2128235769
C,0,3.0261715698,-1.8773438104,0.1499021391
C,0,2.1287431304,-0.8537087063,0.0117758807
C,0,0.7169694243,-1.0619779246,-0.0726474176
C,0,0.2820190774,-2.4262214973,-0.0328181591
C,0,1.1455363212,-3.4641161724,0.1036257232
C,0,-0.1630761547,0.0519985948,-0.2615540818
C,0,0.4420068911,1.3450530542,-0.295481967
C,0,1.8636339541,1.4863201975,-0.239458514
C,0,2.4934173199,2.698227142,-0.3092159952
H,0,3.5775045768,2.7479508692,-0.2667637369
C,0,1.7440511801,3.932817166,-0.42160548
C,0,0.2858455383,3.7857362941,-0.395389374
C,0,-0.3081522375,2.5667413491,-0.3265589904
H,0,4.0897241147,-1.6612123583,0.1890110672
H,0,-0.7822426169,-2.626108304,-0.1214484535
H,0,0.7898278547,-4.4909260816,0.1347721079
H,0,-0.3022742746,4.7002466461,-0.4116467381
H,0,-1.3920265254,2.4961215013,-0.2881836374
O,0,2.667535957,0.3958685454,-0.1010167285
O,0,2.2885155421,5.0449541103,-0.5045057825
O,0,3.3826272432,-4.2059127167,0.3371245959
C,0,-1.5949600187,-0.1068220422,-0.5194582246
C,0,-2.0982378026,0.4276092635,-1.7281707319
C,0,-2.5053525276,-0.8251393973,0.3114333567
C,0,-3.3911065127,0.2007353938,-2.1473264165
H,0,-1.4159901083,0.9816624486,-2.3690548077
C,0,-3.8118728744,-1.0652700594,-0.1497439543
C,0,-4.2606520125,-0.5732709721,-1.3574078195
H,0,-3.723254075,0.5984910938,-3.1038714387
H,0,-4.4693933116,-1.6362384416,0.5003234105
H,0,-5.2776099216,-0.7720684907,-1.6865830023
C,0,-2.2467404394,-1.24956143,1.7152796426
O,0,-2.9822457805,-1.9957422897,2.3262752865
O,0,-1.1801793582,-0.728044899,2.3534872584
H,0,-0.6651935874,-0.171023027,1.7523174063

Fluorescein methyl ester monoanion (2⁻), ground state

C,0,3.9167768455,-1.9051896184,-0.0612855069
C,0,3.6640844589,-0.4834352032,0.0200346678
C,0,2.404777213,0.0235660867,-0.1327212799
C,0,1.2617521278,-0.7966709903,-0.391567406
C,0,1.4940244535,-2.2083352182,-0.4427626594
C,0,2.7329216975,-2.7388605061,-0.2903452199
C,0,0.0138682975,-0.1874144722,-0.5289808952
C,0,-0.1184889127,1.2000972116,-0.4236544094
C,0,1.0424175006,1.9802952675,-0.1274870136
C,0,1.0012328859,3.3337725516,0.0568313235
H,0,1.9137301544,3.8781661801,0.2824466932
C,0,-0.2405904625,4.0685405976,-0.0398695981
C,0,-1.4208813825,3.261186414,-0.3598568976
C,0,-1.3511696304,1.9177233579,-0.5390068677
H,0,4.4980412751,0.1847646264,0.2146184173
H,0,0.6406071919,-2.8643269435,-0.6029266942
H,0,2.8932645561,-3.8142643484,-0.3301160867
H,0,-2.3666724527,3.7911066305,-0.4493616301
H,0,-2.2548300978,1.3601655669,-0.7786316182
O,0,2.2592979145,1.374365792,-0.0156913992
O,0,-0.3165086028,5.2980941895,0.1316049741
O,0,5.0501197277,-2.4014374589,0.0637398316
C,0,-1.1865058509,-1.0251608557,-0.8150839676
C,0,-1.3168105561,-1.5722968441,-2.0936037729
C,0,-2.2111727349,-1.2509672855,0.116991172
C,0,-2.4262394712,-2.3310212536,-2.4417991267
H,0,-0.5261431401,-1.3898980973,-2.8171169817
C,0,-3.3344153027,-1.9962882623,-0.2454141267
C,0,-3.442088371,-2.5458116059,-1.5143783339
H,0,-2.5004739068,-2.7484966396,-3.4435321718
H,0,-4.1219895001,-2.1318762817,0.4910284779
H,0,-4.317118726,-3.1336773723,-1.7809576603
C,0,-2.1991011288,-0.6798964344,1.5010240228
O,0,-3.2034076507,-0.3880141545,2.1105872131
O,0,-0.9678988952,-0.546479698,1.9865823466
C,0,-0.8380118948,0.216605501,3.1850489683
H,0,0.233252853,0.2505573358,3.3879906514
H,0,-1.2281671836,1.2260750745,3.0226127611
H,0,-1.3776033753,-0.2622633055,4.0078991186

Fluorescein methyl ester monoanion (2⁻), excited state

C,0,4.0274105111,-1.9049556592,-0.4390316371

C,0,3.7693322864,-0.4839438668,-0.2978224795
 C,0,2.4976143591,0.004340821,-0.2810270489
 C,0,1.3385983819,-0.8304867681,-0.4318435634
 C,0,1.5864575415,-2.2461113422,-0.4734355651
 C,0,2.8370847676,-2.7629768964,-0.4883067821
 C,0,0.0450065717,-0.2711630522,-0.4723924169
 C,0,-0.0490761995,1.1381926,-0.2794931322
 C,0,1.1284462714,1.9174405523,-0.0491653019
 C,0,1.0960993419,3.2638147775,0.1737712568
 H,0,2.0196446249,3.8127397742,0.3313695986
 C,0,-0.1571488417,3.9915272359,0.176910588
 C,0,-1.3547079129,3.1941170522,-0.1127769275
 C,0,-1.2844590293,1.8591409422,-0.3310659795
 H,0,4.6132666945,0.1897646803,-0.1834237449
 H,0,0.7207032566,-2.901364925,-0.487226792
 H,0,3.0066228784,-3.8366168307,-0.5125563608
 H,0,-2.3029919118,3.7241459795,-0.1478585444
 H,0,-2.1885584947,1.2981251453,-0.545099311
 O,0,2.363790878,1.3444034055,-0.0877038478
 O,0,-0.2225082473,5.2100714008,0.3916596755
 O,0,5.1721353856,-2.3748653304,-0.4791695895
 C,0,-1.1269698277,-1.1070879732,-0.7214976027
 C,0,-1.140848431,-1.8721402586,-1.9068458953
 C,0,-2.3029294084,-1.1340514064,0.1097659066
 C,0,-2.2557829764,-2.5625664761,-2.3304832995
 H,0,-0.2542698133,-1.8583896593,-2.5383396414
 C,0,-3.4481358412,-1.818720984,-0.370650848
 C,0,-3.4403881476,-2.5160352538,-1.5523119609
 H,0,-2.2316594659,-3.1058641855,-3.2720477228
 H,0,-4.3386386086,-1.7905348413,0.2523714338
 H,0,-4.3369603288,-3.0344313061,-1.8852351814
 C,0,-2.3992251206,-0.5796101985,1.4485490406
 O,0,-3.4283456175,-0.4713097745,2.1077230455
 O,0,-1.1982806449,-0.1774434954,1.9525512172
 C,0,-1.2523059434,0.5264311634,3.1799747116
 H,0,-0.2188720048,0.7976285975,3.4093937874
 H,0,-1.8640820611,1.4301515291,3.0791793856
 H,0,-1.6711889491,-0.0983656393,3.9764808448

Fluorescein piperidino amide monoanion (3⁻), ground state

C	-0.022431405300	0.418224848200	0.088751027800
C	-0.064249985700	0.390691993800	1.479977348400
C	1.112870125300	0.253608578500	2.199242902300
C	2.354556042000	0.147693435600	1.560633966000
C	2.388616990100	0.143223485300	0.156515977200

C	1.194404287800	0.272224330400	-0.558739772200
C	3.568013761500	0.073152778800	2.426616309200
C	3.861004887000	1.168168863200	3.257332586200
C	5.013793094000	1.108867412900	4.101401524300
O	5.818692857500	0.008663873000	4.074685497300
C	5.580206721100	-1.036695779400	3.232606233700
C	4.401949932600	-1.045873771300	2.418650734600
C	3.140550469200	2.405630205900	3.275276050100
C	3.500756023400	3.442146707500	4.074123426900
C	4.649540567800	3.369373811300	4.979573052100
C	5.391456571100	2.130227843200	4.927217272200
C	6.507415048100	-2.038550389800	3.211943528500
C	6.340894972100	-3.198226553900	2.362897019200
C	5.105885634800	-3.223198438900	1.574069136100
C	4.202525444200	-2.213939899300	1.612118722000
O	4.963292146300	4.320241474500	5.717192792000
O	7.174692016200	-4.117519720900	2.303383320300
C	3.606356515900	-0.194698443200	-0.675761722400
N	4.762811244100	0.492326366400	-0.509512868900
C	5.954508115200	0.003534549900	-1.191952026200
O	3.499537473600	-1.127723014200	-1.466857055400
H	7.388675641200	-1.975291859300	3.843657777100
H	6.281011444800	2.027231547500	5.541734663100
H	2.281876355800	2.513588286200	2.616781508300
H	2.941175402600	4.375156303800	4.067082179600
H	4.942107866000	-4.095892365200	0.946477526900
H	3.302746205000	-2.279689953500	1.005859784700
H	1.089489937600	0.235381001000	3.285989975400
H	-1.012602537600	0.474770217200	2.005688782400
H	1.237898860500	0.231029639900	-1.643752397700
H	-0.936976067700	0.528291986500	-0.489412018200
C	4.855157575500	1.849222848700	0.015300528900
C	7.172108971300	0.119518833800	-0.282107586400
C	6.088013677900	2.036347341500	0.893600905700
C	7.356653251200	1.558398250100	0.193635642200
H	5.766775229500	-1.030556328700	-1.481677378300
H	6.110784051000	0.588533596500	-2.114397328700
H	4.910293086200	2.543387789300	-0.840842079300
H	3.947635535700	2.088628463900	0.571393753800
H	7.031834736500	-0.545685368600	0.581043431500
H	8.056648111900	-0.231385720200	-0.827105865800
H	6.158799164600	3.091916341400	1.179492014800
H	5.956859674500	1.468354781500	1.817075900000
H	8.210995152900	1.634119791100	0.875849459000
H	7.576199963800	2.205501273600	-0.670353310100

Fluorescein piperidino amide monoanion (3⁻), excited state

C,0,-0.040889952,0.4019674619,0.0382511085
C,0,-0.0609108614,0.5906422738,1.4245608664
C,0,1.1084743979,0.495724776,2.1527151946
C,0,2.3569469978,0.219618657,1.5484189877
C,0,2.3651203976,0.0502338847,0.1373458449
C,0,1.1663848091,0.1172855823,-0.5791133424
C,0,3.5369654087,0.1285408554,2.4083023185
C,0,3.8480846111,1.1859369625,3.32275224
C,0,4.9836075235,1.0902405683,4.1835447433
O,0,5.8198235817,0.0130578461,4.1272618668
C,0,5.6094505706,-0.9734163082,3.2056835027
C,0,4.4498318627,-0.9737262416,2.3750774512
C,0,3.1538314539,2.4399926765,3.3662169855
C,0,3.4858092929,3.43906348,4.2282904502
C,0,4.5963879833,3.3096914314,5.1706320958
C,0,5.3420900278,2.0750905304,5.0667578296
C,0,6.5661740454,-1.9538565203,3.1559233735
C,0,6.4452755315,-3.0833950645,2.2593811149
C,0,5.2104928086,-3.1227078948,1.4772897807
C,0,4.280083334,-2.1336648627,1.5528593976
O,0,4.8896727993,4.2130096477,5.9749369056
O,0,7.3142534325,-3.9700512781,2.1722526964
C,0,3.5747610884,-0.2941989645,-0.6885609141
N,0,4.7458386349,0.3750042289,-0.4800481586
C,0,5.9369106435,-0.1159909025,-1.1589239974
O,0,3.4894023472,-1.2009308616,-1.5139855843
H,0,7.4315042921,-1.8956082601,3.8099371049
H,0,6.2223607171,1.9429522338,5.6892604371
H,0,2.3342705551,2.5939565312,2.6697429695
H,0,2.9402885238,4.3801061743,4.2327785653
H,0,5.0590079333,-3.9827691969,0.8299317897
H,0,3.373836614,-2.2173212576,0.9605537111
H,0,1.0748529433,0.6007128233,3.2346629495
H,0,-0.9988480864,0.7885546177,1.9395856122
H,0,1.207660063,-0.0592292073,-1.6510079714
H,0,-0.9561572596,0.4628859755,-0.5453912032
C,0,4.8220701494,1.7535418233,-0.0119328679
C,0,7.1642249949,0.0578499431,-0.2714353009
C,0,6.0574044503,1.99619328,0.8501185978
C,0,7.3273079957,1.5149127828,0.1541908461
H,0,5.7673456883,-1.1650340084,-1.4035109442
H,0,6.0726073428,0.4290553789,-2.1094869285
H,0,4.8650966783,2.4150157099,-0.8952420039
H,0,3.9126071294,2.0030491162,0.5356666832
H,0,7.0497418919,-0.5797235388,0.6159163068

H,0,8.04924771,-0.2934201137,-0.8155022661
H,0,6.1135370498,3.0644671344,1.0901358053
H,0,5.9454222299,1.4637414245,1.7981619996
H,0,8.1891470322,1.6296334865,0.8217932163
H,0,7.5234014313,2.135766429,-0.7343490154