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Supplementary Information

Photoenolization *via* excited state double proton transfer induces "turn on" fluorescence in diformyl diaryl dipyrromethane

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1. Materials and Methods

All the chemicals were of the best grade commercially available and are used without further purification. NMR spectra were recorded on a Bruker Avance Bruker AMX 500 spectrophotometer with $CDCl_3$ as solvent. Chemical shifts are reported as δ in units of parts per million (ppm) relative to TMS. FAB mass spectra were obtained on a JEOL SX-120/DA6000 spectrometer using argon (6 KV, 10 mA) as the FAB gas. FT-IR spectra were recorded on a Nicolet Impact 400D Infrared spectrophotometer. Melting points were determined on a Buchi melting point apparatus and are uncorrected. The single crystal X-ray diffraction data was collected on a Bruker AXS Kappa Apex 2 CCD diffractometer at 293(2) K for $\mathbf{DA_{KK}}$. Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and the emission spectra were measured on a SPEX-Fluorolog F112X spectrofluorimeter. Fluorescence quantum yield was determined using optically matching solutions of quinine sulphate (Φ_f = 0.54 in 1N H_2SO_4), fluorescein (Φ_f = 0.75 in 1M NaOH) or rhodamine B (Φ_f = 0.7 in ethanol) as standard.

Photoirradiation experiments:

Photoirradiation of $\mathbf{DA_{KK}}$ was carried out using an Oriel optical bench with thermostatic cell holders and a 200 W high pressure mercury lamp. Irradiation of the sample was carried out using an Oriel optical bench with thermostatic cell holders and a 200 W high pressure mercury lamp. Stock solutions of the samples were prepared in various solvents (2.75×10^{-5}M). The required sample solution (3 mL) was taken in a 1 cm quartz cuvette and irradiated with 350 nm UV light ($\lambda_{band\ pass}$ = 300 ± 30 nm, 0.1 W/cm^2) for 5 seconds. After recording absorption and emission spectra, the sample is

again subjected to the irradiation for another 5 seconds. This experiment was repeated until photostationary state was reached. The percent of conversion was calculated from the change in the absorption OD at $\mathbf{DA_{KK}}$ maximum at different intervals, with respect to irradiation which corresponds to the increase in the concentration of $\mathbf{DA_{EE}}$. The keto-enol tautomerism can be expressed by a first-order rate equation:

$$kt = A_0/A_t \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where A_0 and A_t are the values of the absorbance at time t_0 and t, respectively, and k is the rate constant.

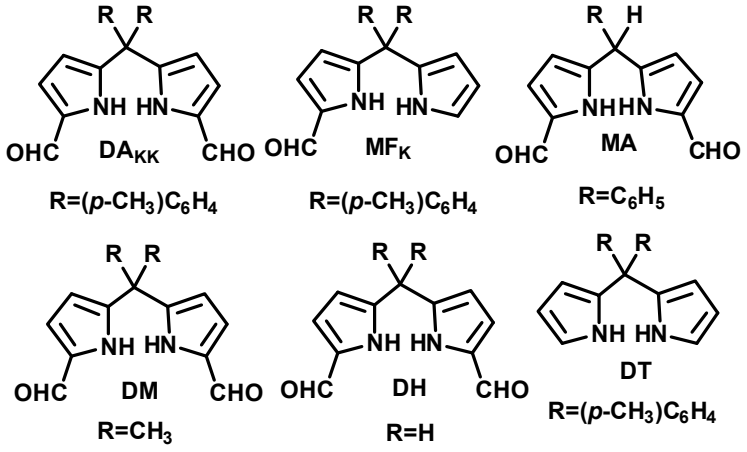
Theoretical Calculations:

DH, **DM**, and **DA** structures were optimized using the B3LYP [1,2,3] functional and 6-31+G* basis set in the ground state and the first excited states. The excited state calculations were performed using TDDFT approach. The stationary points were characterized by frequency calculations. The vertical emission energies were computed as the difference between the S1 minimum and its S0 energies for the S1 minimum geometry. All calculations were performed using GAMESS [4,5] computer program.

2. Synthesis of DA_{KK}

To an ice cold solution of $POCl_3$ (1.43 mL, 15.34 mmol) in DMF (5mL) and CH_2Cl_2 (5mL) mixture, **DT** (1 g, 3.06 mmol) in DMF (5mL) was added and allowed to stir for 1h at 0°C. It was then quenched with 2N NaOH solution and extracted with CH_2Cl_2 solvent to yield $\mathbf{DA_{KK}}$. Purification was done by column chromatography (silica gel 100-200) with 5% EtOAc/ hexane to give $\mathbf{DA_{KK}}$ as white powder and yield was found to be 72%. m.p: 263°C; ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 9.40 (s, CHO, 2H), 9.08 (brs, NH, 2H), 7.12 (d, CH-phenyl, 4H), 6.92 (d, CH-phenyl, 4H), 6.91 (m, CH-pyrrole, 2H), 6.16 (m, CH-Pyrrole, 2H), 2.35 (s, CH3, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 178.91, 143.75, 139.97, 137.65, 132.29 129.21, 121.21, 113.01, 55.89, 20.97; FT-IR: (KBr, cm^{-1}) = 3211, 3092, 3021, 2957, 2918, 2799, 2352, 11741, 1656, 1510, 1474, 1429, 1345, 1313, 1187, 1156, 1050,804, 791, 719; FAB MS (m/z): Calcd. for $C_{25}H_{22}N_2O_2$ 382.45; Observed 383.84 (M+1); Anal. Calcd. for $C_{25}H_{22}N_2O_2$: C, 78.51; H, 5.80; N, 7.32; Found: C, 78.50; H, 5.79; N, 7.21.

Other model compounds such as $\mathbf{MF_K}$, **MA**, **DM**, and **DT** were synthesized according to the literature procedure.[6]



Scheme S1. Structure of $\mathbf{DA_{KK}}$, $\mathbf{MF_K}$, **MA**, **DM**, **DT** and **DH**.

3. Spectral analyses of DA_{KK}

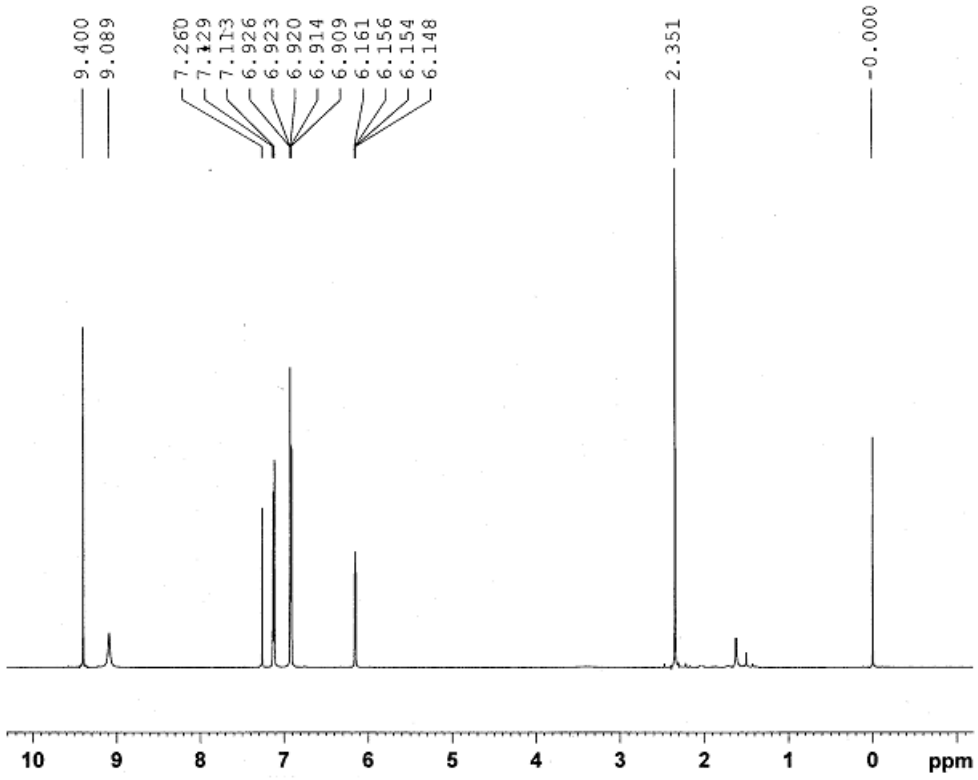


Fig. S1 ^{1}H-NMR Spectrum of $\mathbf{DA_{KK}}$ in $CDCl_3$

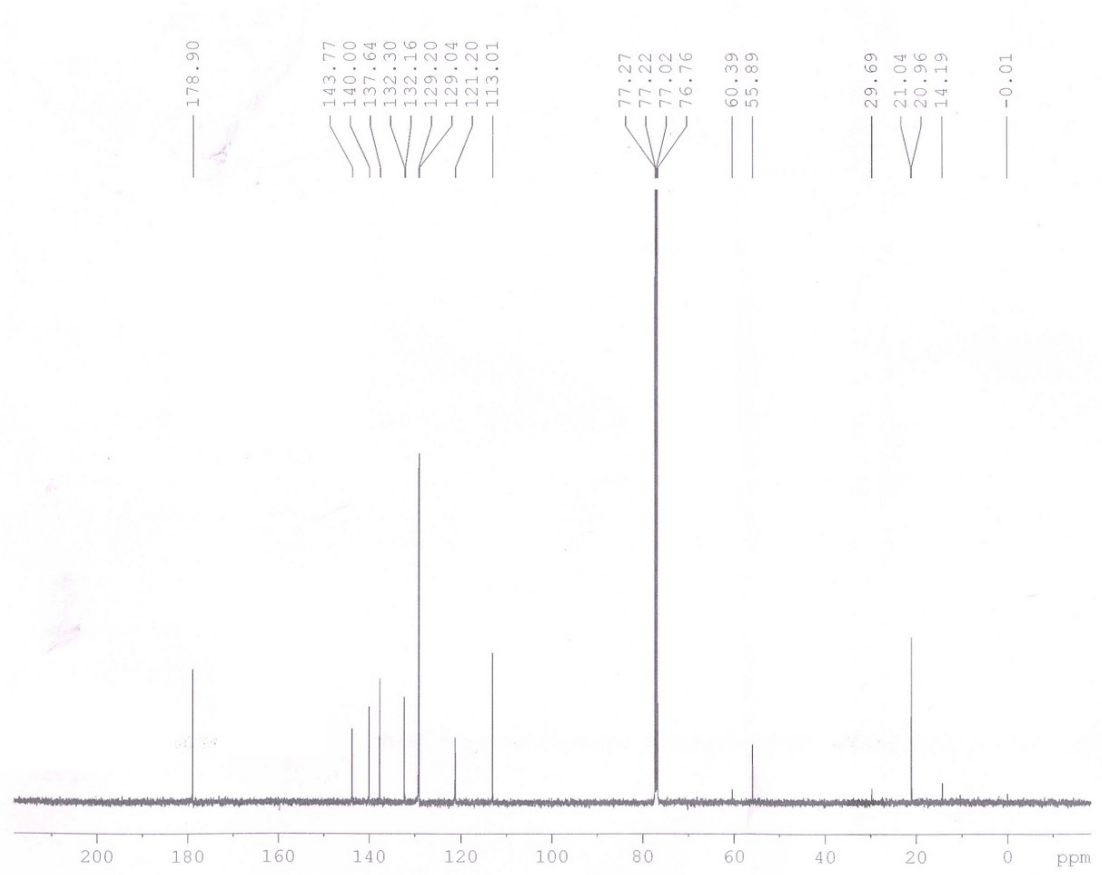


Fig. S2 ^{13}C-NMR Spectrum of $\mathbf{DA_{KK}}$ in $CDCl_3$.

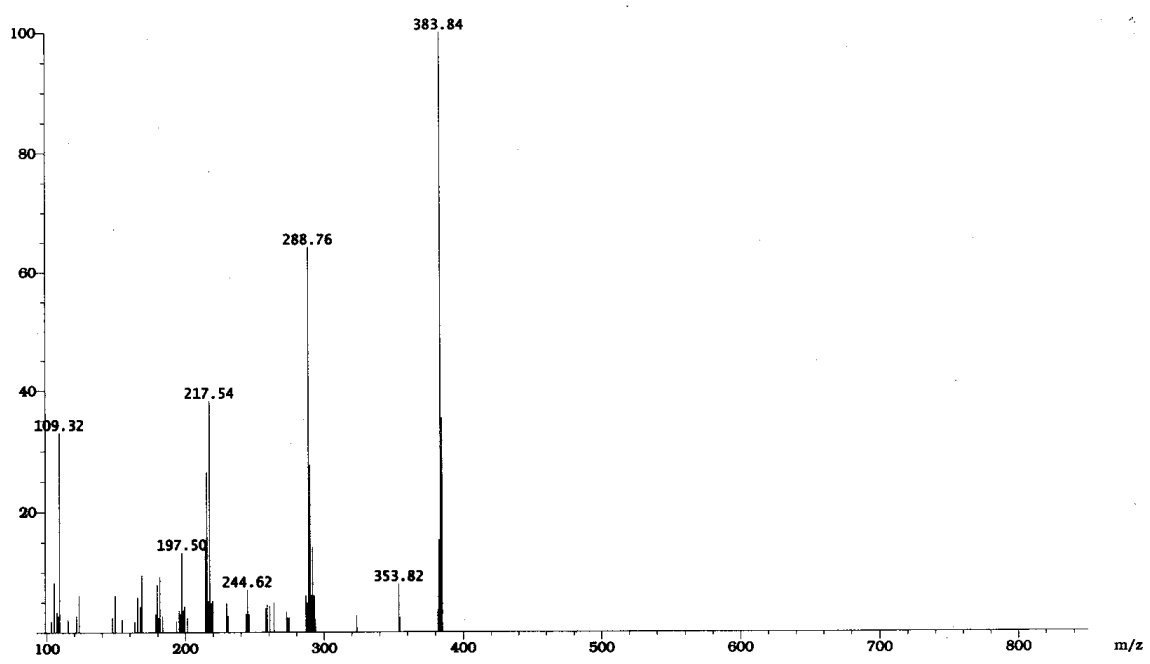


Fig. S3 FAB MS spectrum of $\mathbf{DA_{KK}}$

4. Photoirradiation Experiments

a) b)

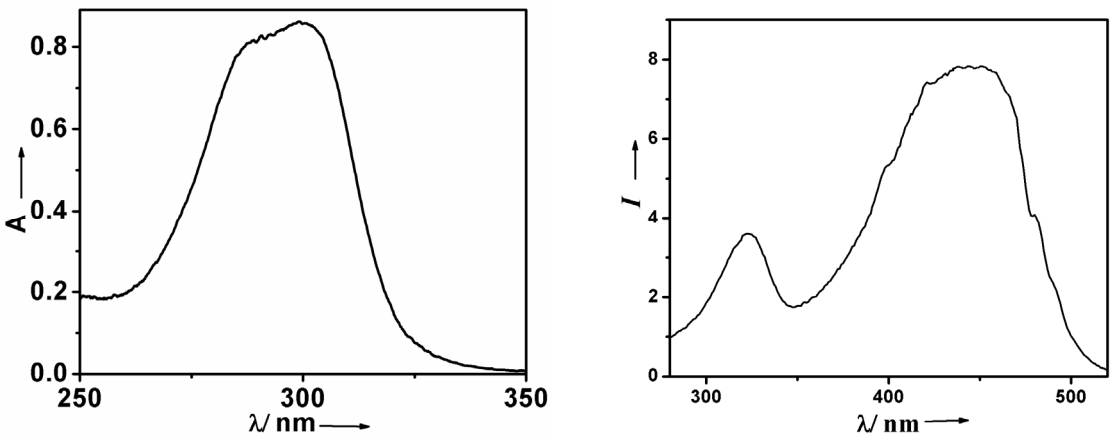
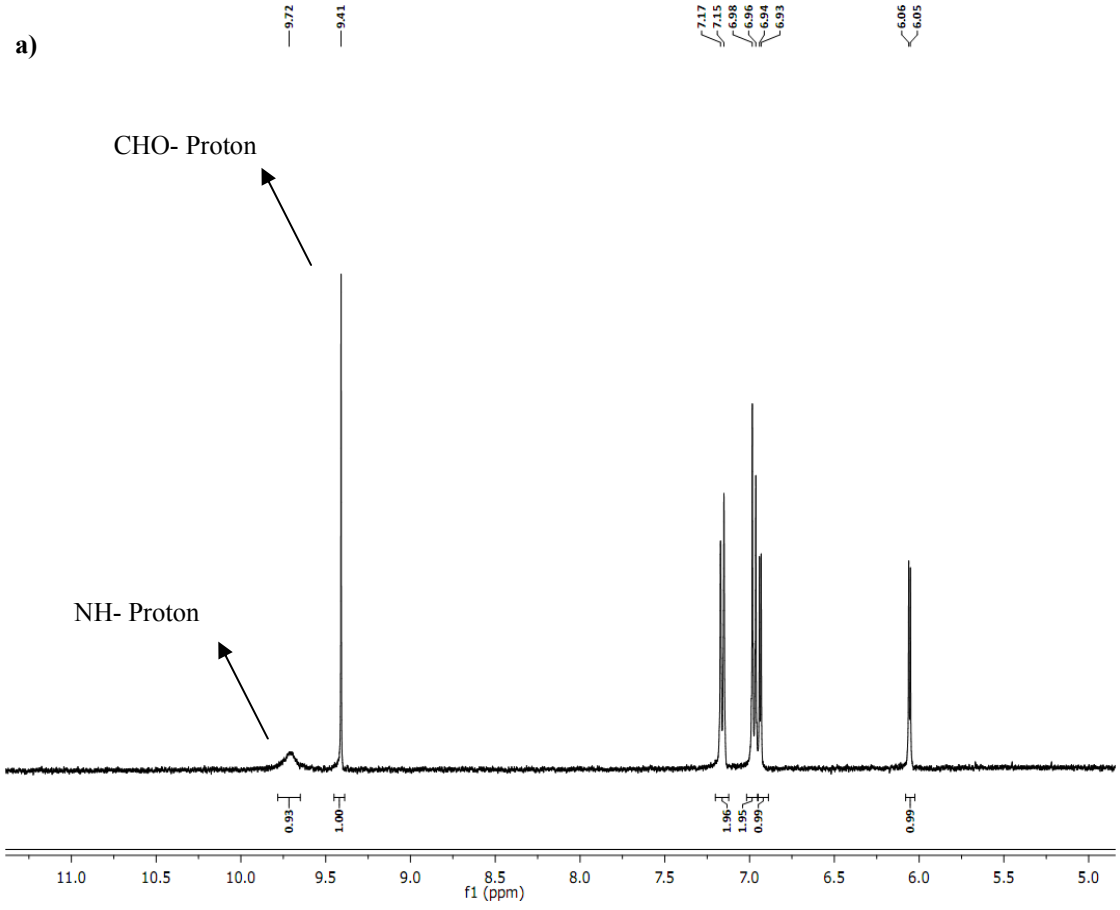


Fig. S4 a) Absorption and b) excitation spectra (λ_{em}= 560 nm) of $\mathbf{DA_{KK}}$ in acetonitrile.

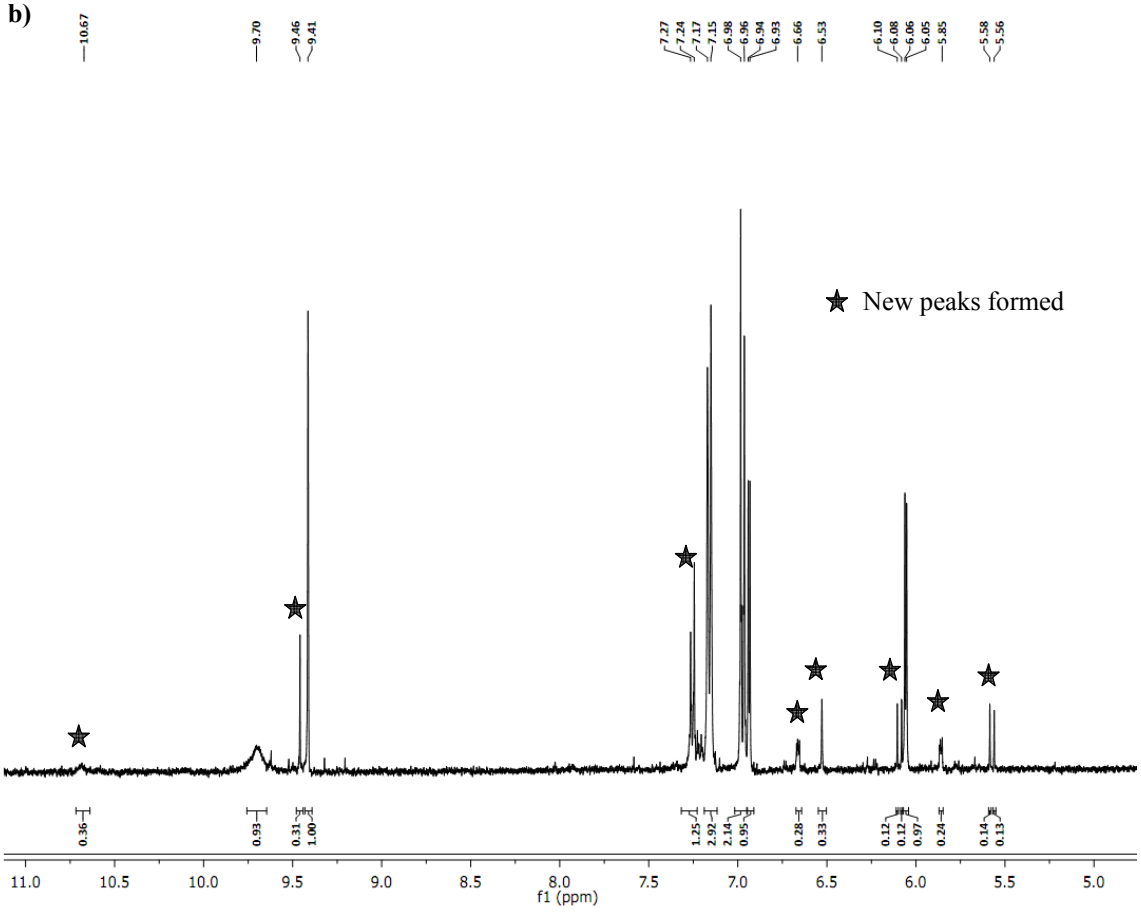
Table S1. Absorption and emission maxima of $\mathbf{DA_{EE}}$ in different solvents.

Solvents	Cyclohexane	THF	CH_3CN	DMSO	Methanol
λ_{abs}^{max}	397 nm	406 nm	393 nm	440 nm	443 nm
λ_{em}^{max}	544 nm	561 nm	564 nm	584 nm	607 nm
ϕ_f	0.023	0.028	0.020	0.074	<0.01

a)


9.72
9.41
7.17
7.15
6.98
6.96
6.94
6.93
6.06
6.05
CHO- Proton
NH- Proton
0.93
1.00
1.96
1.95
0.99
0.99
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)

b)


10.67
9.70
9.46
9.41
7.27
7.24
7.17
7.15
6.98
6.96
6.94
6.93
6.66
6.53
6.10
6.08
6.06
6.05
5.85
5.58
5.56
New peaks formed
0.36
0.93
0.31
1.00
1.25
2.92
2.14
0.95
0.28
0.33
0.12
0.12
0.97
0.24
0.14
0.13
11.0
10.5
10.0
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7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)

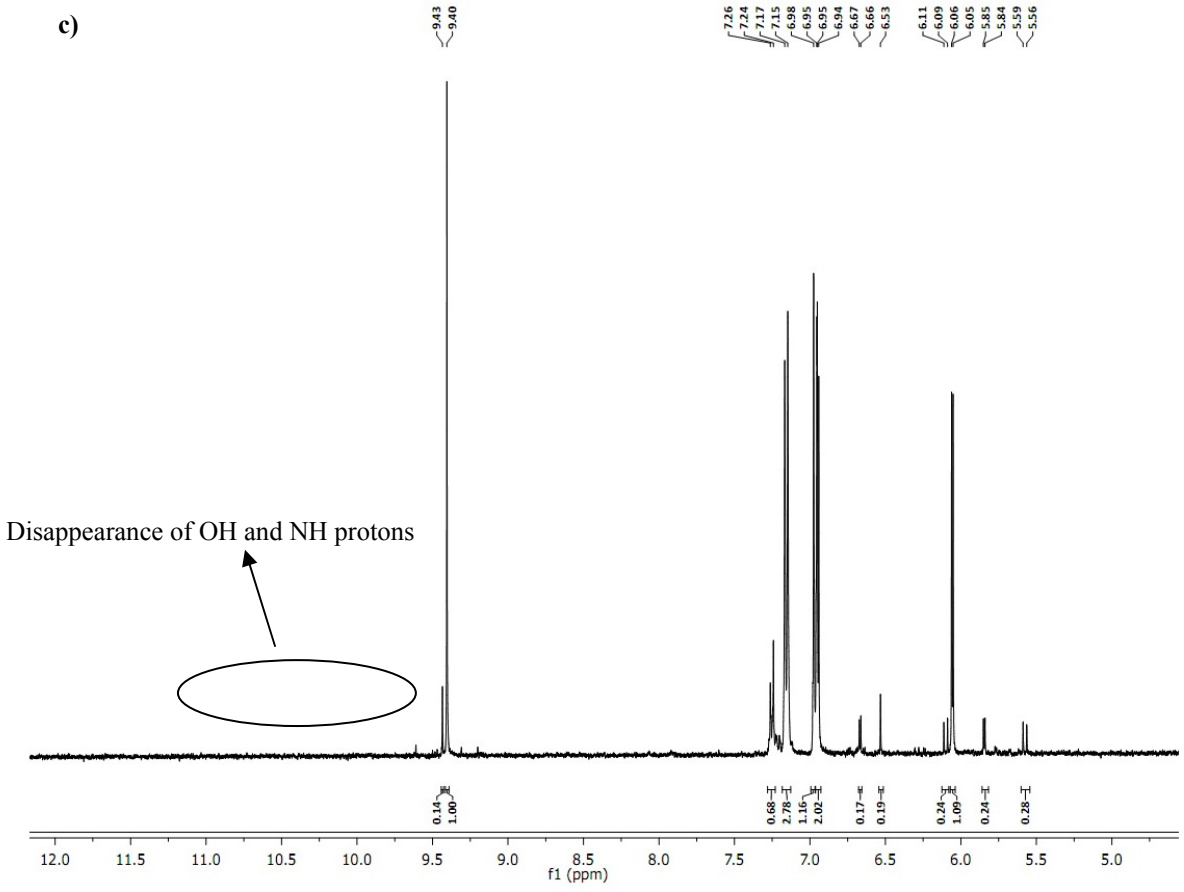

Fig. S5 ^{1}H NMR spectrum of $\mathbf{DA_{KK}}$ in CD_3CN a) before, b) after UV irradiation and c) after the addition of D_2O.

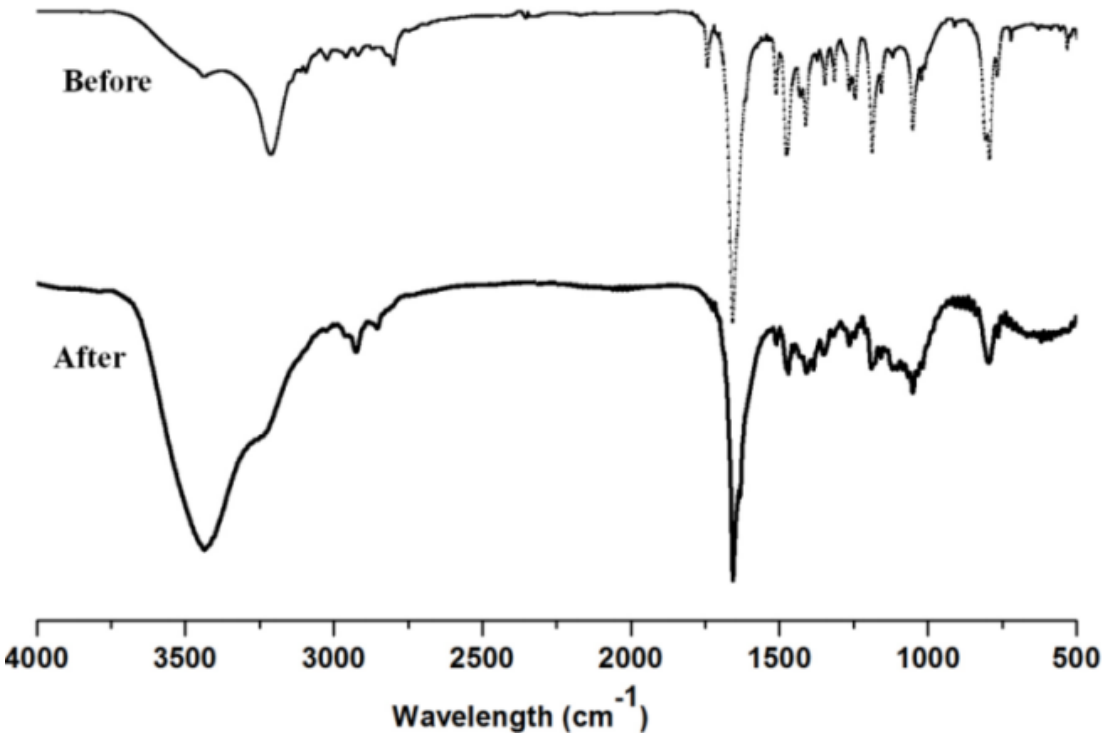

Fig. S6 Change in IR before and after UV irradiation of $\mathbf{DA_{KK}}$.

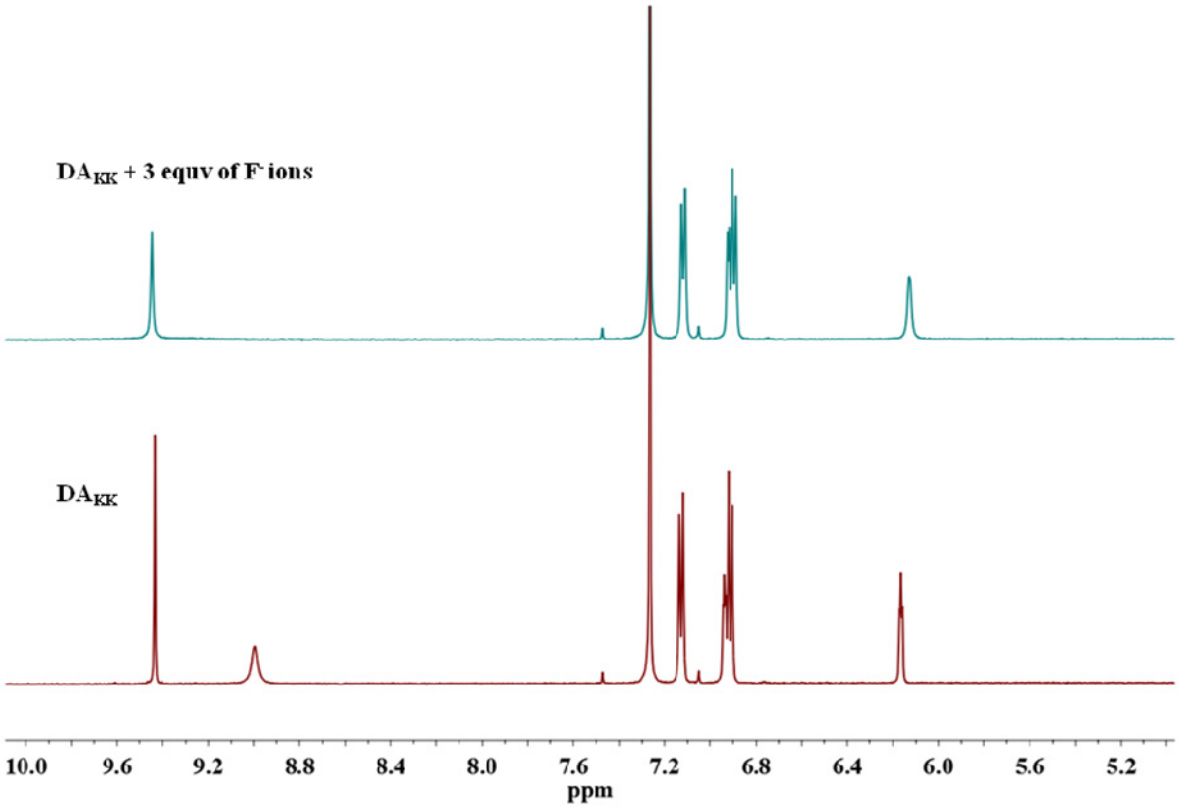

Fig. S7 ^{1}H NMR changes of **DA$_{KK}$** with the addition of F^- ions as its tetrabutyl ammonium salt in $CDCl_3$.

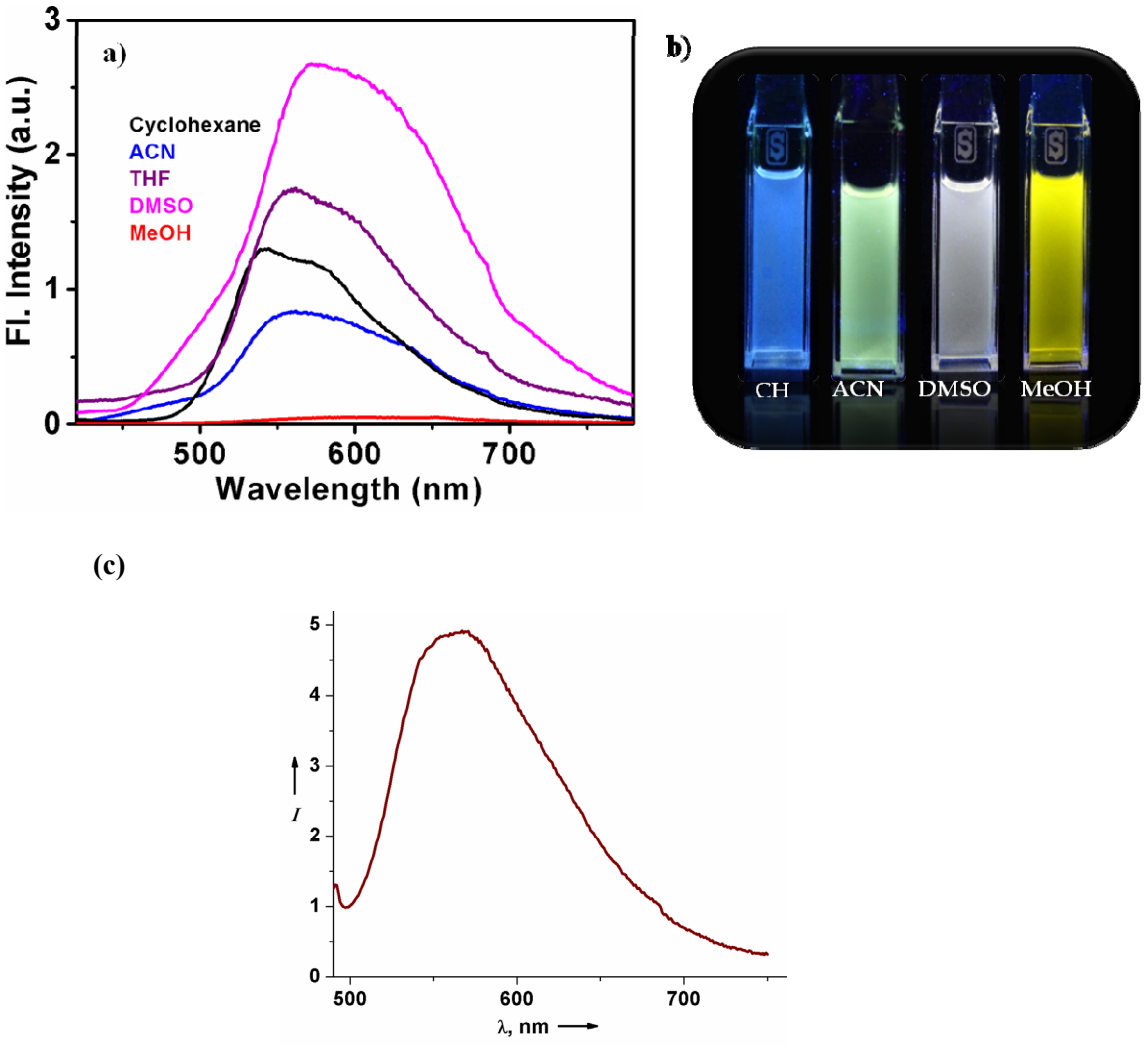

Fig. S8 a) Emission spectra of $\mathbf{DA_{EE}}$ in different solvents, b) corresponding emission colour changes under 365 nm UV light and c) solid state emission spectrum of $\mathbf{DA_{EE}}$ excited at 400 nm.

Table S2. Photoenolization of DA_{KK} in various solvents

Solvents	Rate Constant (k) min^{-1}	Keto-enol ratio in the PS state
Cyclohexane	2.4212	57:43
THF	3.4971	52:48
Acetonitrile	3.2343	51:49
DMSO	4.5107	45:55
MeOH	2.9113	35:65
Acetonitrile + 10% water	5.1529	36:64
Acetonitrile + 30% water	6.0366	29:71
MeOH/Glycerol (50:50)	4.0959	45:55

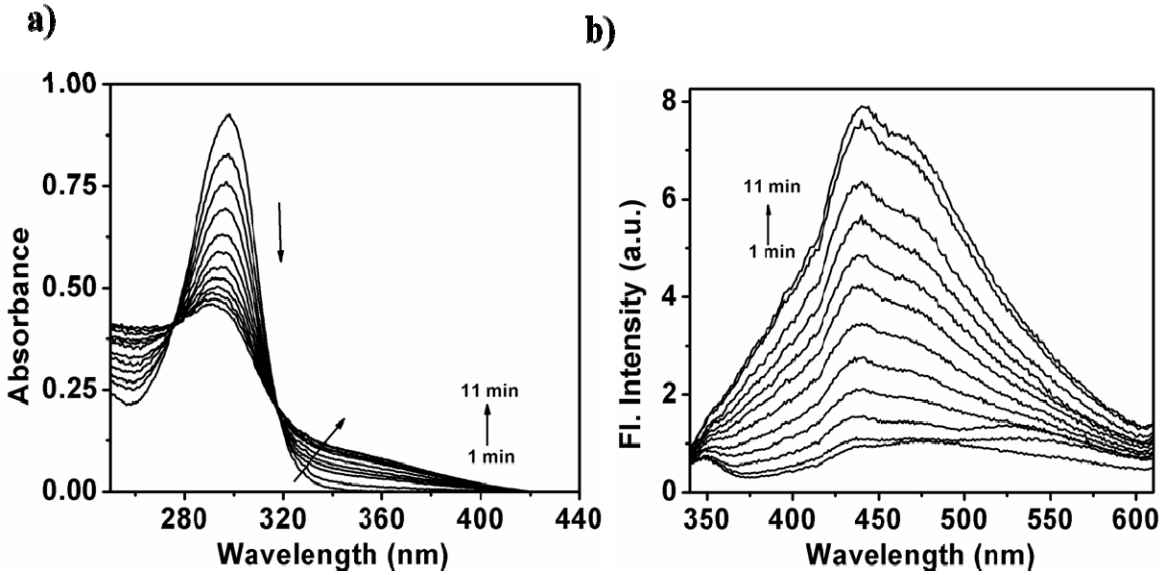

Fig. S9 a) Absorption and b) emission spectra of $\mathbf{MF_K}$ (2.14 x 10^{-5} M) in CH_3CN upon UV irradiation.

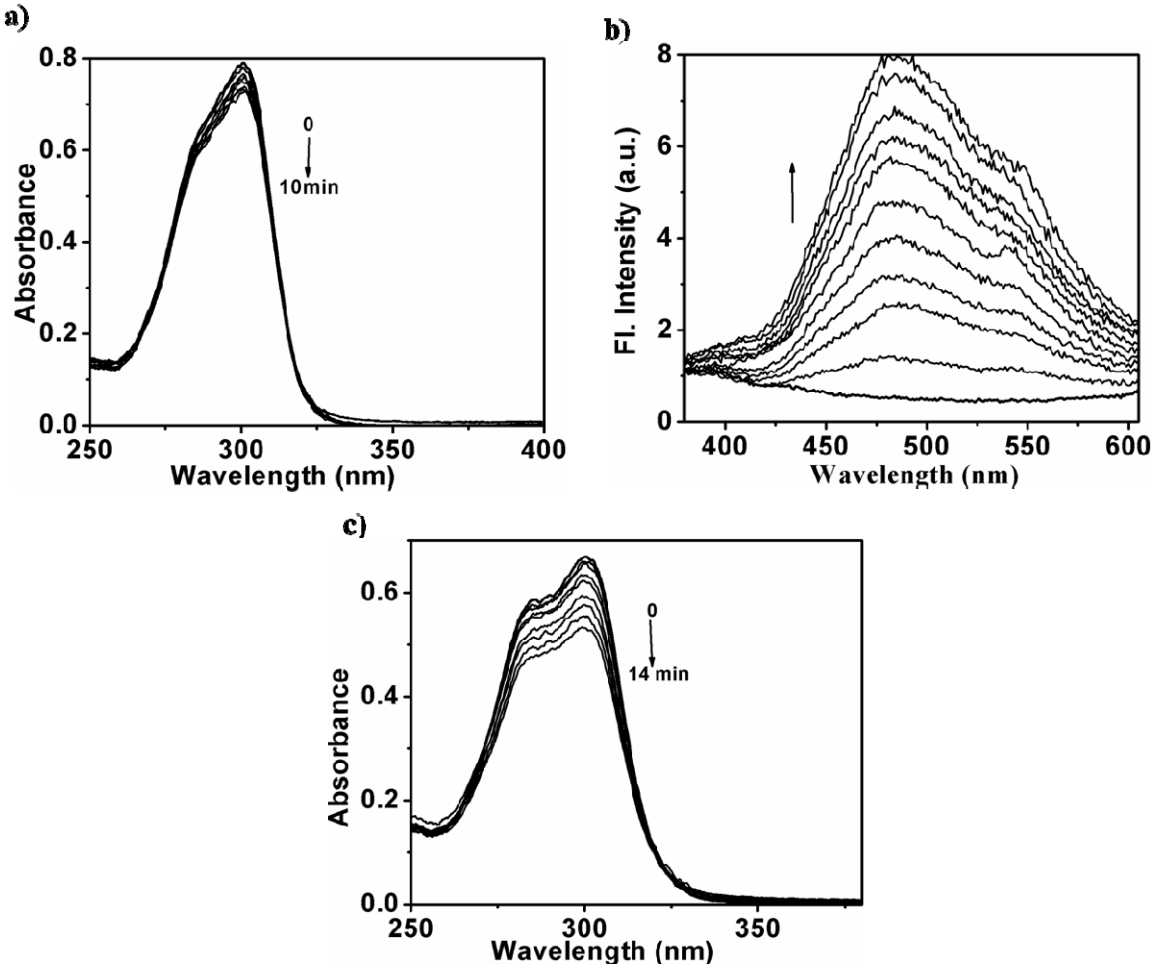

Fig. S10. a) Absorption and b) emission spectra of $\mathbf{MA_{KK}}$ and c) Absorption spectra of $\mathbf{DM_{KK}}$ upon photoirradiation in CH_3CN (2.14×10^{-5} M).

5. Single crystal X-ray structure of DA_{KK}

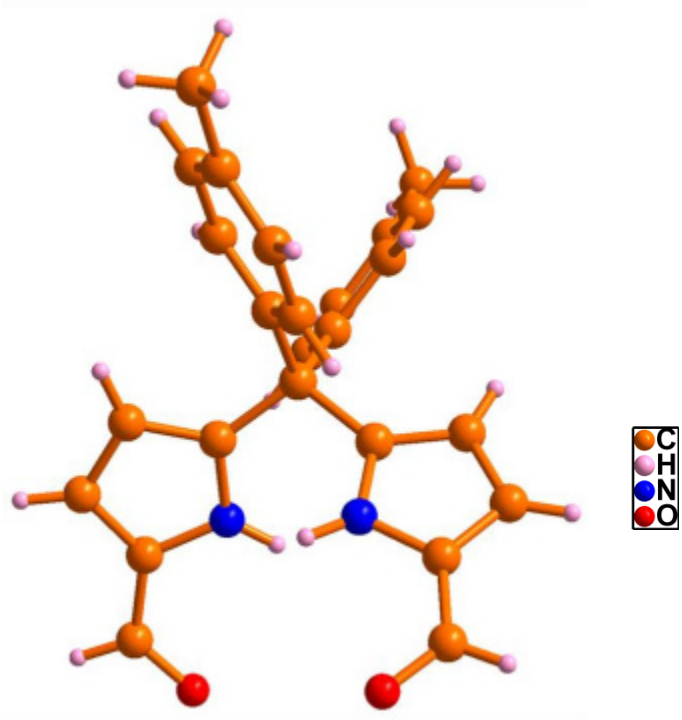

Fig. S11 Single crystal X-ray structure of $\mathbf{DA_{KK}}$

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Crystallographic data of $\mathbf{DA_{KK}}$ (CH_3CN/*n*-hexane): $C_{25}H_{22}N_2O_2$, M_w = 382.45, Orthorhombic, space group Fdd2, a = 41.923 (5) Å, b = 11.100 (5) Å, c = 19.335 (5) Å, α = 90.000 (5)º, β = 90.000 (5)º, γ = 90.000 (5)º, V = 3446.0 (5) $Å^3$, Z = 4, D_{calc} = 1.185 mg/m^3, T = 296 (2) K, R1 = 0.0421 {I > 2σ (I)}, $R2_w$ = 0.1137, GOF = 1.053. The crystal has been deposited in the Cambridge Crystallographic Data Centre with reference no. CCDC-923773. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S3. Crystallographic data for $\mathbf{DA_{KK}}$

Parameters	**DA_{KK}**
Solvent of crystallization	CH_3CN / Hexane
Empirical formula	$C_{25}H_{22}N_2O_2$
M_w	382.45
T [K]	296(2)
λ [Å]	0.71073
Crystal system	Orthorhombic
Space group	Fdd2
a[Å]	41.923(5)
b[Å]	11.100(5)
c[Å]	19.335(5)
α [˚]	90.000(5)
β [˚]	90.000(5)
γ [˚]	90.000(5)
V[Å^3]	3446.0(5)
Z, ρ_{calcd} [Mg m^{-3}]	4, 1.185
μ ($Mo_{K\alpha}$) [mm^{-1}]	0.076
F (000)	3384
Crystal size [mm]	0.11 × 0.09× 0.07
θ range for data collection [˚]	1.94 to 26.49
Limiting indices	$-52 \leq h \leq 51$, $-13 \leq k \leq 13$, $-24 \leq l \leq 24$
Reflections collected	27734
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4628 / 8 / 277
Goodness-of- fit on F^2	1.053
Final R indices[I>2σ(I)]	R1 = 0.0421, wR2 = 0.1137
R indices (all data)	R1 = 0.0509, wR2 = 0.1207
Largest $\Delta\rho$ [e Å^{-3}]	0.246 and -0.193

6. Theoretical calculations

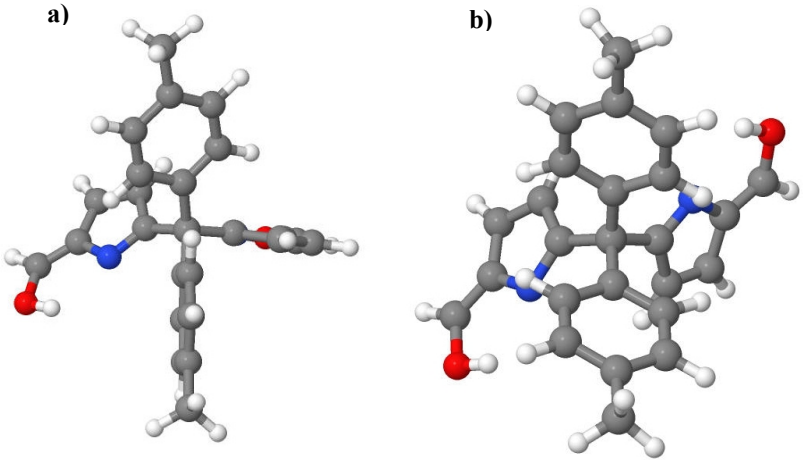


Fig. S12 Optimized structure of $\mathbf{DA_{EE}}$ form (a) in the ground state and (b) excited state.

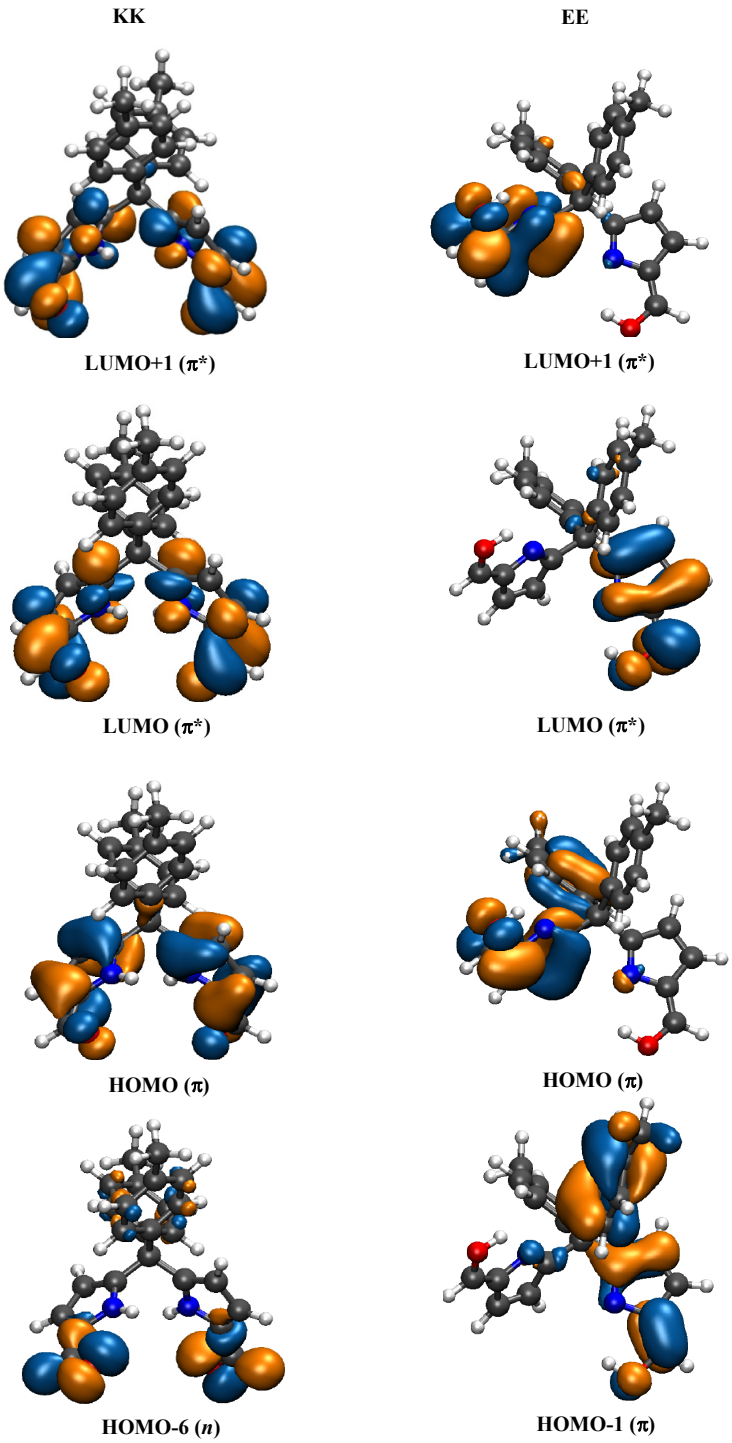


Fig. S13 Molecular orbital diagram of $\mathbf{DA_{KK}}$ and $\mathbf{DA_{EE}}$ in ground state calculated at the B3LYP/6-31+G* level.

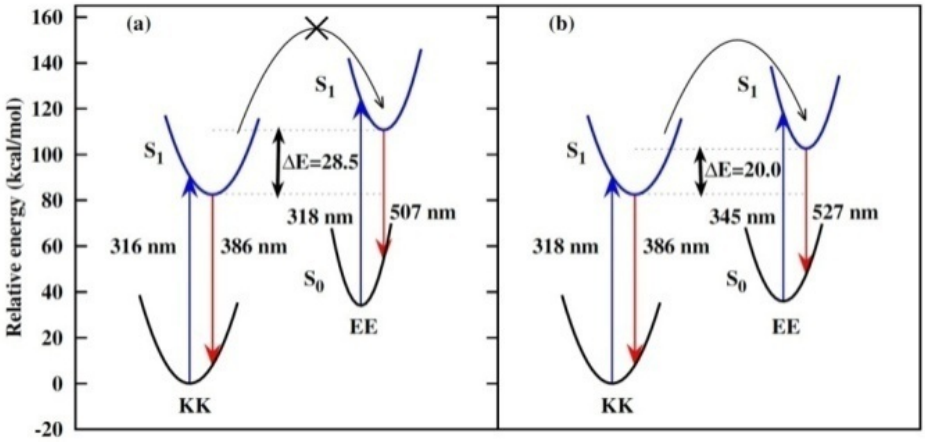
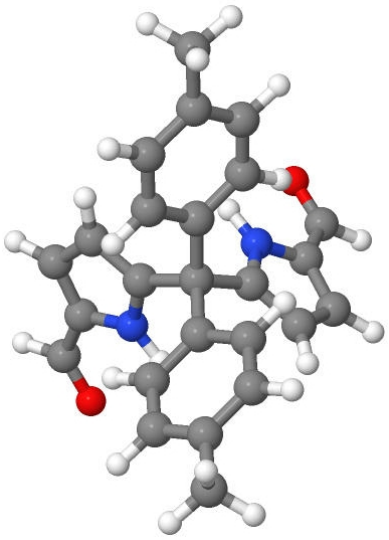


Fig. S14 Photophysical processes taking place in (a) **DH** and (b) **DA** upon UV irradiation.

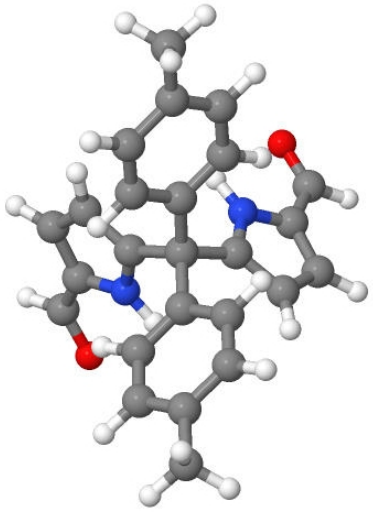
(a) DA_{KK} in ground state:



	X	Y	Z
N	-1.110037	1.217999	-1.794622
C	-0.160481	1.208675	-0.810371
C	0.571627	2.392414	-0.934216
C	0.030124	3.123073	-2.015933
C	-1.020051	2.373035	-2.542695
C	0.000856	0.000875	0.116171
C	1.232902	0.213061	1.039330
C	1.202816	1.263664	1.974019
C	2.265092	1.483138	2.846336
C	3.399973	0.653787	2.836047

C	3.420112	-0.399831	1.918090
C	2.355589	-0.619948	1.033054
C	4.543877	0.891177	3.795698
C	-1.921466	2.632332	-3.645030
O	-2.820081	1.869259	-3.989018
C	0.161341	-1.207903	-0.809185
C	-0.573147	-2.390125	-0.933307
C	-0.032903	-3.121847	-2.014902
C	1.018770	-2.373855	-2.541447
N	1.111231	-1.219181	-1.793099
C	1.918547	-2.633729	-3.644884
O	2.817722	-1.871812	-3.989912
C	-1.230638	-0.210851	1.040261
C	-2.354173	0.620918	1.032993
C	-3.419303	0.399562	1.917021
C	-3.398818	-0.654109	2.834930
C	-2.262577	-1.481493	2.846954
C	-1.199794	-1.260773	1.975649
C	-4.544004	-0.894016	3.792346
H	-0.326944	-1.905988	2.029977
H	-2.206053	-2.305882	3.555865
H	-4.278503	1.066683	1.885007
H	-2.413828	1.459452	0.346988
H	1.403493	2.684352	-0.309835
H	4.278426	-1.068176	1.887072
H	2.208889	2.307630	3.555143
H	0.330691	1.910020	2.027471
H	-1.776674	0.481371	-1.995718
H	2.414822	-1.458597	0.347150
H	0.362731	4.086647	-2.381280
H	1.779440	-0.483919	-1.993994
H	-0.367263	-4.084698	-2.380547
H	-1.405594	-2.680611	-0.309036
H	1.745772	-3.589405	-4.179202
H	-1.751015	3.588541	-4.179070
H	-5.373172	-0.203803	3.603670
H	-4.932285	-1.916669	3.702648
H	-4.227145	-0.758906	4.834968
H	4.224817	0.755858	4.837619
H	5.372023	0.199488	3.608201
H	4.934264	1.913115	3.707530

(b) DA_{KK} in excited state:



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N	-1.131356	1.216744	-1.785856
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C	0.069225	3.111072	-2.033146
C	-1.018873	2.367416	-2.571728
C	-0.004917	0.003900	0.122194
C	1.226396	0.213985	1.045254
C	1.193800	1.261652	1.983048
C	2.256927	1.482335	2.854381
C	3.394285	0.656756	2.840070
C	3.416959	-0.394043	1.918659
C	2.352093	-0.614882	1.034321
C	4.538797	0.895051	3.798871
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C	-0.558577	-2.401560	-0.918816
C	-0.020002	-3.124713	-2.006596
C	1.011931	-2.358788	-2.547956
N	1.093098	-1.202045	-1.801361
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O	2.779216	-1.834692	-4.029633
C	-1.235540	-0.216571	1.048011
C	-2.356017	0.619538	1.046501
C	-3.420561	0.397804	1.931079
C	-3.401845	-0.659674	2.845023
C	-2.268318	-1.490583	2.852273
C	-1.206529	-1.270143	1.979034
C	-4.545911	-0.898550	3.804348

H	-0.335076	-1.917743	2.030224
H	-2.212503	-2.316510	3.559561
H	-4.277607	1.068167	1.904535
H	-2.408599	1.461230	0.363829
H	1.420814	2.667656	-0.328515
H	4.277807	-1.059067	1.884238
H	2.199245	2.304892	3.565422
H	0.319244	1.904316	2.038108
H	-1.757542	0.447344	-1.978724
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H	0.420583	4.064641	-2.404038
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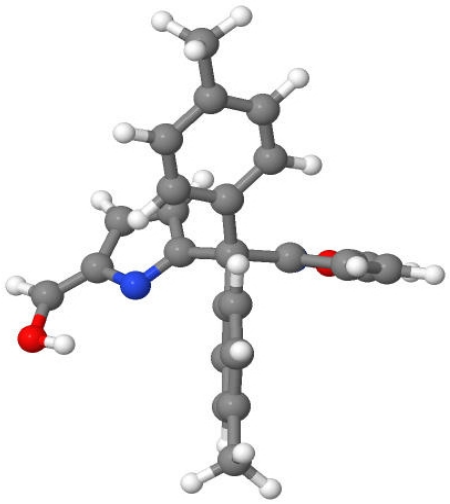
H	-5.373407	-0.205587	3.618687
H	-4.937149	-1.919921	3.713355
H	-4.227650	-0.766092	4.846777
H	4.221762	0.756415	4.840858
H	5.368743	0.206231	3.608587
H	4.926008	1.918387	3.713068

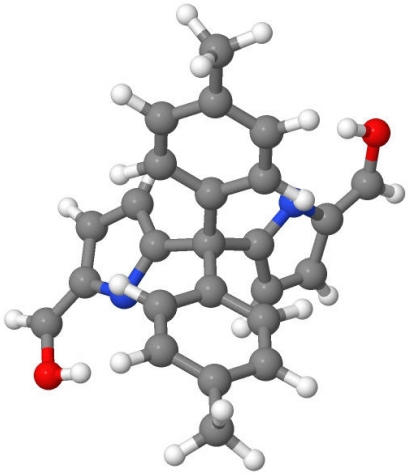
(c) DA_{EE} in ground state:



	X	Y	Z
C	2.079210	-1.408433	0.524543
C	1.625372	-0.318968	-0.241988
C	2.568992	0.371852	-1.008421
C	3.913410	-0.023779	-1.026264
C	4.362683	-1.115205	-0.277606
C	3.414760	-1.800264	0.502157

C	0.131515	0.091845	-0.144035
C	-0.092846	0.405973	1.339272
C	0.597523	1.461343	2.079138
C	0.201391	1.347737	3.380139
C	-0.714776	0.227016	3.408088
N	-0.854458	-0.321902	2.125013
C	-1.412427	-0.333462	4.434593
O	-2.220899	-1.383936	4.256764
C	5.812285	-1.544865	-0.291889
C	-0.183758	1.316298	-1.006130
N	-0.569092	2.473023	-0.511761
C	-0.819659	3.297379	-1.617179
C	-0.570537	2.580385	-2.848919
C	-0.175027	1.329600	-2.468375
C	-1.244078	4.573500	-1.395974
O	-1.429388	5.058531	-0.165617
C	-0.823636	-1.018049	-0.655937
C	-0.379067	-2.140476	-1.360585
C	-1.285236	-3.078626	-1.873026
C	-2.664255	-2.925935	-1.705147
C	-3.109628	-1.787755	-1.011421
C	-2.212010	-0.852901	-0.502937
C	-3.646728	-3.940991	-2.244367
H	1.372589	-1.952968	1.145575
H	3.729471	-2.649502	1.106849
H	4.620757	0.537432	-1.634304
H	2.271989	1.231041	-1.601787
H	0.084259	0.493642	-3.106033
H	-4.177990	-1.629356	-0.870853
H	-0.901696	-3.941566	-2.414794
H	0.682102	-2.298470	-1.522710
H	-2.592969	0.018348	0.021076
H	-0.687057	2.966832	-3.854842
H	0.498645	1.958542	4.224892
H	1.283922	2.182434	1.655596
H	-1.374445	0.015194	5.461914
H	-1.463946	5.289553	-2.181763
H	6.414975	-0.897241	-0.937977
H	6.247751	-1.511254	0.715395
H	5.920832	-2.574971	-0.656151
H	-4.173061	-4.459001	-1.431257
H	-4.411893	-3.464453	-2.870767
H	-3.143433	-4.701948	-2.850905
H	-1.209012	4.328341	0.456595
H	-2.173413	-1.607288	3.299299

(d) DA_{EE} in excited state:



	X	Y	Z
C	-0.933147	1.454463	1.657727
C	-0.914625	0.873153	0.362942
C	-1.756824	1.447064	-0.637393
C	-2.603645	2.497516	-0.332972
C	-2.643608	3.049454	0.963476
C	-1.788915	2.499590	1.951713
C	0.032871	-0.277784	0.014096
C	0.539909	-1.047172	1.221357
C	-0.315372	-1.832819	2.087709
C	0.514342	-2.458716	2.982285
C	1.854864	-2.052536	2.625832
N	1.823380	-1.176208	1.534297
C	3.060814	-2.399396	3.170639
O	4.223389	-1.941045	2.667609
C	-3.548893	4.205256	1.283313
C	-0.606365	-1.325583	-0.886717
N	-1.952287	-1.435385	-0.989992
C	-2.173922	-2.562702	-1.769270
C	-0.930011	-3.161761	-2.142206
C	0.066526	-2.372068	-1.561906
C	-3.486394	-2.932015	-2.062544
O	-4.525153	-2.200623	-1.560329
C	1.090533	0.611262	-0.655192
C	1.976933	1.413461	0.120067
C	2.902641	2.247011	-0.488188
C	2.977107	2.349961	-1.889738
C	2.081189	1.571662	-2.662654
C	1.152122	0.738457	-2.066787
C	3.958540	3.273788	-2.556550
H	-0.304850	1.034114	2.435524

H	-1.819023	2.901976	2.961526
H	-3.258297	2.898170	-1.103090
H	-1.753263	1.019538	-1.630294
H	1.137979	-2.534595	-1.601017
H	2.135223	1.622455	-3.747876
H	3.584622	2.829795	0.126596
H	1.946209	1.342500	1.199301
H	0.495880	0.127725	-2.675310
H	-0.797089	-4.055654	-2.741093
H	0.240429	-3.145274	3.775039
H	-1.390492	-1.925624	1.994376
H	3.184035	-3.053284	4.026782
H	-3.786802	-3.774591	-2.670349
H	-4.491745	4.139017	0.729360
H	-3.773839	4.260694	2.353275
H	-3.073415	5.155330	0.997592
H	4.378558	2.822137	-3.462538
H	3.461499	4.205421	-2.864819
H	4.780516	3.544959	-1.886623
H	-4.095636	-1.501359	-1.024192
H	3.979288	-1.389273	1.893063

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