Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Exploring excited state properties of 7-hydroxy and 7-methoxy 4-Methycoumarin: A combined time-dependent density functional theory / effective fragment potential study

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EQUILIBRIUM GEOMETRY OF 4-METHYLUMBELLIFERONE WITH FIVE WATER MOLECULES

(4MU-$(H_2O)_5$) IN S_0 STATE

O	8.0	-4.1916045940	3.1786721510	3.3456310406
C	6.0	-3.5903553628	4.3708406348	3.6795130110
C	6.0	-2.9922452211	5.1269577105	2.6082661854
C	6.0	-3.0478290326	4.7081734961	1.3077818157
C	6.0	-3.7259939714	3.4703277482	0.9913330996
C	6.0	-3.8892214570	2.9245269377	-0.3033546256
C	6.0	-4.5755563257	1.7420098744	-0.5148217741
C	6.0	-5.1296864331	1.0450703354	0.5830840872
C	6.0	-4.9657443871	1.5424514263	1.8773596117
C	6.0	-4.2849595129	2.7371852933	2.0546472763
O	8.0	-3.6324630683	4.6598966612	4.8722311473
O	8.0	-5.8134330888	-0.0937305901	0.3540785048
C	6.0	-2.4155110055	5.5251966436	0.2139544144
H	1.0	-2.5043158363	6.0515918686	2.8912888281
H	1.0	-3.4727291052	3.4501161082	-1.1566055912
H	1.0	-4.7011595092	1.3380023515	-1.5129359477

H 1.0 -5.3500412682 1.0280082675 2.7435094517

H 1.0 -6.2054152982 -0.4229683363 1.1820796913

H 1.0 -3.1640662697 5.8444228226 -0.5205086800

H 1.0 -1.6649523468 4.9377927342 -0.3269138467

H 1.0 -1.9313683499 6.4160202246 0.6185682770

FRAGNAME=H2ODFT

O1 -2.3334093249 7.0727699161 5.2195985572

H2 -2.8610108402 6.2914003940 5.2640593836

H3 -1.6174787026 6.9513610222 5.8225759022

FRAGNAME=H2ODFT

O1 -5.8887339168 -0.8288074043 -2.3210204039

H2 -5.8384682118 -0.7654494993 -1.3806281512

H3 -6.7991645064 -0.7335312317 -2.5510574585

FRAGNAME=H2ODFT

O1 -6.9987045217 -0.8240023191 2.5541293271

H2 -6.7136850407 -0.4314986727 3.3638102748

H3 -7.9340324675 -0.7054184535 2.5096551243

FRAGNAME=H2ODFT

O1 -6.0486961545 0.2540166767 4.8236394732

H2 -5.5061086307 -0.3204159825 5.3398800692

H3 -5.8738465728 1.1324681996 5.1213457040

FRAGNAME=H2ODFT

O1 -5.3346841201 2.6235126230 5.8859092293

H2 -4.6900516465 3.1835048508 5.4837449184

H3 -5.9079512983 3.1839421986 6.3840677252

EQUILIBRIUM GEOMETRY OF 4-METHYLUMBELLIFERONE WITH FIVE WATER MOLECULES

(4MU-$(H_2O)_5$) IN S_1 STATE

O	8.0	-3.2667272130	2.8348883725	3.3081632068
C	6.0	-3.4615417366	4.3023103777	3.6008233346
C	6.0	-2.9816540323	5.1393224990	2.5468225528
C	6.0	-2.7561746405	4.6621049112	1.2659473921
C	6.0	-3.4668409162	3.3942430942	0.9804401994
C	6.0	-3.9523793878	3.0139301052	-0.2687070844
C	6.0	-4.7762029018	1.8927053559	-0.4180904916
C	6.0	-5.1846663261	1.1379409210	0.7293877115
C	6.0	-4.7080850030	1.4867755764	1.9904351833
C	6.0	-3.8263735753	2.5599005284	2.1093268677
O	8.0	-4.0174836671	4.5475533225	4.6697022027
O	8.0	-6.0099058903	0.1053580642	0.5228151552
C	6.0	-2.1190561666	5.4581701967	0.1732554829
H	1.0	-2.8180307267	6.1818759352	2.8065967693
H	1.0	-3.6955346262	3.5974779648	-1.1464256573
H	1.0	-5.1270421473	1.5787609671	-1.3939171696
H	1.0	-4.9653721115	0.9113790936	2.8701505049
H	1.0	-6.3331406086	-0.2720292839	1.3679390796
H	1.0	-2.8431273509	5.7953227617	-0.5860633371
H	1.0	-1.3541095824	4.8788967894	-0.3628759892
H	1.0	-1.6362545673	6.3504177156	0.5800603884

FRAGNAME=H2ODFT

O1	-3.9736476951	7.3015565490	4.9343751169
H2	-4.1691269678	6.3783271172	4.9166628523
H3	-3.4788502077	7.4590130948	5.7225764469

FRAGNAME=H2ODFT

O1	-6.2713874505	-0.3831402015	-2.1949599150
H2	-6.2631523205	-0.4763502076	-1.2557461313
H3	-7.1750694564	-0.4264602088	-2.4639592891

FRAGNAME=H2ODFT

O1	-7.0521943991	-0.8117343201	2.6338261208
H2	-6.8226627739	-0.4411204212	3.4709874106
H3	-7.9916079677	-0.7562815919	2.5609865975

FRAGNAME=H2ODFT

O1	-6.5524154820	0.2053475755	4.9978271924
H2	-6.4714311967	-0.3932863799	5.7230563887
H3	-5.9606639446	0.9204797112	5.1689838469

FRAGNAME=H2ODFT

O1	-4.7300295265	2.0479641654	5.4559215719
H2	-3.9800538002	1.9760434743	4.8873775735
H3	-4.9065294824	2.9696670890	5.5568668057

EQUILIBRIUM GEOMETRY OF CATIONIC FORM OF 4-METHYLUMBELLIFERONE WITH FIVE WATER MOLECULES (4-MU^--$(H_2O)_5$) IN S_0 STATE

O	8.0	-4.5226440098	2.7126074865	3.1452559944
C	6.0	-3.9032129340	3.8424039912	3.5911435045
C	6.0	-3.2794365094	4.6803108481	2.6093750140

C 6.0 -3.3042558994 4.3655048858 1.2796496801

C 6.0 -3.9642807650 3.1819630223 0.8442446082

C 6.0 -4.0700498864 2.7309166516 -0.4954599880

C 6.0 -4.7063461671 1.5654961817 -0.8201085069

C 6.0 -5.3073538258 0.7143984437 0.1834974326

C 6.0 -5.2143574642 1.1868184700 1.5272429966

C 6.0 -4.5674285047 2.3578323573 1.8194192349

O 8.0 -3.9395219356 4.0292496950 4.7997667803

O 8.0 -5.8776299128 -0.3785955069 -0.1122269676

C 6.0 -2.6266528590 5.2637601488 0.2823404094

H 1.0 -2.7842091126 5.5681452595 2.9817955501

H 1.0 -3.6289293111 3.3323847177 -1.2858686871

H 1.0 -4.7721743930 1.2365748213 -1.8524921441

H 1.0 -5.6476628390 0.6200868259 2.3372864146

H 1.0 -3.3419899894 5.6407913547 -0.4546442070

H 1.0 -1.8556763883 4.7172251872 -0.2690127515

H 1.0 -2.1577081184 6.1159991147 0.7771115504

FRAGNAME=H2ODFT

O1 -2.6509748336 5.6125462956 6.6059427664

H2 -2.7176760448 4.9811346296 7.3043328512

H3 -3.0844157386 5.2355139484 5.8570408735

FRAGNAME=H2ODFT

O1 -6.2576877200 -1.8993243259 2.0638627411

H2 -5.5510769192 -2.5098313839 1.9265282502

H3 -6.2810676799 -1.3365956384 1.3064538318

FRAGNAME=H2ODFT

O1	-6.5273236030	-0.9831728431	-2.6601214790
H2	-7.3649970130	-0.5483234818	-2.6507542380
H3	-6.1506258419	-0.8648166152	-1.8028181172

FRAGNAME=H2ODFT

O1	-5.1452606260	1.6078513151	5.8501211845
H2	-5.3026078064	0.9411627058	5.2007779647
H3	-4.7980456895	2.3563610993	5.3918054147

FRAGNAME=H2ODFT

O1	-6.1476891428	-0.6604447721	4.4758147476
H2	-6.1715840371	-1.0898699602	3.6356353049
H3	-7.0422862142	-0.5838225754	4.7668535300

EQUILIBRIUM GEOMETRY OF CATIONIC FORM OF 4-METHYLUMBELLIFERONE WITH FIVE WATER MOLECULES (4-MU^{-}-$(H_2O)_5$) IN S_1 STATE

O	8.0	-4.4986951316	2.6465243961	3.1568370368
C	6.0	-3.8877149384	3.8428162880	3.6317942557
C	6.0	-3.2933544014	4.6826751919	2.6478544702
C	6.0	-3.2812996186	4.4260699843	1.2926404254
C	6.0	-3.9538803408	3.1585265632	0.8544455079
C	6.0	-4.0603999068	2.7001120855	-0.4850618340
C	6.0	-4.6854506763	1.5139514418	-0.8477752869
C	6.0	-5.2654092659	0.6735123390	0.1542641695
C	6.0	-5.1598959179	1.1343200443	1.5175946939
C	6.0	-4.5149383643	2.3545827595	1.8379869620
O	8.0	-3.9543653439	3.9971938464	4.8653923618

O 8.0 -5.8645290690 -0.4358122510 -0.0893047112

C 6.0 -2.6441117390 5.3090218481 0.2802904095

H 1.0 -2.8251966835 5.5815286912 3.0419924413

H 1.0 -3.6229880155 3.3168729706 -1.2669332591

H 1.0 -4.7347519550 1.1979057312 -1.8847083691

H 1.0 -5.5789054057 0.5499577923 2.3247875770

H 1.0 -3.3639349793 5.6703738843 -0.4785468359

H 1.0 -1.8556033256 4.7876887816 -0.2951928421

H 1.0 -2.1873395582 6.1851566470 0.7516358583

FRAGNAME=H2ODFT

O1 -2.5688540179 5.6401775134 6.5233522209

H2 -2.4693084995 4.9909570215 7.2012031608

H3 -3.0727058623 5.2377041332 5.8341302312

FRAGNAME=H2ODFT

O1 -6.4162978215 -1.9470024673 2.0758724423

H2 -5.7911029925 -2.6410363395 1.9404956932

H3 -6.3759909004 -1.3929212532 1.3128207964

FRAGNAME=H2ODFT

O1 -6.6179281535 -0.8962491921 -2.6673420101

H2 -7.2055483041 -0.1595767384 -2.7211445061

H3 -6.2445826091 -0.8827176431 -1.8005614983

FRAGNAME=H2ODFT

O1 -5.3109711964 1.7142460351 5.8365789338

H2 -5.2890375408 1.0696530345 5.1474510556

H3 -4.8820398986 2.4850545956 5.5007954339

FRAGNAME=H2ODFT

O1	-6.0818690699	-0.6497740626	4.4333904359
H2	-6.2392939848	-1.1283565692	3.6352334121
H3	-6.9242837297	-0.5057122919	4.8339677709

EQUILIBRIUM GEOMETRY OF PHOTOTAUTOMER OF 4-METHYLUMBELLIFERONE WITH FIVE WATER MOLECULES (4-MUT-$(H_2O)_5$) IN S_0 STATE

O	8.0	-4.4555371706	2.0788348984	2.6634046597
C	6.0	-4.0453293380	2.9621395815	3.5786708203
C	6.0	-3.3271044039	4.0836637675	3.2406698235
C	6.0	-3.0456162072	4.3406127564	1.8764244701
C	6.0	-3.5085796418	3.4562965450	0.8948412633
C	6.0	-3.3517468238	3.5850081445	-0.5294446011
C	6.0	-3.8874301912	2.6844486296	-1.4027190505
C	6.0	-4.6594084368	1.5261783015	-0.9518421407
C	6.0	-4.7364854292	1.3462356126	0.4746086827
C	6.0	-4.2309979797	2.2891623400	1.3154984839
O	8.0	-4.4125403534	2.6286377263	4.7980346454
O	8.0	-5.2414158163	0.7436965222	-1.7478490783
C	6.0	-2.2607802205	5.5863039337	1.5611525642
H	1.0	-3.0140661591	4.7562645934	4.0277975835
H	1.0	-2.8016165175	4.4345570555	-0.9207818984
H	1.0	-3.7730098090	2.8153526617	-2.4741445143
H	1.0	-5.2345081760	0.4804261159	0.8824107725
H	1.0	-5.0235543188	1.8540362252	4.7552394382
H	1.0	-2.0671201119	5.7194897927	0.4976166851

H 1.0 -1.2984196148 5.5616201069 2.0847678497

H 1.0 -2.7967110280 6.4701627080 1.9255706867

FRAGNAME=H2ODFT

O1 -3.4318671377 4.6212861636 6.4719273097

H2 -3.8056463292 3.8163411009 6.1506314710

H3 -4.1195010283 5.0747163368 6.9328385427

FRAGNAME=H2ODFT

O1 -5.9909517289 0.6941865395 4.5609455936

H2 -6.4122582994 0.6450464049 3.7177584999

H3 -5.6116691037 -0.1544899694 4.7245650531

FRAGNAME=H2ODFT

O1 -7.2320379569 -0.4094438232 -0.2427984808

H2 -7.2883128151 -1.3225760988 -0.4749644595

H3 -6.6147821706 -0.0156311762 -0.8384370856

FRAGNAME=H2ODFT

O1 -7.4632942737 0.3796010782 2.3462885672

H2 -7.3144309098 0.1082668818 1.4546070619

H3 -8.2895612955 0.8357290913 2.3567048250

FRAGNAME=H2ODFT

O1 -4.8679198629 1.3098687226 -4.4045104237

H2 -4.9467263776 1.0038118119 -3.5151302155

H3 -5.7347631317 1.5575777505 -4.6839767704

EQUILIBRIUM GEOMETRY OF PHOTOTAUTOMER OF 4-METHYLUMBELLIFERONE WITH FIVE WATER MOLECULES (4-MUT-$(H_2O)_5$) IN S_1 STATE

O 8.0 -4.4328765300 2.0548433746 2.6432100205

C 6.0 -4.0143480308 2.9242007348 3.5958406572

C 6.0 -3.2702426931 4.0757631553 3.2669258950

C 6.0 -2.9879690512 4.3845759356 1.9605937210

C 6.0 -3.5252130071 3.4615661262 0.9102745013

C 6.0 -3.4199885734 3.6211990251 -0.5019510981

C 6.0 -3.9767977127 2.7490214297 -1.4189920136

C 6.0 -4.7175175827 1.5959538776 -0.9813586379

C 6.0 -4.7740971868 1.3916046901 0.4492316071

C 6.0 -4.2090662558 2.3407256631 1.3380061593

O 8.0 -4.3841665860 2.5747912451 4.8228828746

O 8.0 -5.3084105645 0.7649784523 -1.7412918651

C 6.0 -2.2021825992 5.5816258611 1.5546230576

H 1.0 -2.9427211117 4.7009389862 4.0895171372

H 1.0 -2.8799917109 4.4875037449 -0.8754884660

H 1.0 -3.8800554335 2.9228054218 -2.4845627138

H 1.0 -5.2542730112 0.5154495984 0.8563988584

H 1.0 -5.0065850165 1.8167339139 4.7737270401

H 1.0 -1.3157856879 5.2954246052 0.9674933839

H 1.0 -1.8710936047 6.1567749575 2.4224089499

H 1.0 -2.7920514693 6.2458227853 0.9038163159

FRAGNAME=H2ODFT

O1 -3.4297390584 4.5474347955 6.5243164036

H2 -3.7851886623 3.7452991055 6.1763043809

H3 -4.1485462000 5.0130429369 6.9210578885

FRAGNAME=H2ODFT

O1 -5.9950475058 0.6362254577 4.5558379873

H2 -6.4134551833 0.5892563657 3.7110851395

H3 -5.6281836558 -0.2168774224 4.7246717679

FRAGNAME=H2ODFT

O1 -7.1746031669 -0.5368290519 -0.2232736006

H2 -7.1776533211 -1.4549254517 -0.4422899269

H3 -6.6131402501 -0.1101411640 -0.8506293956

FRAGNAME=H2ODFT

O1 -7.4378548297 0.4078235228 2.2982947890

H2 -7.3307920835 0.0464198509 1.4329605135

H3 -8.2603611955 0.8708150356 2.2990637145

FRAGNAME=H2ODFT

O1 -4.9528612920 1.2810490497 -4.4213869345

H2 -5.0149781026 1.0040021810 -3.5212397308

H3 -5.8182680164 1.5533789610 -4.6817445250

EQUILIBRIUM GEOMETRY OF 7-METHOXY-4METHYL COUMARIN (MMC) IN S_0 STATE

O 8.0 -0.5272610210 1.6237753503 3.0585890802

C 6.0 0.3106630407 2.7369482296 3.2032387731

C 6.0 0.2027372014 3.7600899127 2.1723041102

C 6.0 -0.6526395393 3.6706979883 1.1179432126

C 6.0 -1.5047581536 2.4972347720 1.0130921987

C 6.0 -2.4372496075 2.2755107504 -0.0172364711

C 6.0 -3.2285167316 1.1314936179 -0.0614911795

C 6.0 -3.0972571223 0.1592034114 0.9507882293

C 6.0 -2.1777313570 0.3513335607 1.9892661631

C	6.0	-1.3970739969	1.5035721398	2.0159341388
O	8.0	1.0466511931	2.7588289706	4.1592738939
O	8.0	-3.8134696581	-0.9939335108	1.0073506574
C	6.0	-4.7781829790	-1.2467328487	-0.0057735196
C	6.0	-0.7228358204	4.7559215463	0.0781295719
H	1.0	0.8652442207	4.6165464385	2.3053892586
H	1.0	-2.5478501260	3.0199387567	-0.8070270833
H	1.0	-3.9377848913	1.0013330005	-0.8773564126
H	1.0	-2.0733361924	-0.3965077809	2.7752775398
H	1.0	-5.2235418941	-2.2192488062	0.2412740487
H	1.0	-4.3142520849	-1.3039167503	-1.0064624728
H	1.0	-5.5694875911	-0.4762640495	-0.0148268215
H	1.0	-0.0188047623	5.5674956499	0.3074189171
H	1.0	-1.7374184692	5.1845414622	0.0189935570
H	1.0	-0.4815536581	4.3612581888	-0.9232393899

EQUILIBRIUM GEOMETRY OF 7-METHOXY-4METHYL COUMARIN WITH TWO WATER MOLECULES (MMC-$(H_2O)_2$) IN S_0 STATE

O	8.0	-1.4051262439	1.0298838112	3.2893439493
C	6.0	-0.3586326610	1.8770503128	3.6433950539
C	6.0	0.0136893148	2.9001158028	2.6795584841
C	6.0	-0.6113832381	3.0400457091	1.4777453607
C	6.0	-1.6942516745	2.1291272249	1.1440153646
C	6.0	-2.4231003469	2.1544122607	-0.0600424233
C	6.0	-3.4488172568	1.2505562928	-0.3201385134
C	6.0	-3.7757298373	0.2780247964	0.6448177858

C 6.0 -3.0735068805 0.2289879261 1.8545752631

C 6.0 -2.0487811879 1.1412189859 2.0923788078

O 8.0 0.1530341720 1.6891477047 4.7275161051

O 8.0 -4.7538027873 -0.6573479395 0.4938968082

C 6.0 -5.5336918167 -0.6527696311 -0.7034655945

C 6.0 -0.1986245751 4.1146258207 0.5095493736

H 1.0 0.8329960463 3.5507434373 2.9865215474

H 1.0 -2.1806483352 2.9018882780 -0.8168993418

H 1.0 -3.9842333541 1.3042602663 -1.2666662457

H 1.0 -3.3256419763 -0.5137472265 2.6119603388

H 1.0 -6.2429054400 -1.4825130067 -0.5986640854

H 1.0 -4.9039558346 -0.8277007522 -1.5920016035

H 1.0 -6.0832912019 0.2972386389 -0.8144241930

H 1.0 0.6360617460 4.7061749831 0.9095655428

H 1.0 -1.0379755749 4.7984947019 0.2980928522

H 1.0 0.1153231332 3.6815597959 -0.4550432938

FRAGNAME=H2ODFT

O1 -4.3173106657 -3.3973887270 0.5240307893

H2 -3.4794496195 -3.7311415948 0.8023765176

H3 -4.3577765830 -2.4972880188 0.8052063194

FRAGNAME=H2ODFT

O1 2.1798628313 3.5458059301 5.0426395987

H2 1.6157833351 2.7914861125 5.1034210826

H3 2.0540714511 4.0431596679 5.8349111698

EQUILIBRIUM GEOMETRY OF 7-METHOXY-4METHYL COUMARIN WITH TWO WATER MOLECULES (MMC-$(H_2O)_2$) IN S_1 STATE

O	8.0	-1.4449397722	1.0621270010	3.3137196689
C	6.0	-0.3279989809	1.9240810461	3.6393858974
C	6.0	0.0374235757	2.9079339142	2.6847197878
C	6.0	-0.6202280858	3.0734274523	1.4422273821
C	6.0	-1.6858917692	2.1686294291	1.1368944176
C	6.0	-2.4268574041	2.1731328802	-0.0755307171
C	6.0	-3.4448178645	1.2491666782	-0.3193789686
C	6.0	-3.7693272526	0.2632294971	0.6560659230
C	6.0	-3.0649999498	0.2265695371	1.8698135675
C	6.0	-2.0560775605	1.1496829601	2.1194448712
O	8.0	0.1610888707	1.6783016147	4.7342306741
O	8.0	-4.7356562767	-0.6754001378	0.4994208943
C	6.0	-5.5311024892	-0.6826008762	-0.6903191627
C	6.0	-0.2097792648	4.1368480992	0.4717640421
H	1.0	0.8722771268	3.5492124826	2.9706084529
H	1.0	-2.1942658219	2.9153295692	-0.8385753215
H	1.0	-3.9839739319	1.2870527817	-1.2654144965
H	1.0	-3.3122802828	-0.5132563446	2.6315045192
H	1.0	-6.2314090954	-1.5167668722	-0.5708813734
H	1.0	-4.9067392348	-0.8611316844	-1.5816086369
H	1.0	-6.0839973786	0.2655830870	-0.7977096369
H	1.0	0.6252526277	4.7303617418	0.8706409315
H	1.0	-1.0398822729	4.8341248971	0.2460965787
H	1.0	0.1137610678	3.7134035155	-0.4990261624

FRAGNAME=H2ODFT

O1	-4.4294003006	-3.4156928785	0.4100344648
H2	-3.7843352434	-3.9732379190	0.8148962361
H3	-4.3468098592	-2.5670077837	0.8147453283

FRAGNAME=H2ODFT

O1	2.2301970196	3.4614471761	5.2372359641
H2	1.6438355093	2.7251697337	5.1668501613
H3	2.0030849478	3.9139302252	6.0338272339

Natural charges on atoms of 4-Methylumbelliferone and 7-methoxy-4Methyl coumarin in water complexes

	4MU_S0	**4MU_S1**	MMC_S0	MMC_S1
O 1	-0.519	-0.531	-0.526	-0.517
C 2	0.801	0.721	0.807	0.749
C 3	-0.397	-0.355	-0.359	-0.351
C 4	0.084	-0.068	0.056	-0.051
C 5	-0.182	-0.021	-0.168	-0.043
C 6	-0.187	-0.256	-0.169	-0.263
C 7	-0.308	-0.246	-0.326	-0.240
C 8	0.374	0.378	0.355	0.340
C 9	-0.375	-0.372	-0.311	-0.338
C 10	0.376	0.385	0.381	0.414

O 11	-0.689	-0.678	-0.612	-0.594
O 12	-0.778	-0.732	-0.563	-0.530
C 13	-0.722	-0.712	-0.282	-0.286
H 14 (15)	0.289	0.283	0.281	0.277
H 15 (16)	0.250	0.258	0.240	0.245
H 16 (17)	0.282	0.284	0.244	0.245
H 17 (18)	0.295	0.300	0.258	0.261
H 18 (C14)	0.624	0.630	-0.681	-0.676
H 22	-	-	0.236	0.247
H 23	-	-	0.245	0.232
H24	-	-	0.246	0.233
H 19	0.261	0.243	0.236	0.247
H 20	0.260	0.243	0.202	0.206
H 21	0.260	0.256	0.197	0.200