Supporting Information

Controlling Solid-State Optical Properties of Stimuli Responsive Dimethylamino-Substituted Dibenzoylmethane Materials

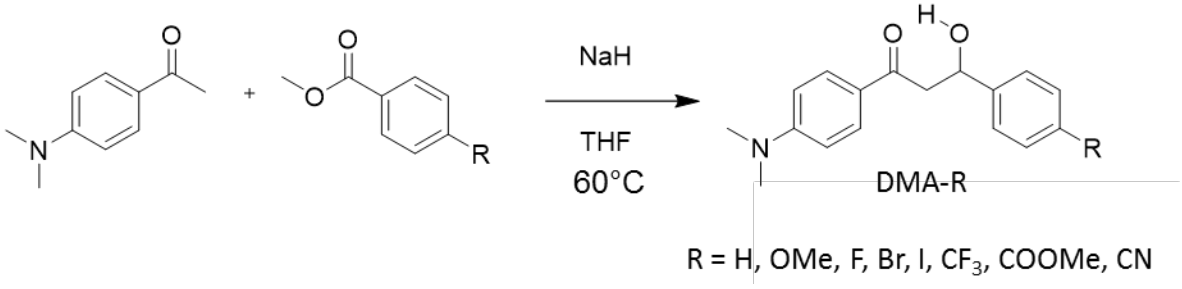
Tristan Butler, [a] *Fang Wang,* [a] *Michal Sabat*[a,b]*, Cassandra L. Fraser*[a,*]

[a] Department of Chemistry, University of Virginia, McCormick Road, Charlottesville, Virginia 22904, United States

[b] Department of Materials Science and Engineering, University of Virginia, 395 McCormick Road, Charlottesville, Virginia, 22904, United States

*Corresponding Author: fraser@virginia.edu

Scheme S1. Synthesis of dimethylamino (DMA) substituted diketones.



Synthesis of β-Diketones. The β-diketones were synthesized by Claisen condensation with NaH using a previously described method[1] involving 1-(4-(dimethylamino)phenyl)ethan-1-one) and the corresponding para substituted esters.

DMA-F. After recrystallization from 1:1 hexanes/EtOAc (2x), a yellow powder was obtained: 1.215g (37%). ^{1}H NMR (600 MHz, DMSO-d6) δ 17.59 (s, 1H, ArCOH) 8.17-

8.15 (t, 2H, J = 12, 2″-ArH) 8.00 (d, 2H, J = 6, 2′-ArH) 7.33 (t, 2H, J = 12, 3″-ArH) 7.11 (s, 1H, COCHCO) 6.74 (d, 2H, J = 6, 3′-ArH) 2.97 (s, 6H, $N(CH_3)_2$) HRMS (ESI, TOF): m/z calculated for $C_{17}H_{17}NO_2F$ 286.1243; found 286.1251 [M+H].

DMA-Br. After recrystallization from 1:1 hexanes/EtOAc (2x), a yellow powder was obtained: 0.420 g (34%). ^{1}H NMR (600 MHz, DMSO-d6) δ 17.53 (s, 1H, ArCOH), 8.03-7.99 (m, 4H, 2″-ArH, 3″-ArH), 7.72 (d, 2H, J = 6, 2′-ArH) 7.14 (s, 1H, COCHCO) 6.75 (d, 2H, 3′-ArH), 3.03 (s, 6H, $N(CH_3)_2$) HRMS (ESI, TOF): m/z calculated for $C_{18}H_{17}N_2O_2Br$ 346.0443; found 346.0445 [M+H].

DMA-I. After recrystallization from 1:1 hexanes/EtOAc (2x), a yellow powder was obtained: 0.843g (39%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 17.07 (s, 1H, ArCOH) 7.92 (d, 2H, J = 6, 3″-ArH) 7.80 (d, 2H, 2′-ArH) 7.66 (d, 2H, J = 6, 2″-ArH) 6.81 (d, 2H, J = H, 3′-ArH) 3.08 (s, 6H, $N(CH_3)_2$) HRMS (ESI, TOF): m/z calculated for $C_{17}H_{17}NO_2I$ 394.0306; found 394.0304 [M+H].

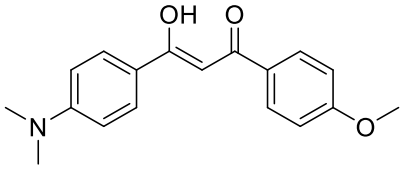
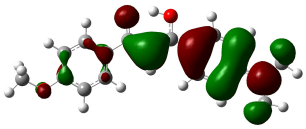
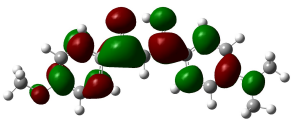
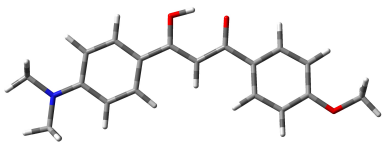
DMA-CF_3. After recrystallization from 1:1 hexanes/EtOAc (2x), a yellow powder was obtained: 1.020 g, (46%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 17.10 (s, 1H, ArCOH), 8.04 (d, 2H, J = 6, 2′-ArH), 7.92 (d, 2H, J = 6, 3″-ArH), 7.71 (d, 2H, J = 6, 2″-ArH), 6.75 (s, 1H, COCHCO), 6.69 (d, 2H, J = 6, 3′-ArH), 3.07 (s, 6H, $N(CH_3)_2$) HRMS (ESI, TOF): m/z calculated for $C_{18}H_{17}F_3NO_2$ 336.1211; found 336.1212 [M+H].

DMA-COOMe. The dye was passed through a silica column with 9:1 hexanes/EtOAc and recrystallized from 1:1 hexanes/EtOAc (2x). An orange powder was obtained: 0.321 g, (32%) ^{1}H NMR (600 MHz, DMSO-d6) δ 17.46 (s, 1H, ArCOH), 8.19 (d, 2H, J = 6, 2″-ArH), 8.04-8.00 (m, 4H, 2′-ArH, 3′-ArH), 7.20 (s, 1H, COCHCO), 6.75 (d, 2H, J = 9,

2″-ArH) 3.85 (s, 3H, OCH_3) 3.05 (s, 6H, $N(CH_3)_2$) HRMS (ESI, TOF): m/z calculated for $C_{19}H_{20}NO_4Br$ 326.1392; found 326.1404 [M+H].

Full Computational Details

All compounds were modeled using the Gaussian 09 suite of programs[2] utilizing density functional theory (DFT). The ground state optimization of the ligands was done using the basis set B3LYP/6-311+G(d) to simulate all atoms with the exception of I, where B3LYP/SDD was used. The vibrational frequencies were calculated in an additional calculation also utilizing B3LYP/6-31G(d), and all vibrational frequencies were positive assuring that the geometries were at least a local minimum. Single point energy calculations were used to generate the molecular orbital diagrams utilizing B3LYP/6-31G(d) for all atoms except I, where B3LYP/SDD. Molecular orbitals were depicted by GaussView software. Absorption spectra at the optimized geometry were estimated using time-dependent density functional theory, TD-B3LYP/6-311+G(d) for all but I atoms, which employed B3LYP/SDD. A Tomasi polarized continuum for dichloromethane solvent was used for all calculations.[4] Cartesian Coordinates are given in Angstroms.

DMA-OMe	Occupied Orbitals	Unoccupied Orbitals
	HOMO 	LUMO 
		

E(TD-HF/TD-KS) = -977.90956420 a.u.
Dipole Moment = 7.0832 Debye

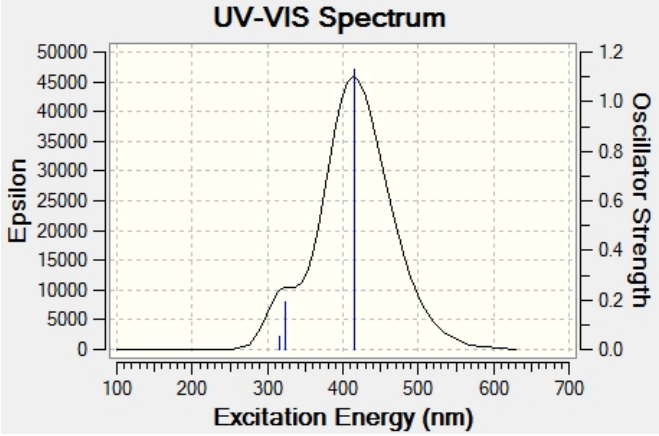
C	4.11607	1.10281	-0.17292
C	5.34217	0.43899	-0.19673
C	5.38049	-0.94766	0.01789
C	4.18334	-1.64708	0.25215
C	2.97059	-0.97193	0.26516
C	2.90941	0.42092	0.05112
H	4.08509	2.17505	-0.33569
H	2.06907	-1.54235	0.46264
C	1.63889	1.19881	0.05864
C	0.37164	0.53123	0.03221
H	0.33669	-0.54641	-0.0167
O	1.70934	2.46994	0.07421
C	-0.82459	1.23942	0.04453
C	-2.15833	0.64266	0.01924
C	-2.37082	-0.75239	0.00134
C	-3.30525	1.46488	0.01265
C	-3.64341	-1.29844	-0.02272
H	-1.52832	-1.43671	0.00817
C	-4.58627	0.93638	-0.01154
H	-3.18312	2.54265	0.02575
C	-4.80053	-0.46939	-0.0307
O	-0.80663	2.5775	0.08149
H	-3.74272	-2.37714	-0.03475
H	-5.42823	1.61809	-0.0164
H	4.22695	-2.71822	0.42597
H	6.24932	1.00304	-0.38055
N	-6.06201	-1.00286	-0.05518
C	-6.2498	-2.44922	-0.0757
H	-5.82017	-2.92497	0.81601
H	-7.31737	-2.66918	-0.09552
H	-5.79161	-2.90328	-0.96448
C	-7.23031	-0.1292	-0.06027
H	-7.24128	0.52449	-0.94267
H	-8.13211	-0.74144	-0.08055
H	-7.26589	0.50195	0.83778
H	0.17529	2.83719	0.08384
O	6.51631	-1.69668	0.02118
C	7.77247	-1.04714	-0.19666
H	8.52298	-1.83652	-0.1451
H	7.80397	-0.57328	-1.18443
H	7.9688	-0.30081	0.58163

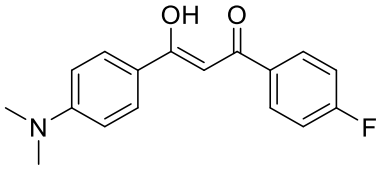
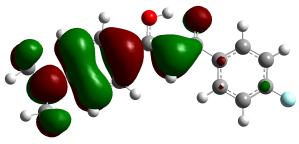
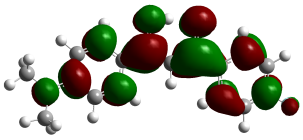
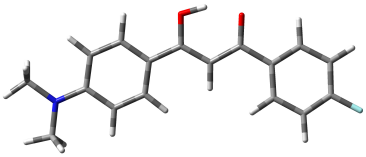
Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.9913 eV 414.48 nm f=1.1302 <S2>=0.000**
79 -> 80 0.70098
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -977.909564199
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.8396 eV 322.91 nm f=0.1929 <S**2>=0.000
74 -> 80 0.12152
75 -> 80 0.24583
78 -> 80 0.63042

Excited State 3: Singlet-A 3.9312 eV 315.39 nm f=0.0546 <S**2>=0.000
74 -> 80 0.30106
75 -> 80 0.53831
76 -> 80 0.12634
77 -> 80 0.11068
78 -> 80 -0.27467



DMA-F	Occupied Orbitals	Unoccupied Orbitals
	HOMO 	LUMO 
		

E(TD-HF/TD-KS) = -962.62392731 a.u.
Dipole Moment = 10.2185 Debye

C	-4.56293	0.9175	0.26184
C	-5.7664	0.21623	0.30781
C	-5.74053	-1.1488	0.04568
C	-4.57016	-1.83339	-0.25832
C	-3.37403	-1.11562	-0.29189
C	-3.35111	0.26612	-0.03067
H	-4.54957	1.98428	0.45693
H	-2.46306	-1.64726	-0.54432
C	-2.09689	1.08219	-0.06056
C	-0.81589	0.4498	-0.03197
H	-0.75114	-0.62548	0.03649
O	-2.21116	2.348	-0.0931
C	0.36177	1.19264	-0.05886
C	1.71009	0.63524	-0.02878
C	1.96258	-0.75353	-0.00153
C	2.83292	1.49109	-0.02806
C	3.25009	-1.26182	0.02613
H	1.14024	-1.46199	-0.00434
C	4.12801	1.00049	0.00032
H	2.67935	2.56467	-0.0486
C	4.38276	-0.39897	0.02896
O	0.30388	2.52761	-0.11467
H	3.38147	-2.33691	0.04474
H	4.94998	1.70616	0.00093
H	-4.59879	-2.89795	-0.46695
H	-6.70483	0.70939	0.54047
N	5.65837	-0.89469	0.0576
C	5.88946	-2.33505	0.08596
H	5.47527	-2.82756	-0.80378
H	6.96309	-2.52258	0.10817
H	5.44393	-2.79735	0.97674
C	6.80066	0.01338	0.05741
H	6.79051	0.67322	0.93498
H	7.71997	-0.57178	0.08361
H	6.81855	0.63823	-0.8454
H	-0.683	2.76236	-0.116
F	-6.91163	-1.84407	0.08495

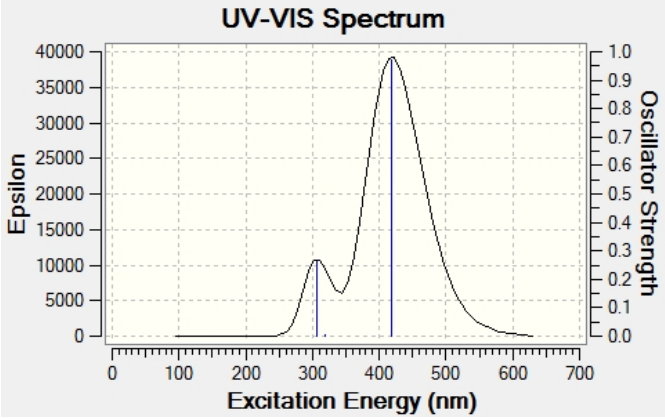
Excitation energies and oscillator strengths:

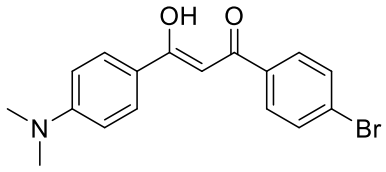
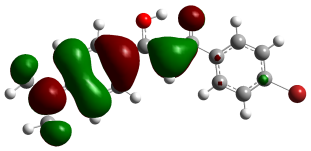
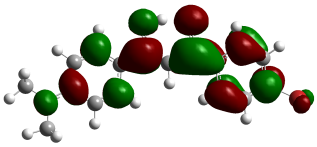
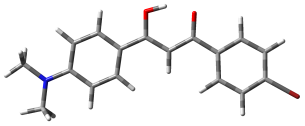
Excited State 1: Singlet-A 2.9599 eV 418.87 nm f=0.9705 <S2>=0.000**
75 -> 76 0.70368
This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -962.623927305
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.8853 eV 319.11 nm f=0.0044 <S**2>=0.000
70 -> 76 0.13347
71 -> 76 0.59372
72 -> 76 0.15155
73 -> 76 0.30077

Excited State 3: Singlet-A 4.0529 eV 305.91 nm f=0.2659 <S**2>=0.000
74 -> 76 0.60199
75 -> 77 -0.33480
75 -> 78 0.11881



DMA-Br	Occupied Orbitals	Unoccupied Orbitals
	HOMO 	LUMO 
		

E(TD-HF/TD-KS) -3436.89947099 a.u.
Dipole Moment 10.3778 Debye

C	-3.3015	1.58916	0.24374
C	-4.57157	1.01631	0.26206
C	-4.69992	-0.34905	0.00354

C	-3.58658	-1.14343	-0.26982
C	-2.32151	-0.5556	-0.28188
C	-2.15936	0.81573	-0.02321
H	-3.1831	2.65006	0.43631
H	-1.46786	-1.1828	-0.51522
C	-0.82789	1.50129	-0.04996
C	0.38097	0.74218	-0.03193
H	0.33614	-0.33445	0.02899
O	-0.81561	2.7721	-0.07518
C	1.62839	1.36203	-0.05706
C	2.9126	0.67087	-0.02996
C	3.02283	-0.73656	-0.00885
C	4.11628	1.40881	-0.02362
C	4.25206	-1.37273	0.01932
H	2.13322	-1.35824	-0.01695
C	5.35473	0.7895	0.00486
H	4.07213	2.49247	-0.0398
C	5.4662	-0.62871	0.02845
O	1.70541	2.6962	-0.10529
H	4.27403	-2.45563	0.03363
H	6.24388	1.40823	0.00947
H	-3.70024	-2.20212	-0.47684
H	-5.44577	1.62252	0.47499
N	6.68505	-1.25042	0.05783
C	6.76953	-2.7071	0.0808
H	6.30961	-3.15199	-0.81157
H	7.81863	-3.00221	0.10393
H	6.27771	-3.12516	0.96902
C	7.91337	-0.46248	0.06176
H	7.96878	0.19239	0.94136
H	8.76886	-1.13753	0.08707
H	7.99567	0.15983	-0.83914
H	0.74778	3.03001	-0.10316
Br	-6.433	-1.14972	0.03392

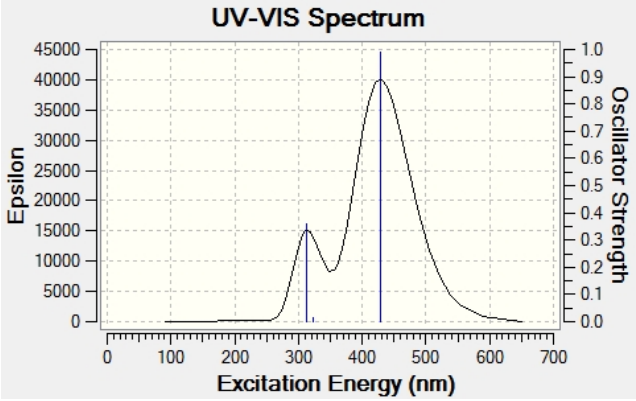
Excitation energies and oscillator strengths:

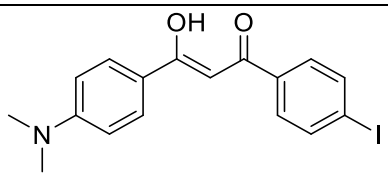
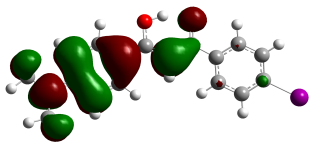
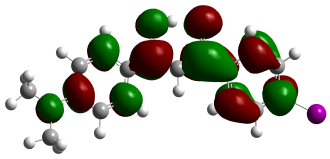
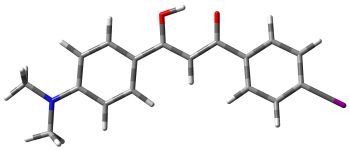
Excited State 1: Singlet-A 2.8961 eV 428.11 nm f=0.9895 <S2>=0.000**
88 -> 89 0.70315
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3436.89947099
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.8409 eV 322.80 nm f=0.0145 <S**2>=0.000
83 -> 89 0.18778
84 -> 89 0.63029
86 -> 89 0.17743

87 -> 89 0.13157

Excited State 3: Singlet-A 3.9564 eV 313.38 nm f=0.3600 <S**2>=0.000
84 -> 89 -0.13085
87 -> 89 0.60094
88 -> 90 0.33396



DMA-I	Occupied Orbitals	Unoccupied Orbitals
	HOMO 	LUMO 
		

E(TD-HF/TD-KS) = -873.93384033 a.u.
Dipole Moment = 10.2066 Debye

C	-2.58045	1.82404	0.2621
C	-3.86942	1.28975	0.28748
C	-2.96212	-0.88082	-0.32867
C	-1.67732	-0.3332	-0.33935
C	-1.46667	1.02381	-0.04287
H	-2.42684	2.87468	0.48523
H	-0.84792	-0.98077	-0.60372
C	-0.11046	1.66053	-0.051
C	1.06765	0.85403	-0.02795
H	0.97856	-0.22044	0.01978
O	-0.04928	2.93016	-0.06344

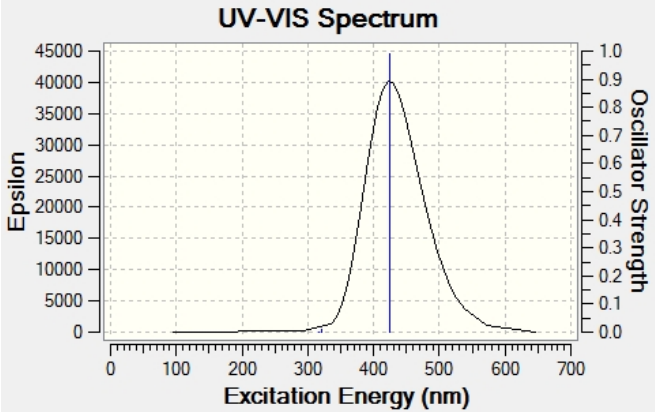
C	2.33932	1.42356	-0.04086
C	3.5941	0.67955	-0.01705
C	3.64435	-0.73089	0.03495
C	4.82849	1.36499	-0.04724
C	4.84561	-1.41903	0.05731
H	2.72891	-1.31326	0.06073
C	6.03987	0.69308	-0.02697
H	4.83059	2.44894	-0.08746
C	6.09071	-0.7282	0.02708
O	2.46961	2.75363	-0.07925
H	4.82151	-2.50117	0.09874
H	6.95481	1.27259	-0.05245
H	-3.10325	-1.92882	-0.57
H	-4.71445	1.92385	0.53463
N	7.28229	-1.40172	0.04954
C	7.30473	-2.85955	0.11459
H	6.80747	-3.30965	-0.75482
H	8.34052	-3.19926	0.12532
H	6.81424	-3.23009	1.02456
C	8.54295	-0.66704	0.02179
H	8.6412	-0.00181	0.89
H	9.3695	-1.3775	0.0432
H	8.63624	-0.06255	-0.89
H	1.52622	3.12545	-0.08055
I	-6.02264	-0.90501	0.02464
C	-4.04734	-0.06343	-0.00902

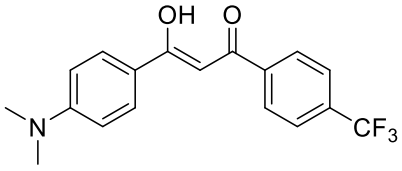
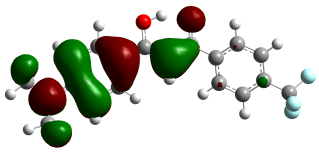
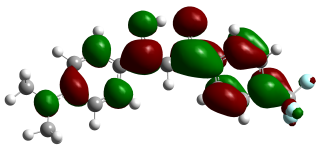
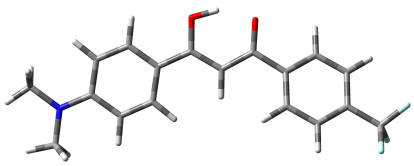
Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.9217 eV 424.35 nm f=0.9907 <S2>=0.000**
74 -> 75 0.70296
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -873.933840332
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.8542 eV 321.69 nm f=0.0119 <S**2>=0.000
68 -> 75 0.17533
70 -> 75 0.65065
72 -> 75 -0.12827
73 -> 75 -0.12320

Excited State 3: Singlet-A 3.9133 eV 316.82 nm f=0.0009 <S**2>=0.000
74 -> 76 0.70039



DMA-CF_3	Occupied Orbitals	Unoccupied Orbitals
	HOMO 	LUMO 
		

E(TD-HF/TD-KS) = -1200.50918528 a.u.
Dipole Moment = 11.7488 Debye

C	-3.3666	1.5491	0.3294
C	-4.62737	0.95789	0.35387
C	-4.77184	-0.38168	-0.02647
C	-3.6546	-1.1246	-0.42366
C	-2.39439	-0.52872	-0.43458
C	-2.23363	0.81433	-0.05637
H	-3.24624	2.58946	0.61115
H	-1.54484	-1.11606	-0.76606
C	-0.90301	1.50872	-0.06674
C	0.30339	0.74987	-0.03768
H	0.25453	-0.32714	0.01764
O	-0.8994	2.77886	-0.08381
C	1.55221	1.37093	-0.05099
C	2.83537	0.68069	-0.02045
C	2.94467	-0.72583	0.04601
C	4.03996	1.41713	-0.05835

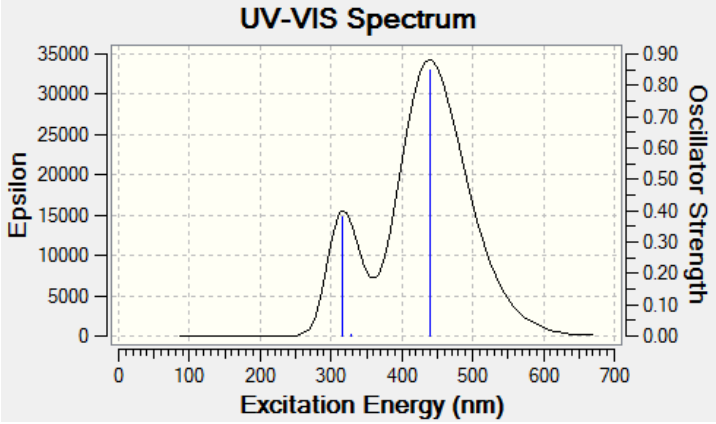
C	4.17335	-1.36221	0.07417
H	2.05456	-1.34588	0.07918
C	5.27779	0.79735	-0.03269
H	3.99651	2.49972	-0.10948
C	5.3883	-0.61993	0.0353
O	1.62675	2.70456	-0.09733
H	4.19477	-2.44386	0.12735
H	6.16753	1.41435	-0.06519
H	-3.76435	-2.15931	-0.73172
H	-5.49185	1.53788	0.66051
N	6.60633	-1.24192	0.0623
C	6.69018	-2.69715	0.13665
H	6.20668	-3.17268	-0.72671
H	7.73926	-2.99303	0.14239
H	6.22144	-3.0817	1.05214
C	7.83568	-0.45588	0.02796
H	7.90484	0.22148	0.88937
H	8.69056	-1.13145	0.05775
H	7.90494	0.14233	-0.88999
H	0.67024	3.03939	-0.10128
C	-6.12264	-1.03988	0.03535
F	-6.35016	-1.62891	1.24651
F	-6.26728	-2.02002	-0.89305
F	-7.14062	-0.16308	-0.15551

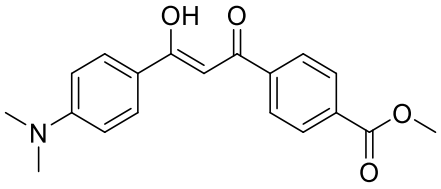
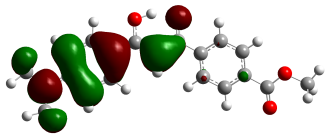
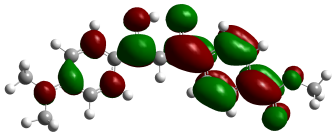
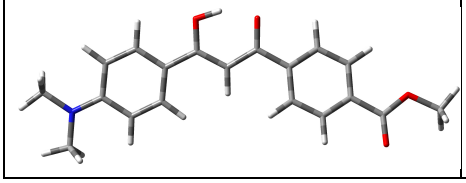
Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.8238 eV 439.06 nm f=0.8475 <S2>=0.000**
87 -> 88 0.70466
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1200.50918528
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.7881 eV 327.30 nm f=0.0048 <S**2>=0.000
82 -> 88 -0.14716
83 -> 88 0.24541
84 -> 88 0.63753

Excited State 3: Singlet-A 3.9142 eV 316.76 nm f=0.3800 <S**2>=0.000
86 -> 88 -0.44506
87 -> 89 0.54068



DMA-COOMe	Occupied Orbitals	Unoccupied Orbitals
	HOMO 	LUMO 
		

E(TD-HF/TD-KS) = -1091.30891292 a.u.
Dipole Moment = 8.4354 Debye

C	-3.34386	1.49949	0.26643
C	-4.60039	0.90095	0.29497
C	-4.74333	-0.45149	-0.05489
C	-3.61048	-1.18864	-0.43024
C	-2.35366	-0.58929	-0.4464
C	-2.20259	0.76381	-0.09572
H	-3.2302	2.54573	0.52926
H	-1.49762	-1.17903	-0.75692
C	-0.87646	1.46469	-0.1066
C	0.33511	0.71339	-0.06361
H	0.29254	-0.36339	0.00002
O	-0.87756	2.73513	-0.13578
C	1.57982	1.34203	-0.0713
C	2.8674	0.66019	-0.02474
C	2.98544	-0.74565	0.03908
C	4.06728	1.40481	-0.04357
C	4.21803	-1.37376	0.08282
H	2.09923	-1.37188	0.05608

C	5.30895	0.79343	-0.00154
H	4.01714	2.48723	-0.09236
C	5.42825	-0.62314	0.06419
O	1.64658	2.67591	-0.12599
H	4.24599	-2.45548	0.13191
H	6.19478	1.41664	-0.01952
H	-3.7246	-2.23053	-0.71104
H	-5.46995	1.47963	0.58614
N	6.65015	-1.23699	0.10744
C	6.74275	-2.69211	0.17115
H	6.27858	-3.16404	-0.70485
H	7.79358	-2.98089	0.19435
H	6.2598	-3.08727	1.07456
C	7.87452	-0.44287	0.08712
H	7.92723	0.23736	0.94735
H	8.73342	-1.11258	0.13104
H	7.95263	0.15336	-0.83155
H	0.68711	3.00372	-0.14104
C	-6.06631	-1.14059	-0.04712
O	-6.23134	-2.31337	-0.3491
O	-7.07247	-0.33139	0.33156
C	-8.39183	-0.91566	0.36967
H	-9.05154	-0.11122	0.69323
H	-8.67574	-1.27145	-0.62356
H	-8.41692	-1.7447	1.08094

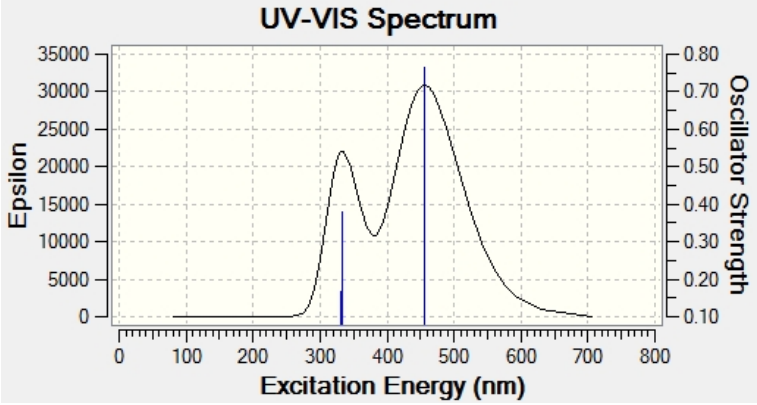
Excitation energies and oscillator strengths:

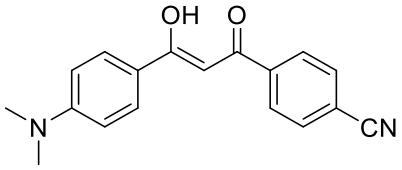
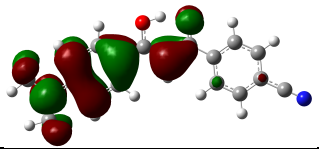
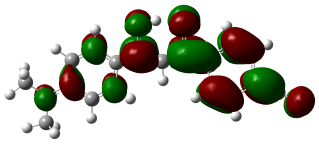
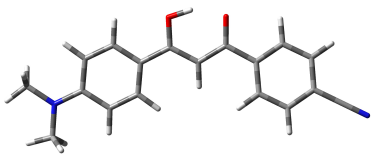
Excited State 1: Singlet-A 2.7174 eV 456.26 nm f=0.7632 <S2>=0.000**
86 -> 87 0.70471
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1091.30891292
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.7129 eV 333.93 nm f=0.3790 <S**2>=0.000
81 -> 87 -0.11965
82 -> 87 0.23192
83 -> 87 0.33320
85 -> 87 -0.23259
86 -> 88 0.50664

Excited State 3: Singlet-A 3.7352 eV 331.93 nm f=0.1661 <S**2>=0.000
81 -> 87 -0.27810
82 -> 87 0.28456
83 -> 87 0.38801
85 -> 87 0.16491

86 -> 88 -0.38745



DMA-CN	Occupied Orbitals	Unoccupied Orbitals
	HOMO 	LUMO 
		

E(TD-HF/TD-KS) = -955.40196265 a.u.
Dipole Moment = 12.5894 Debye

C	-4.27916	1.14948	0.302
C	-5.50255	0.4902	0.34689
C	-5.56523	-0.87935	0.03111
C	-4.39631	-1.57385	-0.32708
C	-3.17718	-0.90274	-0.35833
C	-3.101	0.46465	-0.04222
H	-4.22062	2.20646	0.53705
H	-2.29066	-1.45354	-0.65276
C	-1.81411	1.2383	-0.07007
C	-0.56374	0.5565	-0.0399
H	-0.54305	-0.52062	0.02583
O	-1.89003	2.50613	-0.10107
C	0.64448	1.25501	-0.06045
C	1.96733	0.64621	-0.02747
C	2.16342	-0.7521	0.0082

C	3.12431	1.45671	-0.03207
C	3.42862	-1.31159	0.03859
H	1.31335	-1.42677	0.01068
C	4.39766	0.91439	-0.0014
H	3.0143	2.53548	-0.059
C	4.59556	-0.4947	0.03549
O	0.63468	2.58986	-0.11386
H	3.51614	-2.39095	0.0642
H	5.24764	1.58585	-0.00554
H	-4.44708	-2.62768	-0.58116
H	-6.40577	1.02534	0.62223
N	5.84884	-1.04098	0.06607
C	6.02128	-2.48988	0.10065
H	5.58608	-2.96855	-0.78645
H	7.08633	-2.7207	0.12227
H	5.5586	-2.92912	0.99414
C	7.02854	-0.18119	0.05865
H	7.04661	0.48408	0.93181
H	7.92239	-0.80436	0.08816
H	7.07126	0.43579	-0.84855
H	-0.34104	2.86414	-0.11915
C	-6.82285	-1.56763	0.07007
N	-7.84401	-2.12663	0.10246

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.7624 eV 448.83 nm f=0.7127 <S2>=0.000**
77 -> 78 0.70513
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -955.401962651
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.6828 eV 336.66 nm f=0.0062 <S**2>=0.000
73 -> 78 -0.22932
74 -> 78 0.65358

Excited State 3: Singlet-A 3.8194 eV 324.62 nm f=0.5300 <S**2>=0.000
76 -> 78 0.47424
77 -> 79 0.51477

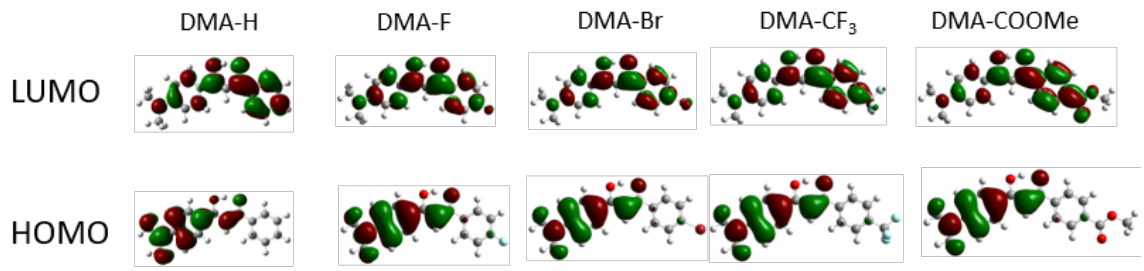


Fig. S1. Molecular orbitals of selected DMA substituted diketones.

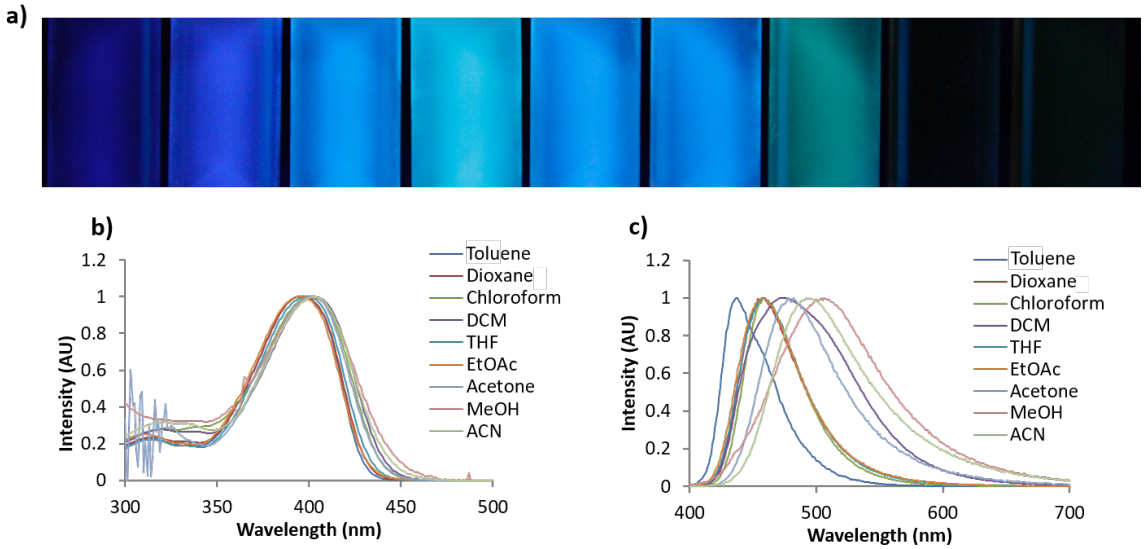


Fig. S2. Image of DMA-OMe dissolved (from left to right) in toluene, dioxane, $CHCl_3$, CH_2Cl_2, THF, EtOAc, MeOH, and ACN (1 x 10^{-5}M) (λ_{ex} = 365 nm) (a), and corresponding absorption (b), and emission (c) spectra. (λ_{ex} = 385 nm)

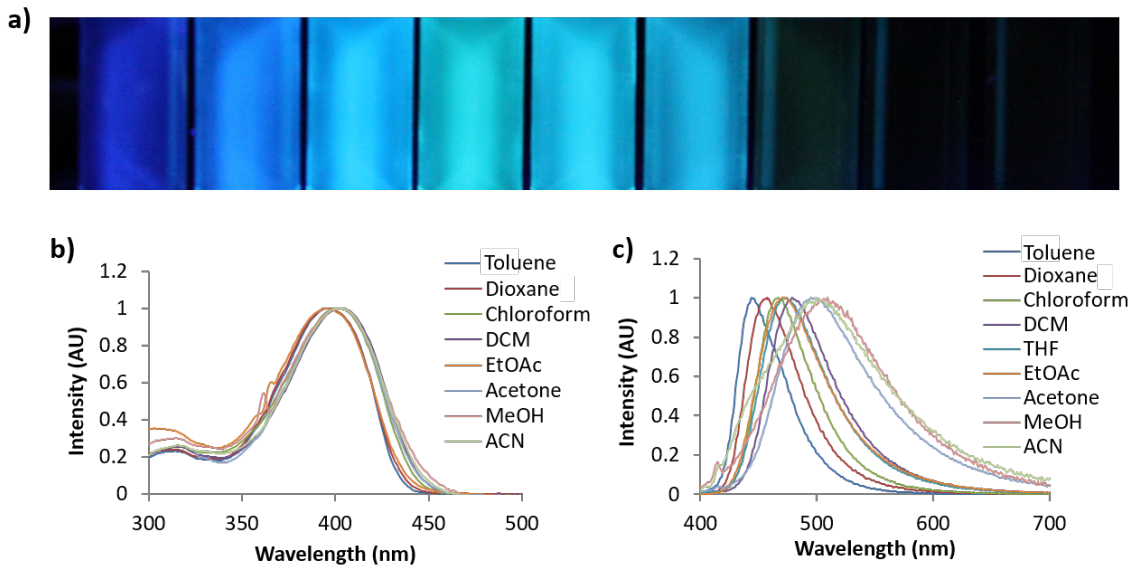


Fig. S3. Image of DMA-F dissolved (from left to right) in toluene, dioxane, $CHCl_3$, CH_2Cl_2, THF, EtOAc, MeOH, and ACN (1 x 10^{-5}M) (λ_{ex} = 365 nm) (a), and corresponding absorption (b), and emission (c) spectra. (λ_{ex} = 385 nm).

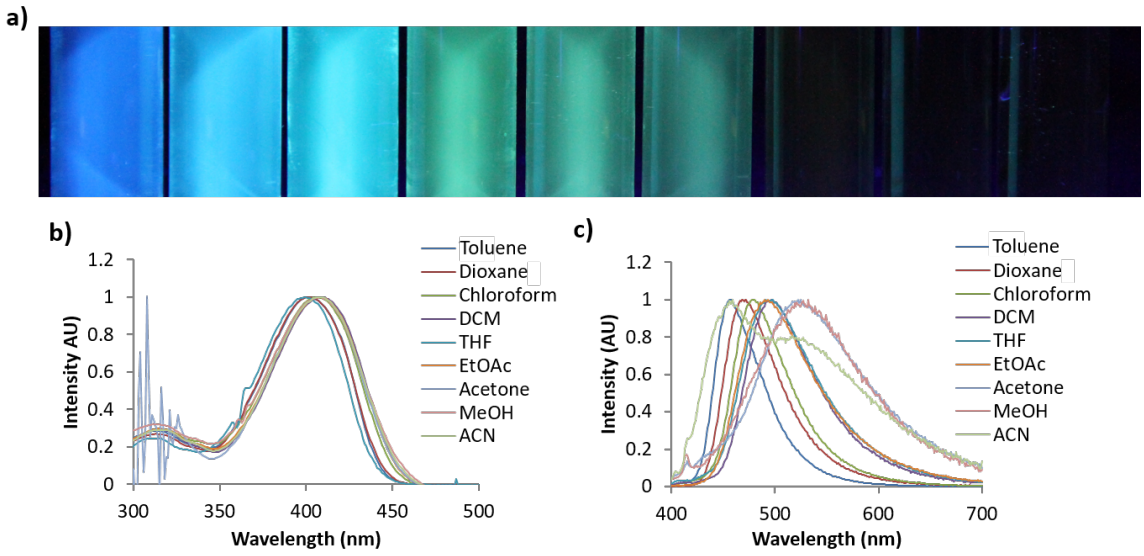


Fig. S4. Image of DMA-Br dissolved (from left to right) in toluene, dioxane, $CHCl_3$, CH_2Cl_2, THF, EtOAc, MeOH, and ACN (1 x 10^{-5}M) (λ_{ex} = 365 nm) (a), and corresponding absorption (b), and emission (c) spectra. (λ_{ex} = 385 nm).

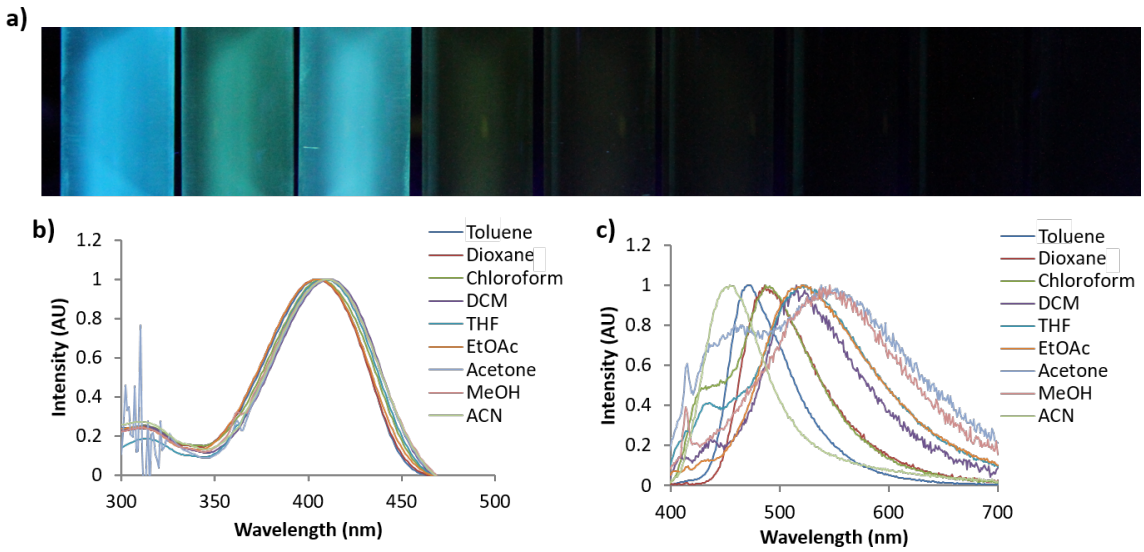


Fig. S5. Image of DMA-CF_3 dissolved (from left to right) in toluene, dioxane, $CHCl_3$, CH_2Cl_2, THF, EtOAc, MeOH, and ACN (1 x 10^{-5}M) (λ_{ex} = 365 nm) (a), and corresponding absorption, (b) and emission (c) spectra (λ_{ex} = 385 nm).

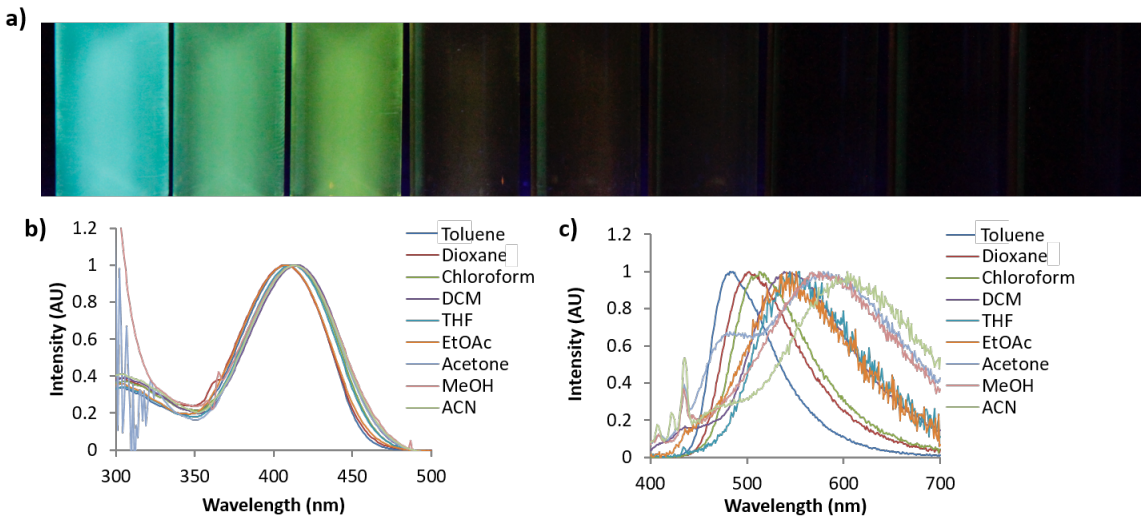


Fig. S6. Image of DMA-COOMe dissolved (from left to right) in toluene, dioxane, $CHCl_3$, CH_2Cl_2, THF, EtOAc, MeOH, and ACN (1 x 10^{-5}M) (λ_{ex} = 365 nm) (a), and corresponding absorption (b), and emission (c) spectra (λ_{ex} = 385 nm).

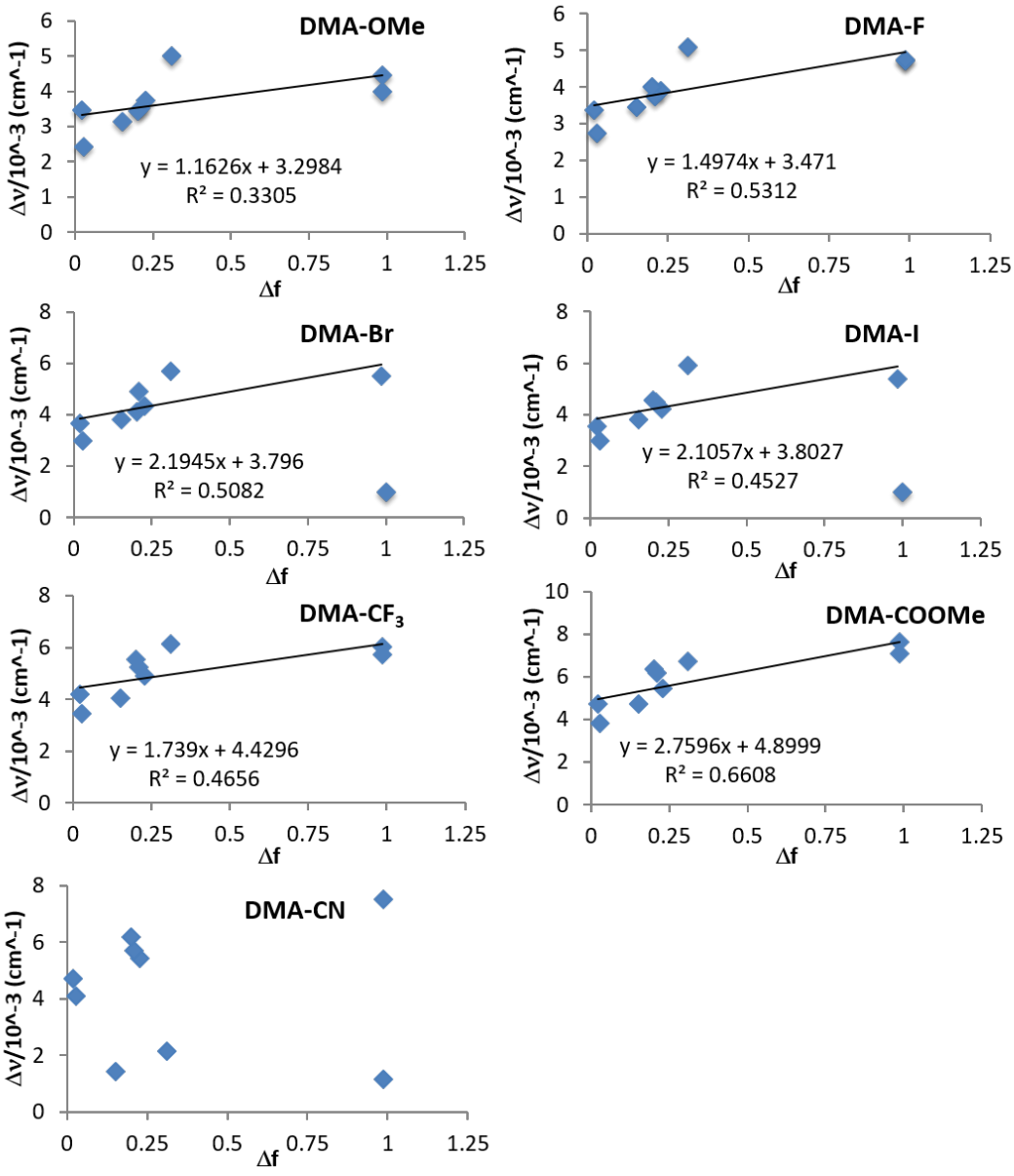


Fig. S7. Lippert Mataga plots of DMA substituted diketones.

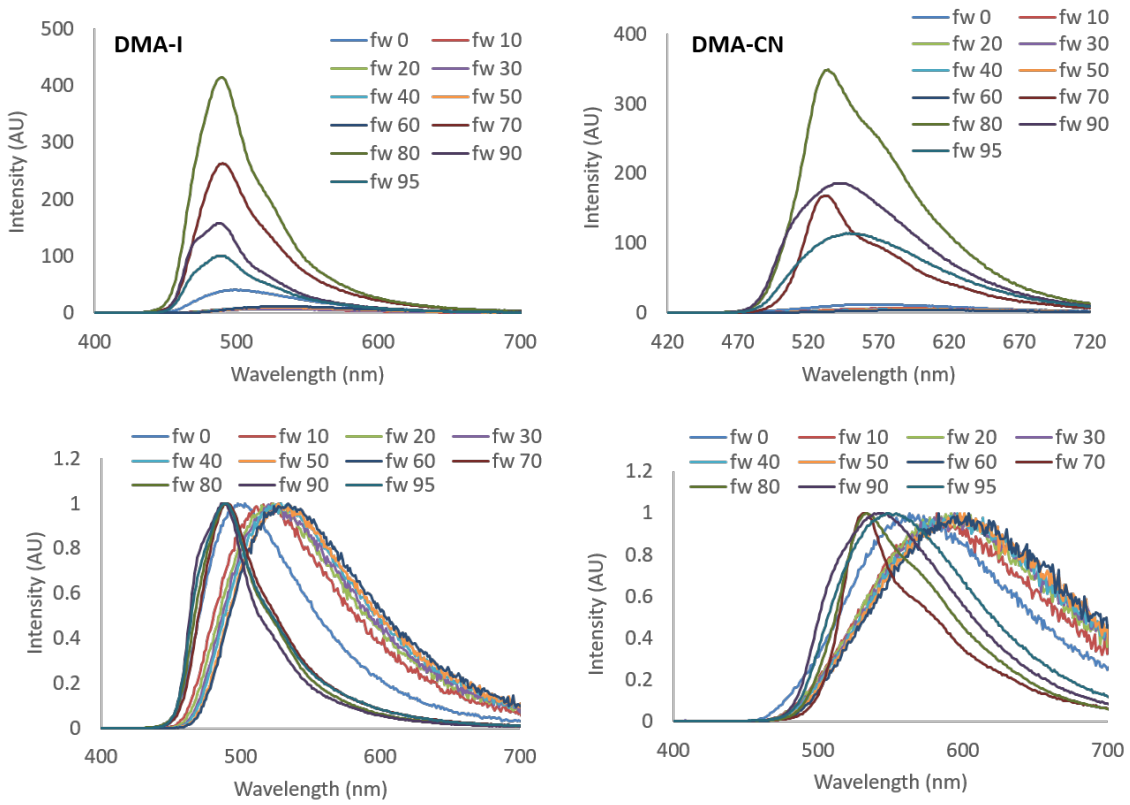


Fig. S8. Raw (top) and normalized by peak wavelength (bottom) emission spectra of DMA-I and DMA-CN in THF/H_2O solutions with increasing water fractions (fw, %). (λ_{ex} = 369 nm).

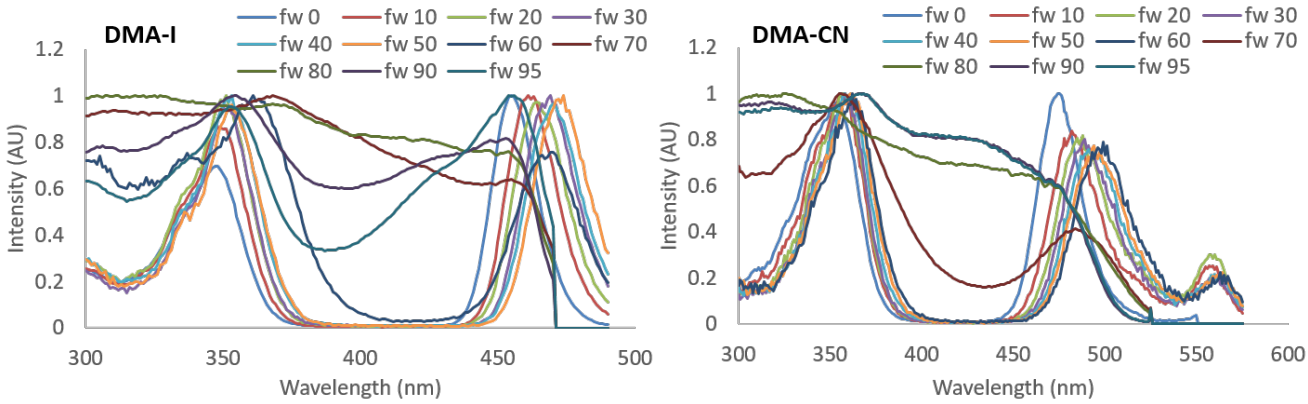


Fig. S9. Excitation spectra of DMA-I and DMA-CN in THF/H_2O solutions with increasing water fractions (fw, %). (λ_{ex} = 369 nm)

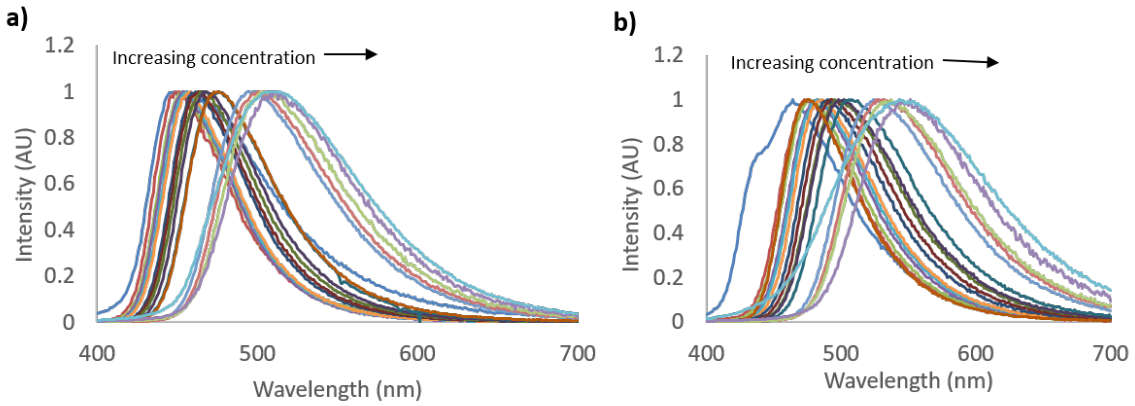


Fig. S10. Emission spectra of Dye/PS thin films of DMA-I (a) and DMA-CN (b) with increasing dye concentration.

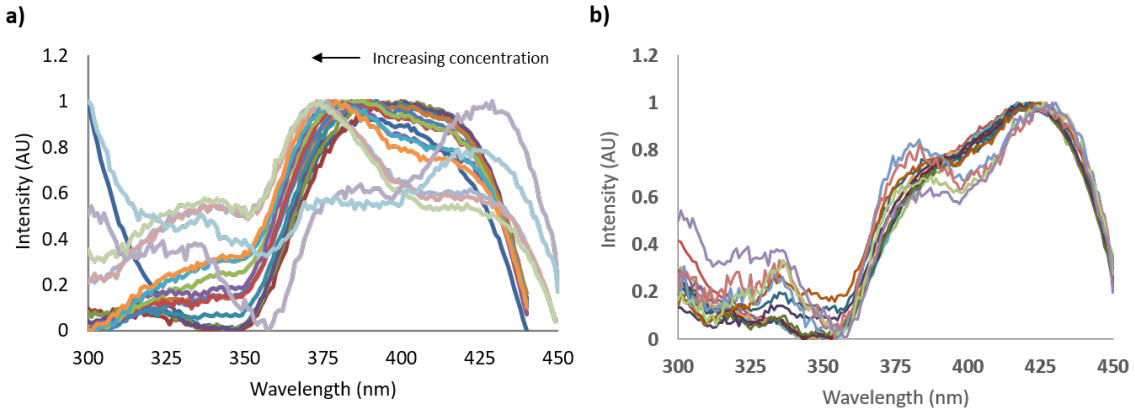


Fig. S11. Excitation spectra of Dye/PS thin films of DMA-I (a) and DMA-CN (b) with increasing dye concentration.

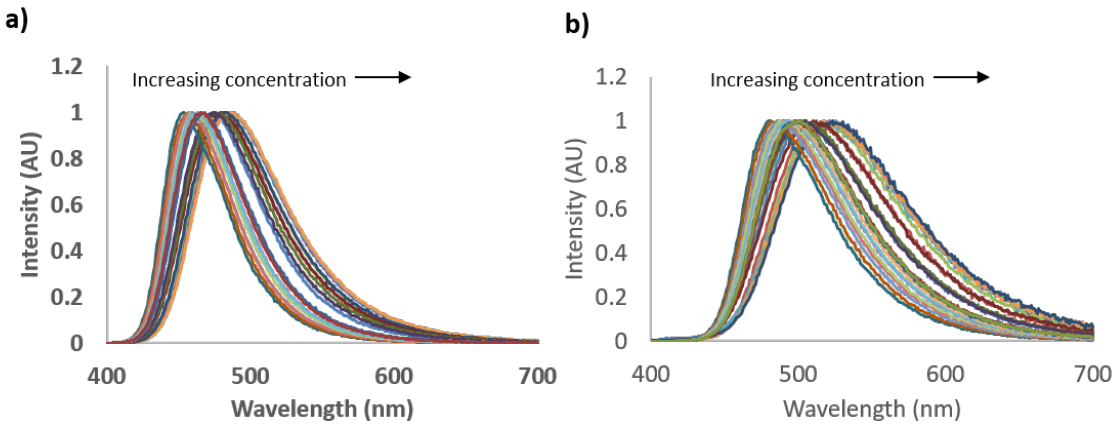


Fig. S12. Emission spectra of Dye/CA/PS thin films of DMA-I (a) and DMA-CN (b) with increasing CA concentration.

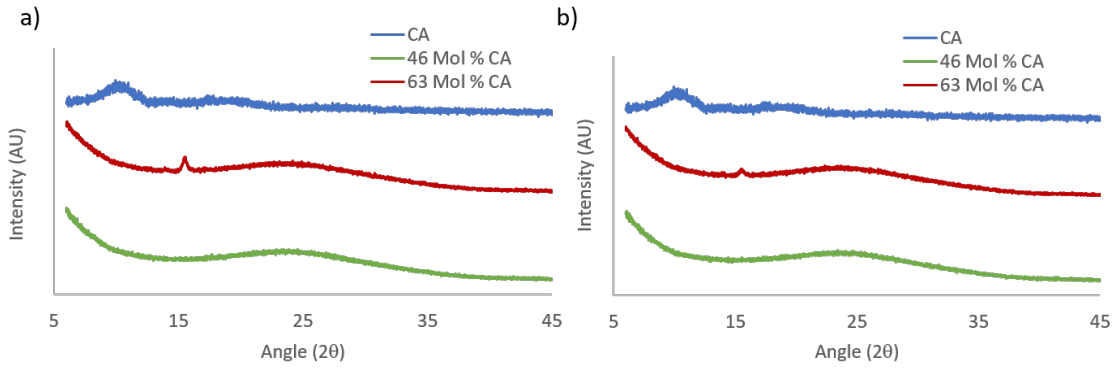


Fig. S13. Powder XRD patterns of DMA-I (a) and DMA-CN (b) polystyrene (PS) films doped with camphoric anhydride (CA).

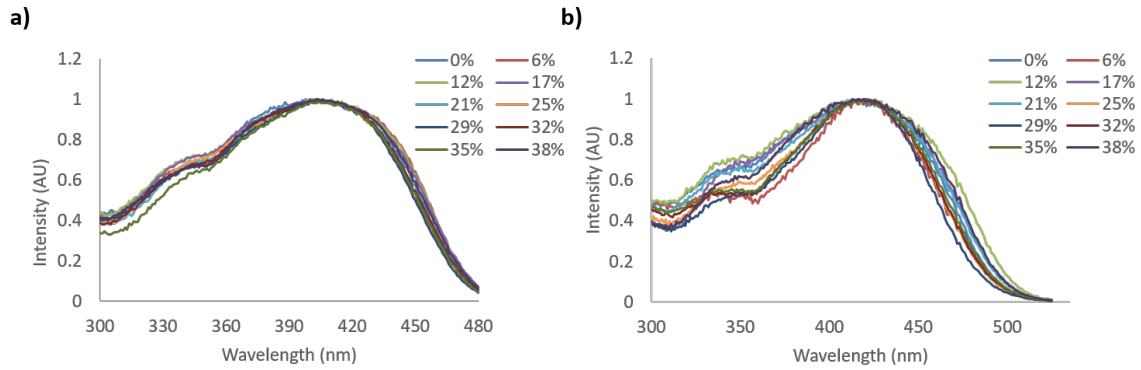


Fig. S14. Excitation spectra of dye/CA/PS thin films of DMA-I (a) and DMA-CN (b) with increasing CA concentration.

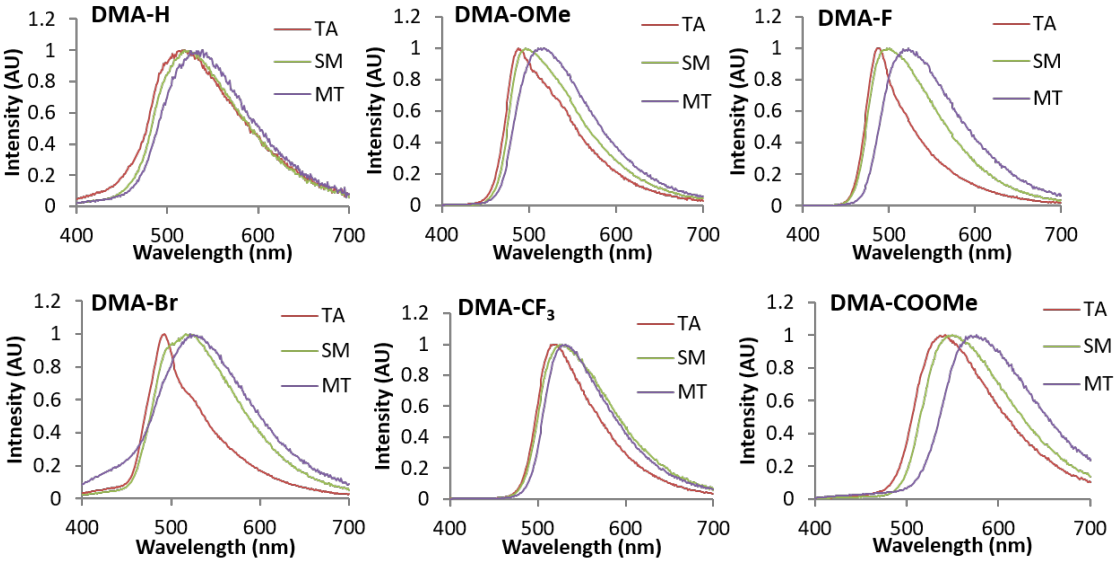


Fig. S15. Total emission spectra of diketone films on weigh paper substrates in thermally annealed (TA), smeared (SM) and melted (MT) phases. (λ_{ex}= 369 nm).

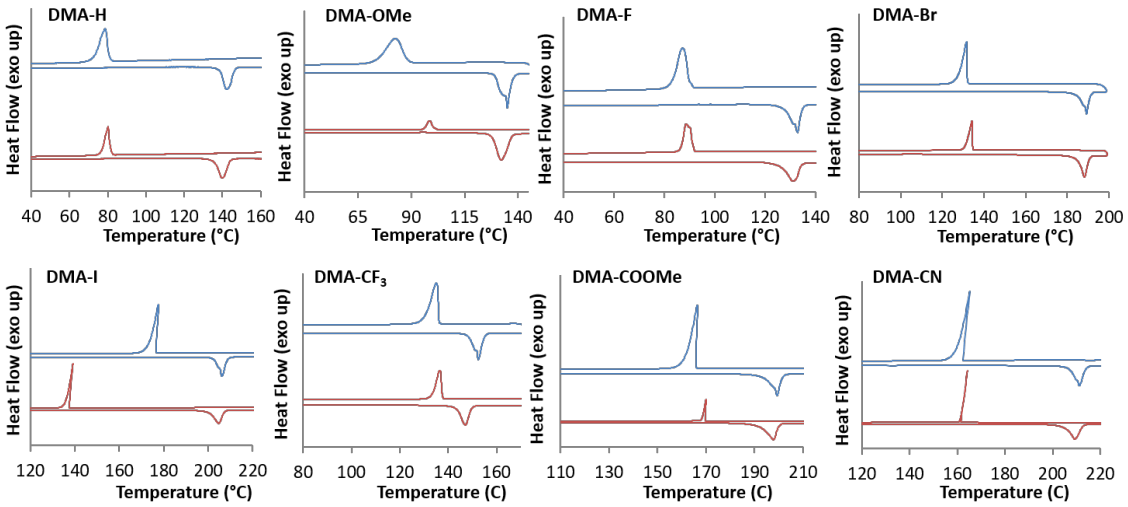


Fig. S16. Differential scanning calorimetery (DSC) thermograms of diketones. Cooling rate varied between first (blue, 10 °C/min) and second (red, 1 °C/min) cycles. (Heating rate = 5 °C/min)

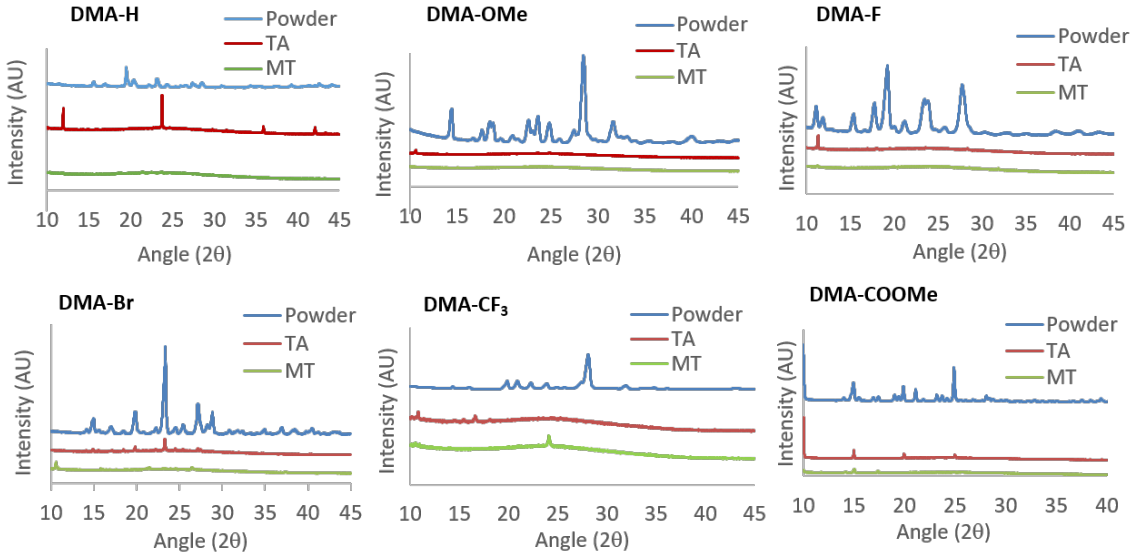


Fig. S17. Powder X-ray diffraction patterns of diketones as bulk powders and glass films in the thermally annealed (TA) and melted (MT) states.

References

1 N. D. Nguyen, G. Zhang, J. Lu, A. E. Sherman and C. L. Fraser, *J. Mater. Chem.*, 2011, **21**, 8409–8415.

2 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson, *Gaussian 09 Revis. A.1; Gaussian, Inc. Wallingford, CT*, 2009.

4 R. Tomasi, J.; Mennucci, B.; Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.