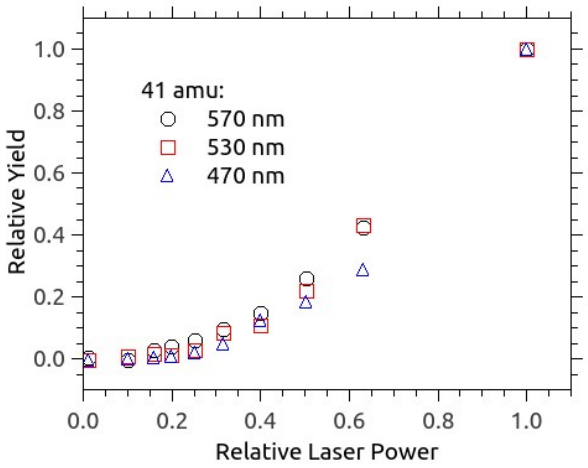
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

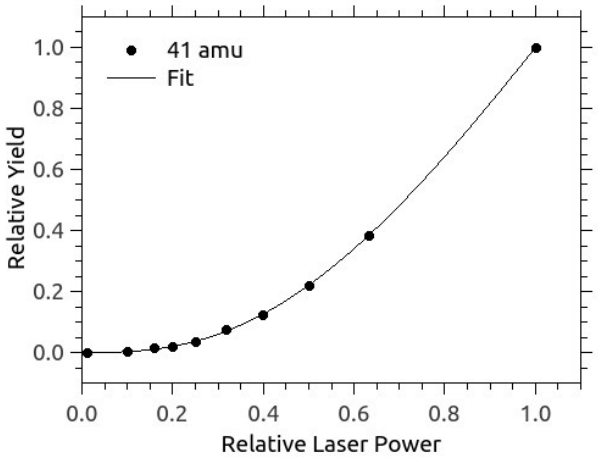
Sibling rivalry: intrinsic luminescence from two xanthene dye monoanions, resorufin and fluorescein, provides evidence for excited-state proton transfer in the latter

Christina Kjær, Steen Brøndsted Nielsen,* and Mark H. Stockett*

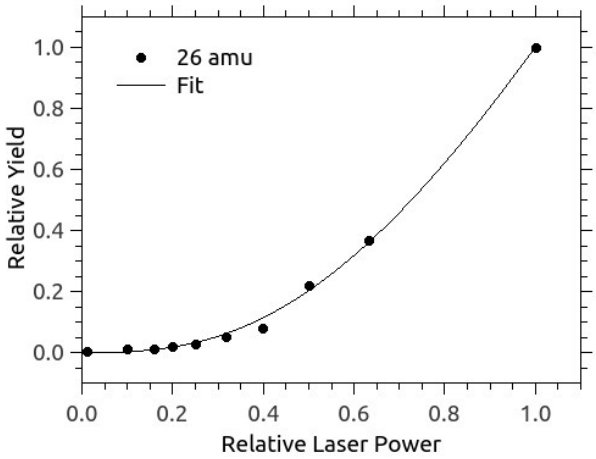
Supplementary Information



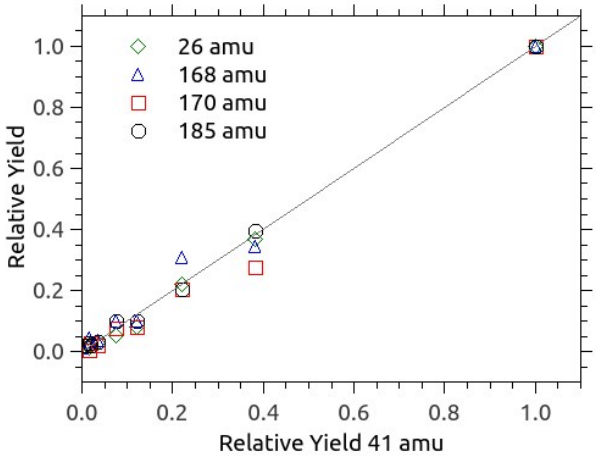
S1: Photo-fragment yield as a function of laser power for the 41 amu daughter ion (CHCOH—) of resorufin, recorded with three different laser excitation wavelengths. The laser power is reduced by use of neutral density filters, and the laser power is given relative to the maximum power (*i.e.* no filter), and the yield is given relative to that at maximum power. The laser power dependence is the same for the three wavelengths.



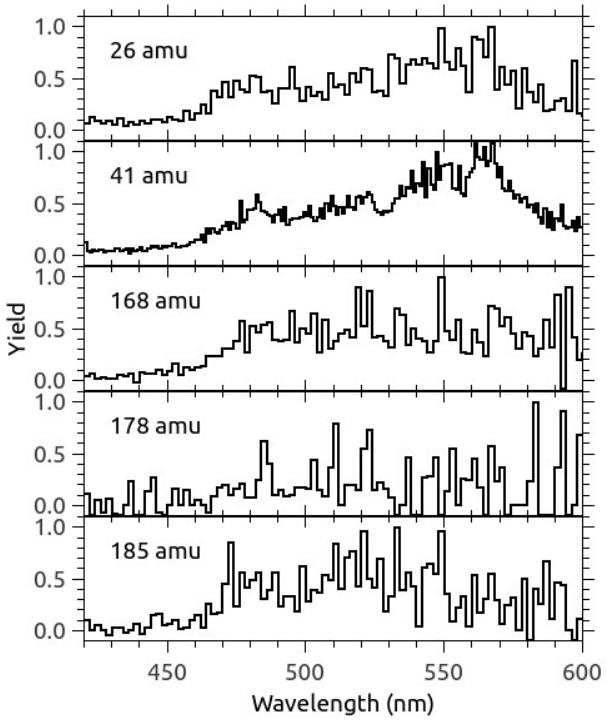
S2: Same as S1, but the yields for the three wavelengths have been summed. The solid line is a fit to the function $Y = A \times P^3 \times \exp(-s \times P)$, where the yield Y is assumed to depend on the third power of the laser power P, and the amplitude A and a saturation term s are fit parameters. The formation of this daughter ion thus required the absorption of 3 photons.



S3: Same as S2, for the 26 amu daughter ion (CN—) of resorufin.



S4: Yield of various daughter ions of resorufin plotted *versus* the yield of CHCOH— (41 amu). The solid line represents direct proportionality. This shows that all photofragments are formed following the same number of photon absorptions as CHCOH— *i.e.* 3 photons.



S5: Action spectra for various daughter ions of resorufin. Although the data quality is poor for the heavier daughter ions, all channels show absorption in the same region.

Computational results B3LYP/6-311++G(2d,p)//B3LYP/6-31+G(d)

Resorufin anion

Charge = -1, Spin multiplicity = 1

Geometry:

C,0,-9.9499717994,-1.0890202666,-0.9736021742
C,0,-8.4983560601,-1.0236602171,-0.9683746115
C,0,-7.8472264617,0.1805392955,-0.9689651165
C,0,-8.5431833529,1.4425836094,-0.974914544
C,0,-9.9746180825,1.3911109671,-0.9802395852
C,0,-10.6475386049,0.2033287947,-0.979582137
C,0,-6.5590432568,2.6090037166,-0.9713269594
C,0,-5.7947857662,1.3871117241,-0.9652476676
C,0,-4.4259307557,1.3704077406,-0.9603936929
H,0,-3.8854755969,0.4284318886,-0.9557558464
C,0,-3.6628441875,2.6070103371,-0.9612886901
C,0,-4.4527979835,3.8450466242,-0.9674386541
C,0,-5.8179063983,3.8347269866,-0.9721943008
H,0,-7.9381361024,-1.9540172044,-0.9637729695
H,0,-10.4978749433,2.3452197785,-0.9847729603
H,0,-11.7342460861,0.1669436004,-0.9834354836
H,0,-3.8925001919,4.7768932706,-0.9679736774
H,0,-6.3970910581,4.7559578215,-0.9767663663
O,0,-6.472269956,0.190599171,-0.9644495744
O,0,-10.5781180488,-2.1746717507,-0.9726366434
O,0,-2.4087512903,2.6278760759,-0.9565139801
N,0,-7.8984807665,2.6166913565,-0.9757704854

Vibrational frequencies:

58.3305	82.2397	171.9073
183.4979	184.9277	249.6323
287.0260	348.7300	355.4273
437.7649	449.9046	452.3755
452.8355	472.8849	524.9038
576.4993	589.2929	613.8907
638.4350	662.6887	695.3717
726.6778	728.5505	757.9169
814.5897	815.4666	850.8627
853.2205	855.7652	874.8197
909.4795	952.7287	968.7893
969.2038	1113.9375	1129.6120
1165.8470	1174.4878	1235.2371
1257.7476	1309.3294	1311.3162
1333.0768	1375.8898	1431.0541
1461.7499	1497.0893	1512.1829
1549.3110	1567.6274	1608.8905
1619.2458	1645.7860	1690.4464
3174.1192	3174.4494	3195.8956
3196.3227	3207.4650	3207.9806

ZKE = 0.151983

E = -741.5957062

Resorufin neutral (anion geometry)

Charge = 0, Spin multiplicity = 2

E = -741.4660156

Resorufin neutral (optimized geometry)

Charge = 0, Spin multiplicity = 2

Geometry:

C,0,-9.9448999516,-1.0654689506,-0.9733506879
C,0,-8.4843649612,-1.0350883649,-0.9682572341
C,0,-7.8266907758,0.1564110461,-0.9692028324
C,0,-8.5292501954,1.423423733,-0.9751946956
C,0,-9.9662869917,1.4062429104,-0.9802816047
C,0,-10.6493067288,0.2305435419,-0.9794711018
C,0,-6.5490782175,2.587512647,-0.9713175528
C,0,-5.7836903637,1.3574351386,-0.9651983229
C,0,-4.422749568,1.3526242911,-0.9602881162
H,0,-3.8594711824,0.4254246181,-0.9557332553
C,0,-3.6858901483,2.6140318242,-0.9610735729
C,0,-4.4757183996,3.8598272983,-0.9673739417
C,0,-5.8351802279,3.8348075615,-0.9721918386
H,0,-7.9481555103,-1.9782011585,-0.9637621555
H,0,-10.466808257,2.3700960048,-0.9847317393
H,0,-11.7342630654,0.1928919502,-0.9832473745
H,0,-3.9151639666,4.7895264825,-0.9679277958
H,0,-6.433937198,4.7409105506,-0.9768387361
O,0,-6.4572153541,0.1649908712,-0.9643670437
O,0,-10.5757025553,-2.1345962077,-0.9727039339
O,0,-2.4449421542,2.6452555784,-0.956752992
N,0,-7.8883807222,2.5995121039,-0.976149592

Vibrational frequencies:

54.5474	73.6688	161.8553	870.1479	880.0463	881.6296
174.4206	187.4574	239.3718	899.5848	945.8344	992.6988
285.4666	346.6524	353.5499	992.7873	1105.1846	1136.9772
407.4723	423.2636	429.7232	1153.4012	1173.4376	1237.0175
447.6466	472.1721	516.2545	1257.7407	1289.0464	1324.8432
573.2534	578.8688	604.4722	1328.7185	1337.0907	1377.7571
632.5355	645.0746	706.4238	1431.7635	1453.2304	1479.5432
713.2540	734.1762	736.1278	1541.1584	1574.0319	1609.4734
823.4638	826.5814	846.3395	1611.4298	1624.3871	1670.6881
			3210.8682	3211.0465	3228.3416
			3228.4299	3232.1148	3232.4145

ZKE = 0.151537

E = -741.4683188

Resorufin minus CN^-

Charge = 0, Spin multiplicity = 1

Geometry:

C,0,3.6101491193,-0.2811575894,0.4038516256
C,0,2.4298363017,-1.1417248951,0.7206975751
C,0,1.4078690439,-0.653057114,-0.0029411289
C,0,1.8416581446,0.5137118678,-0.8487447163
C,0,3.1406257675,0.7428870653,-0.608235639
C,0,-0.9687547046,0.8959459309,0.3410787667
C,0,-0.9649807687,-0.463591534,-0.0363579716
C,0,-2.1289057474,-0.9323713314,-0.5897803698
H,0,-2.1373549818,-1.7790417087,-1.2714830131
C,0,-3.3976042599,-0.2151346412,-0.3706467248
C,0,-3.3476245107,1.0180098711,0.4485086993
C,0,-2.140201401,1.4725006535,0.8975603086
H,0,2.4381947314,-1.9795329694,1.4035073429
H,0,1.183351637,1.0387486838,-1.5277029856
H,0,3.7886150394,1.4957912697,-1.0386807602
H,0,-4.284527176,1.537864271,0.6280950852
H,0,-2.0630435556,2.367152414,1.5130211179
O,0,0.1677414231,-1.2301593967,-0.0810236706
O,0,4.734658044,-0.3751143668,0.8624573327
O,0,-4.4605041461,-0.6279424803,-0.8418978741

Vibrational frequencies:

31.0365	39.5559	87.1955	850.0557	878.4125	880.0237
161.9603	172.6990	195.8064			
251.2632	264.5704	323.3106			
350.3323	428.8554	491.5575			
496.5731	523.5021	568.1174			
608.2305	632.2925	659.7544			
677.5564	708.4109	727.8738			
760.8953	796.1037	843.2835			

884.8184 939.0178 941.5247
971.0168 1092.5311 1119.3837
1134.8339 1166.2311 1216.9316
1240.7129 1266.7204 1294.5242
1354.6057 1386.6469 1425.4593
1506.4406 1546.9344 1612.8061
1677.4177 1682.2251 1790.6615
3177.1596 3209.5950 3218.2416
3254.6252 3276.9836 3281.7967
ZKE = 0.136870
E = -648.4349848

Resorufin minus $CHCO^-$
Charge = 0, Spin multiplicity = 1
Geometry:
C,0,1.2328083917,0.2048839671,-0.0003594259
C,0,0.9704198557,1.554526406,-0.0000501169
C,0,2.5078473532,1.7669615489,-0.0002569522
C,0,2.7369511349,0.4300187174,0.0003144983
C,0,-1.2233573456,1.2031675019,0.000191335
C,0,-1.008886141,-0.2441091878,-0.0001073899
C,0,-2.0089025411,-1.1602533029,-0.0000280336
H,0,-1.8001955203,-2.2251716706,-0.0003770777
C,0,-3.4055468333,-0.7237643265,0.0007546578
C,0,-3.6189831061,0.7301382672,0.0002361762
C,0,-2.5887213284,1.6248042675,0.0001819164
H,0,3.1582602183,2.6337527016,-0.0003739938
H,0,3.6084269149,-0.208703258,0.0007000983
H,0,-4.6525283707,1.0641869454,0.0000976497
H,0,-2.7650061638,2.6972316071,0.0000963389
O,0,0.3353449209,-0.7375522948,-0.0004278896
O,0,-4.3494420878,-1.5313867601,-0.0004019235
N,0,-0.2257993515,2.1143008706,0.0001441327
Vibrational frequencies:
82.4109 95.8602 191.8528
203.8640 251.8262 340.1515
386.0838 424.7124 428.6480
443.5131 499.8397 526.8169
579.2629 603.8268 663.3518
683.3481 705.5814 732.0974
744.4124 812.4000 829.5591
834.0493 868.2828 886.6326
905.7467 987.3880 1015.8425
1041.9763 1056.4502 1127.9975
1228.2689 1253.7325 1279.2667
1297.2796 1356.7614 1404.9850
1473.4613 1504.4090 1542.5496
1572.7174 1609.8705 1653.8370
1684.7779 3198.6324 3217.0641
3224.3123 3257.4914 3299.9739
ZKE = 0.123051
E = -589.273037

CN^-
Charge = -1, Spin multiplicity = 1
Geometry:
C,0,0.,0.,-0.0917263903
N,0,0.,0.,1.0917263903
Vibrational frequency:
2124.8908
ZKE = 0.004841
E = -92.8904464

$CHCO^-$
Charge = -1, Spin multiplicity = 1
Geometry:
C,0,-1.7768908887,-0.6961345132,0.
H,0,-2.8492529678,-0.7152090659,0.
C,0,-0.7706049966,-1.4633948682,0.
O,0,0.2915123931,-2.0846021927,0.
Vibrational frequencies:
431.4657 571.2017 573.0233
1236.3152 2080.4128 3373.4610
ZKE = 0.018831
E = -152.0614691