Supporting Information

Dramatic Changes of Excited-state Behavior of Green Fluorescent Protein Chromophore by a Strong π-Donating Group through Significantly Pulling down Excited-state Potential Energy Surface with Photoinduced Intramolecular Charge Transfer

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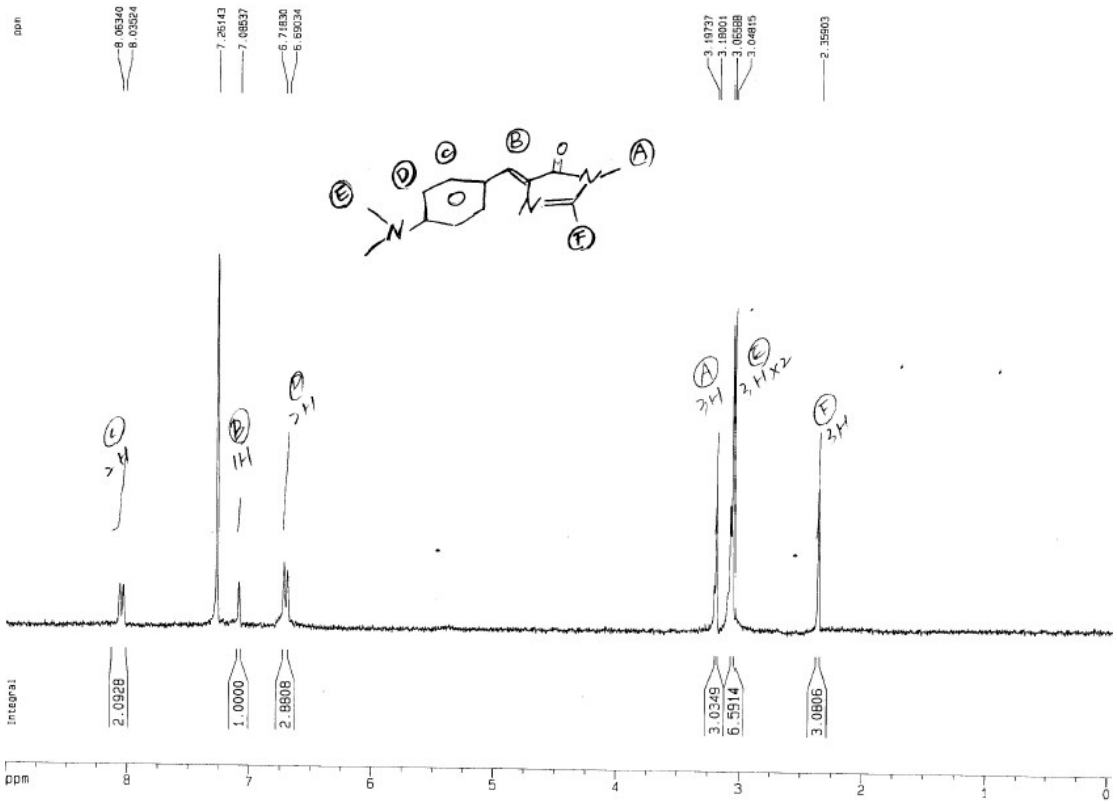

Figure S1. [1]H-NMR spectrum of *p*-DMABDI

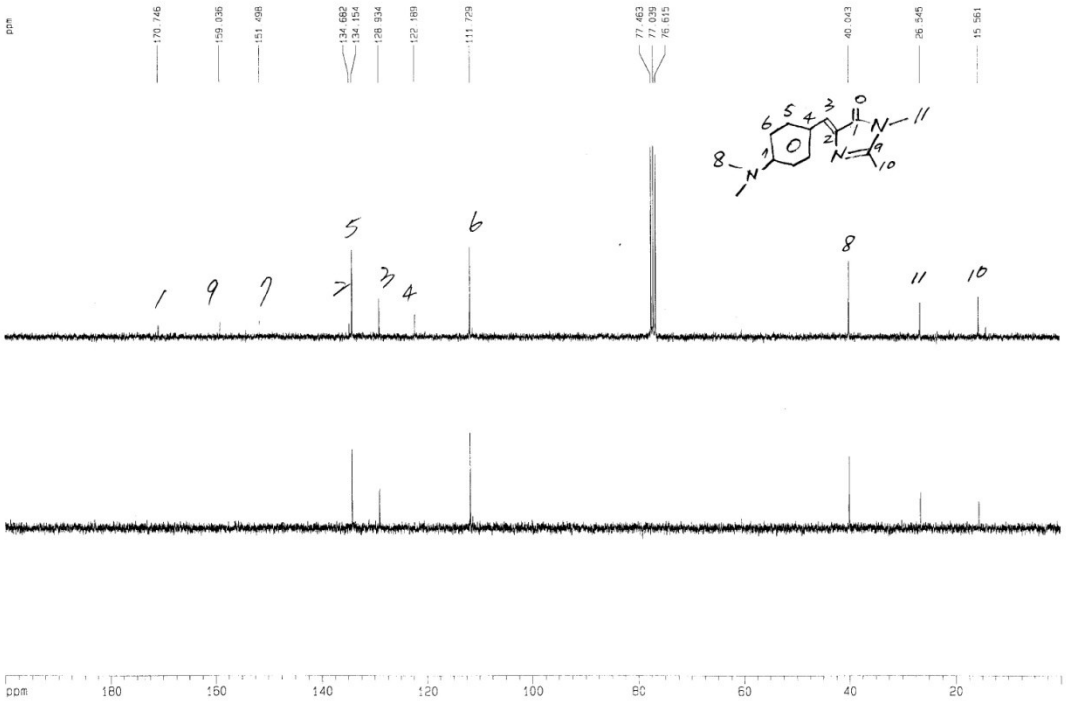

Figure S2. [13]C-NMR spectrum of *p*-DMABDI

Compound: ground-state *Z*-*p*-DMAbDI
Method/basis set: CASSCF(8, 8)/6-31G*
Energy of the optimized structure: -700.28431 Hartree
Cartesian coordinate of the optimized structure:

6	-3.511308	-0.141784	0.109866
6	-2.534832	-1.172252	0.072084
6	-1.200446	-0.898159	0.042379
6	-0.723740	0.434631	0.051231
6	-1.679617	1.437230	0.095356
6	-3.049251	1.162989	0.130083
1	-2.839358	-2.199590	0.060946
1	-1.367023	2.467118	0.110435
1	-3.727651	1.990808	0.174402
6	0.692744	0.809737	0.022765
1	0.891650	1.867596	0.033769
6	1.800302	0.042842	-0.015619
7	1.892182	-1.369815	-0.038884
6	3.177464	0.620077	-0.040739
7	3.973465	-0.499353	-0.077196
6	3.162703	-1.625529	-0.073999
8	3.537266	1.757592	-0.032319
1	-0.500535	-1.709161	0.011820
7	-4.865429	-0.452166	0.105641
1	4.966795	-0.477979	-0.101570
1	3.583133	-2.610406	-0.098966
6	-5.812974	0.618366	0.320795
1	-5.696996	1.385895	-0.433949
1	-6.815969	0.226313	0.229028
1	-5.714993	1.084394	1.301661
6	-5.279008	-1.772286	0.537006
1	-4.920371	-2.536239	-0.141153
1	-4.935566	-2.015918	1.541659
1	-6.358391	-1.821371	0.528064

Compound: ES(τ=0°) (S_1 excited state of *p*-DMAbDI with constrained τ=0°)
Method/basis set: CASSCF(8, 8)/6-31G*
Energy of the optimized structure: -700.08670 Hartree
Cartesian coordinate of the optimized structure:

6	-3.346722	0.514972	0.500205
6	-2.276766	1.455648	0.433392
6	-0.989148	1.060253	0.311706
6	-0.629150	-0.356973	0.242557
6	-1.745608	-1.296945	0.312910
6	-3.016856	-0.893245	0.433352
1	-2.489464	2.504240	0.479782
1	-1.524276	-2.347820	0.265351
1	-3.797221	-1.624777	0.480814
6	0.647199	-0.807970	0.121330
1	0.814591	-1.869529	0.078437
6	1.915013	-0.021694	0.034381
7	2.038551	1.332174	0.060545
6	3.187854	-0.655881	-0.090719
7	4.051672	0.433819	-0.134360
6	3.322648	1.584386	-0.041675
8	3.509130	-1.835412	-0.149690
1	-0.199147	1.780915	0.262926
7	-4.625290	0.911888	0.621481
1	5.037618	0.353342	-0.220702
1	3.758417	2.560331	-0.052296
6	-5.708442	-0.057180	0.685832
1	-6.644832	0.468968	0.779228
1	-5.752136	-0.662715	-0.212522
1	-5.604260	-0.711511	1.544125
6	-4.953902	2.326973	0.689790
1	-4.485049	2.798391	1.546312
1	-4.641213	2.847212	-0.208770
1	-6.021936	2.437132	0.788039

Compound: ES(τ=70°) (S_1 excited state of *p*-DMAbDI with constrained τ=70°)
Method/basis set: CASSCF(8, 8)/6-31G*
Energy of the optimized structure: -700.13189 Hartree
Cartesian coordinate of the optimized structure:

6	-2.276603	-1.270999	-2.849078
6	-1.111234	-0.457226	-2.983581
6	-0.198348	-0.387383	-1.984202
6	-0.357738	-1.120110	-0.764159
6	-1.533410	-1.931372	-0.647046
6	-2.455958	-2.007582	-1.630686
1	-0.954656	0.111904	-3.875600
1	-1.678115	-2.494565	0.257119
1	-3.319356	-2.625372	-1.498857
6	0.568577	-1.042761	0.253122
1	0.286794	-1.576680	1.155060
6	1.758372	-0.203318	0.246309
7	1.662073	1.188954	0.342181
6	2.984675	-0.589073	-0.347623
7	3.658314	0.633396	-0.438485
6	2.809935	1.641019	-0.041735
8	3.442947	-1.669323	-0.709339
1	0.667502	0.235611	-2.081735
7	-3.181590	-1.341720	-3.825740
1	4.576170	0.728171	-0.803993
1	3.086539	2.675298	-0.073518
6	-4.378498	-2.163714	-3.682278
1	-4.978146	-2.066374	-4.572335
1	-4.123945	-3.209434	-3.558958
1	-4.974979	-1.841747	-2.837533
6	-2.993415	-0.603730	-5.070925
1	-2.962821	0.463982	-4.891418
1	-2.080376	-0.905672	-5.568678
1	-3.820807	-0.811866	-5.729316

Compound: ES (The only real S_1 excited-state minimum of *p*-DMAbDI)
Method/basis set: CASSCF(8, 8)/6-31G*
Energy of the optimized structure: -700.088368 Hartree
Cartesian coordinate of the optimized structure:

6	-3.255960	-0.064164	0.008117
6	-2.584945	-0.208465	1.273899
6	-1.314525	-0.707021	1.331095
6	-0.583464	-1.105269	0.166600
6	-1.268426	-0.952642	-1.082624
6	-2.543626	-0.471605	-1.175017
1	-3.081780	0.084721	2.175288
1	-0.741685	-1.226821	-1.976069
1	-3.008741	-0.378114	-2.134394
6	0.792389	-1.584208	0.246895
1	0.990644	-2.636842	0.166655
6	1.840617	-0.658735	0.142866
7	1.659169	0.726883	0.123092
6	3.237955	-0.973273	0.057842
7	3.829735	0.283399	-0.008144
6	2.842377	1.242090	0.034426
8	3.844834	-2.031242	0.036764
1	-0.822725	-0.799223	2.279661
7	-4.480290	0.426650	-0.065163
6	-5.160260	0.572906	-1.354661
1	-5.259349	-0.384824	-1.847383
1	-6.146669	0.970204	-1.184766
1	-4.621906	1.255819	-1.998324
6	-5.193626	0.861455	1.138514
1	-6.158980	1.243156	0.851989
1	-5.341813	0.033061	1.818388
1	-4.650911	1.649454	1.642900
1	4.809430	0.426524	-0.074180
1	3.061738	2.290131	-0.002680

Compound: The conical intersection CI of *p*-DMAbDI
Method/basis set: CASSCF(8,8)/6-31G*
Energy of the optimized structure: -700.11592 Hartree

Cartesian coordinate of the optimized structure:

6	-1.336046	-2.305974	-3.171831
6	-0.205201	-1.402876	-3.259944
6	0.323231	-0.903306	-2.132902
6	-0.263577	-1.156776	-0.831659
6	-1.435145	-2.009891	-0.781421
6	-1.971468	-2.555210	-1.872209
1	0.293006	-1.263262	-4.193121
1	-1.880461	-2.195982	0.178321
1	-2.850050	-3.159482	-1.814718
6	0.511927	-0.968456	0.257643
1	0.103165	-1.454551	1.145618
6	1.800371	-0.285692	0.293763
7	1.799991	1.143686	0.320335
6	2.849298	-0.785443	-0.422635
7	3.666204	0.357262	-0.553783
6	2.949353	1.467861	-0.155990
8	3.093255	-1.876126	-0.988189
1	1.225091	-0.333619	-2.143869
7	-1.769852	-2.910321	-4.222746
1	4.525072	0.344936	-1.050419
1	3.369996	2.454896	-0.148921
6	-1.251172	-2.612658	-5.572892
1	-0.317993	-3.132653	-5.735758
1	-1.981929	-2.950581	-6.288963
1	-1.116928	-1.552880	-5.702310
6	-2.794593	-3.969666	-4.185092
1	-2.699102	-4.565657	-3.295041
1	-3.783763	-3.536904	-4.246335
1	-2.633753	-4.613021	-5.034497