Electronic Supplementary Information

Primary Photodegradation Pathways of an Exciplex-Forming A-D Molecular System

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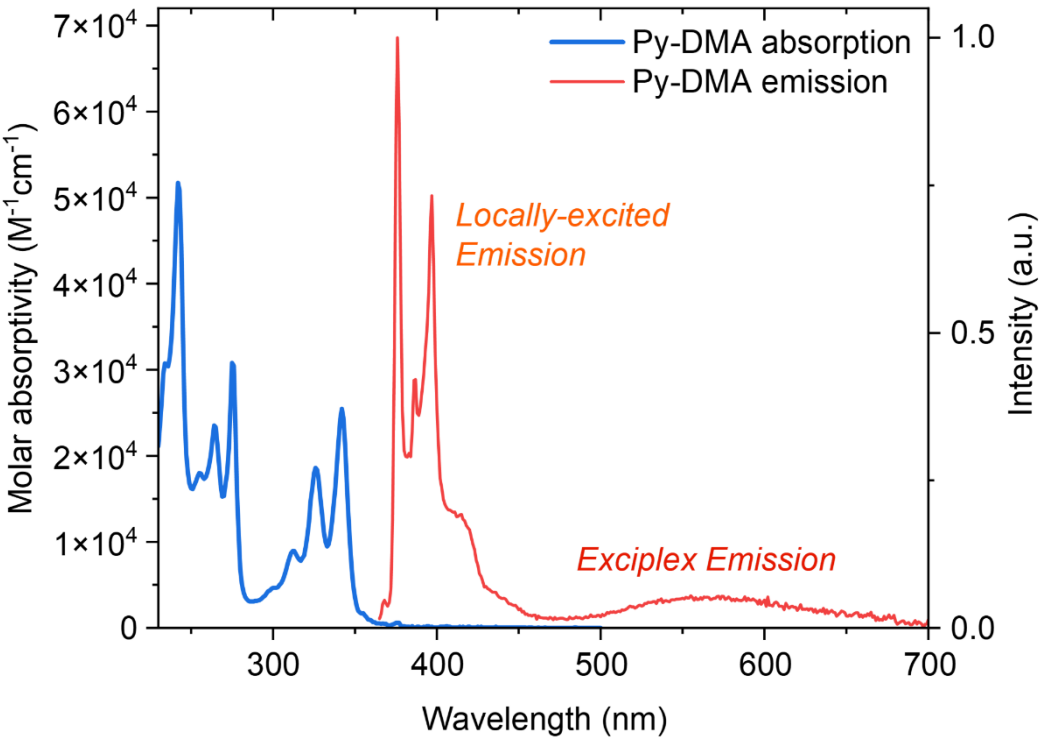

Figure S1. Absorption spectrum and normalized emission spectrum (λ_{ex}= 355 nm) of Py-DMA in ACN.

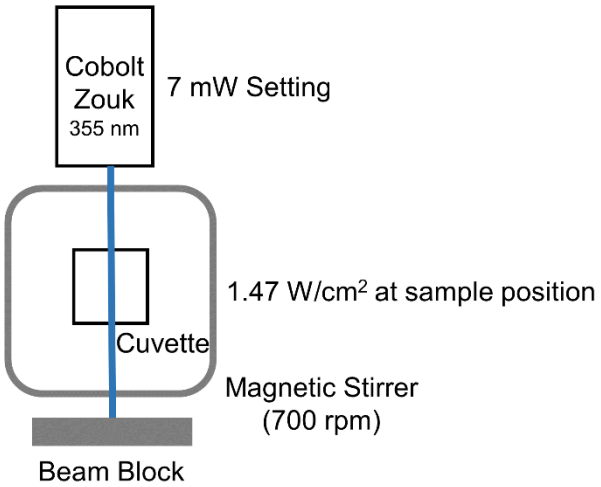

Figure S2. The diagram for photodegradation setup. Magnetic stirrer was used to keep homogenous environment in solution during photodegradation.

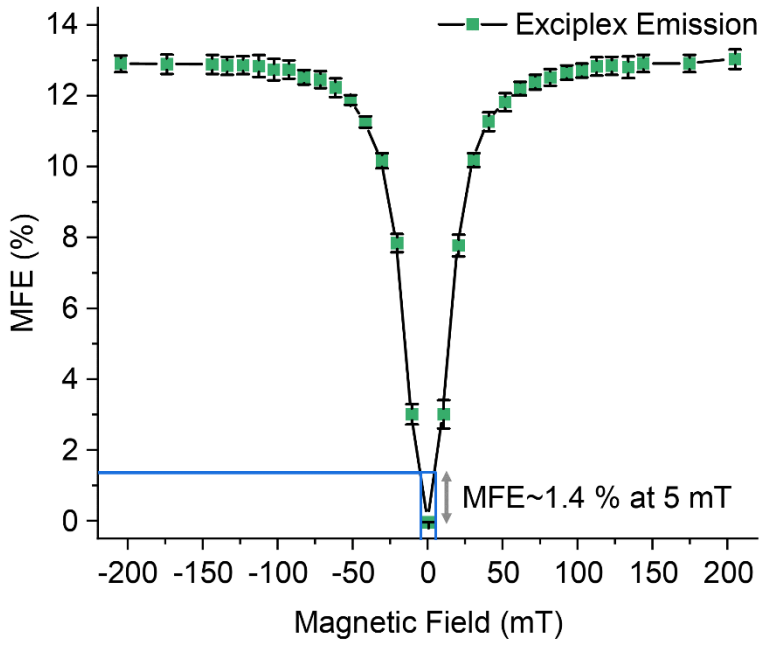

Figure S3. Magnetic field effect (MFE) plot for exciplex emission of Py-DMA (30 μM in ACN) with 355-nm excitation. (n = 10) It shows approximately 1.4 % MFE at a magnetic field strength of 5 mT. See Ref. 7 for details.

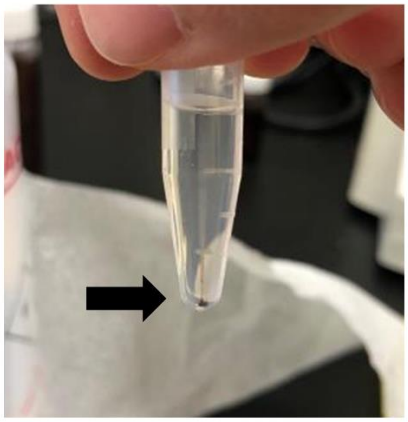

Figure S4. After centrifugation, the black precipitates were observed in 600 μM Py-DMA solution irradiated for 180 min.

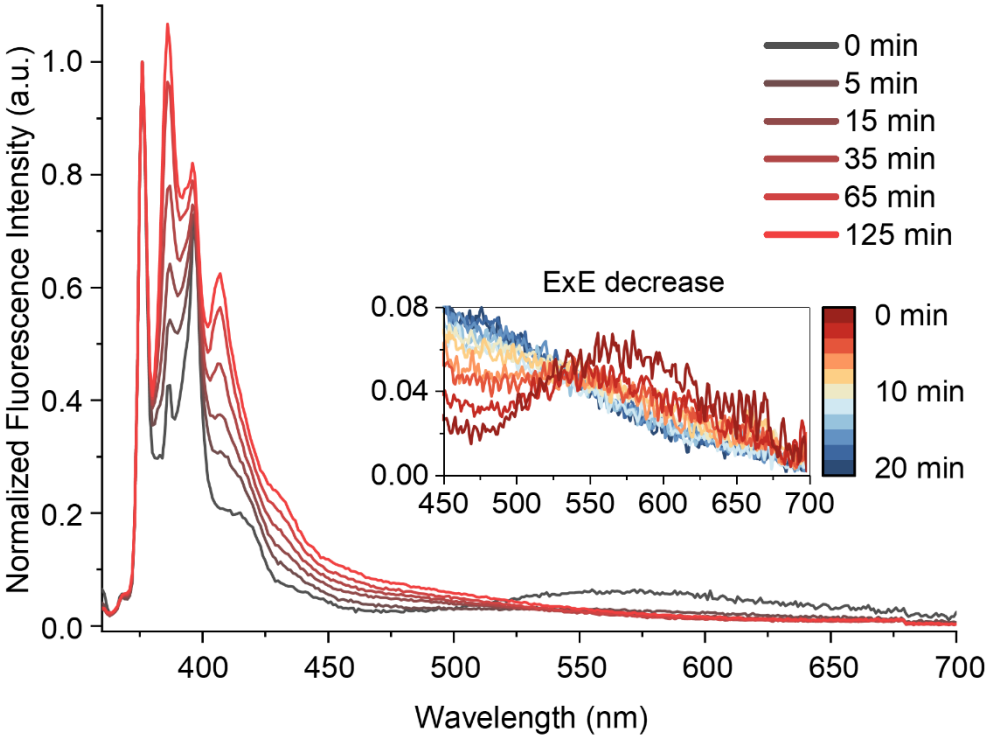

Figure S5. Emission spectra of Py-DMA normalized at 376 nm after photodegradation. Decrease in exciplex emission and increase in peaks at 386 nm and 405 nm are observed distinctively. Inset plot is emission spectra taken at shorter intervals, which exhibits a gradual decrease in exciplex emission.

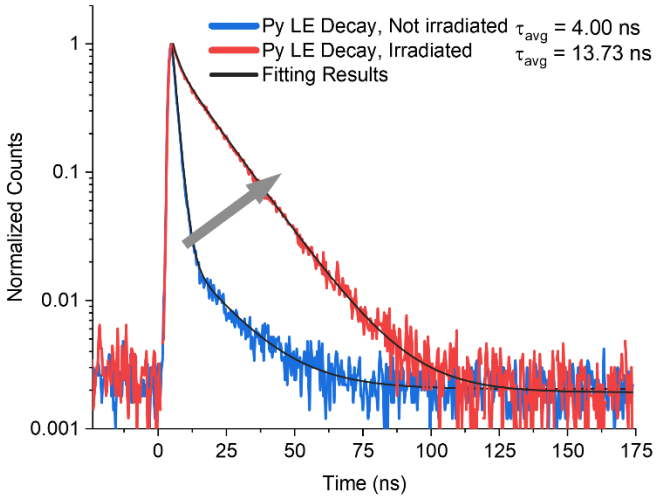

Figure. S6. Py-DMA's LE (377 nm, slit size 10 nm) fluorescence decay data before/after irradiation for 60 min. Py-DMA solution was prepared at 25 μM. The data were measured using the Time-Correlated Single Photon Counting (TCSPC) method on an FLS980 fluorometer.

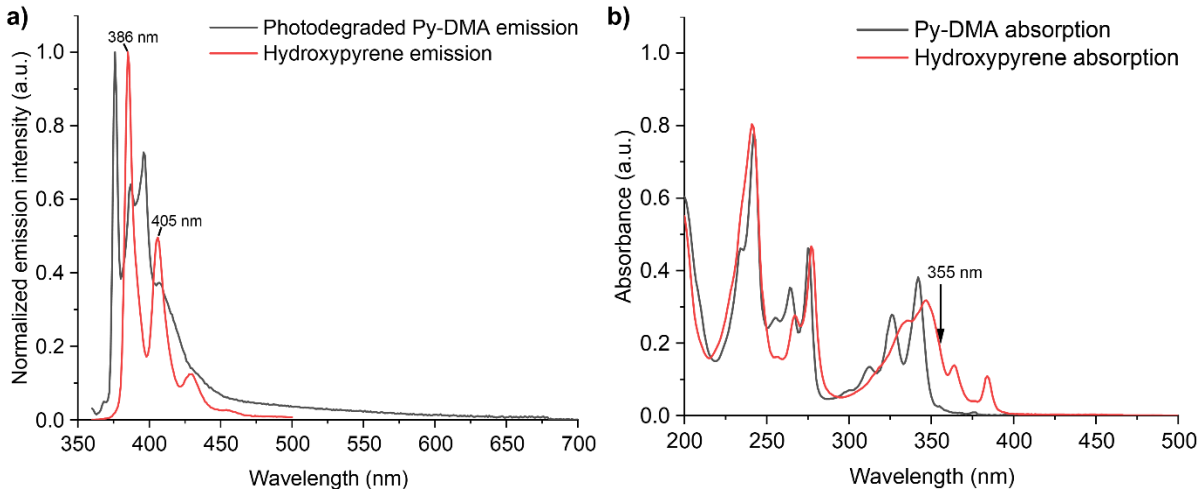

Figure S7. Absorption/emission spectra of 15 μM Py-DMA and hydroxypyrene (PyOH). a) The 386-nm and 405-nm peaks observed in Py-DMA emission spectrum after photodegradation match those of pure PyOH, suggesting the formation of PyOH. b) Larger absorbance of PyOH compared to Py-DMA at 355 nm makes the emission of PyOH observable despite the small amount of PyOH generated by the irradiation.

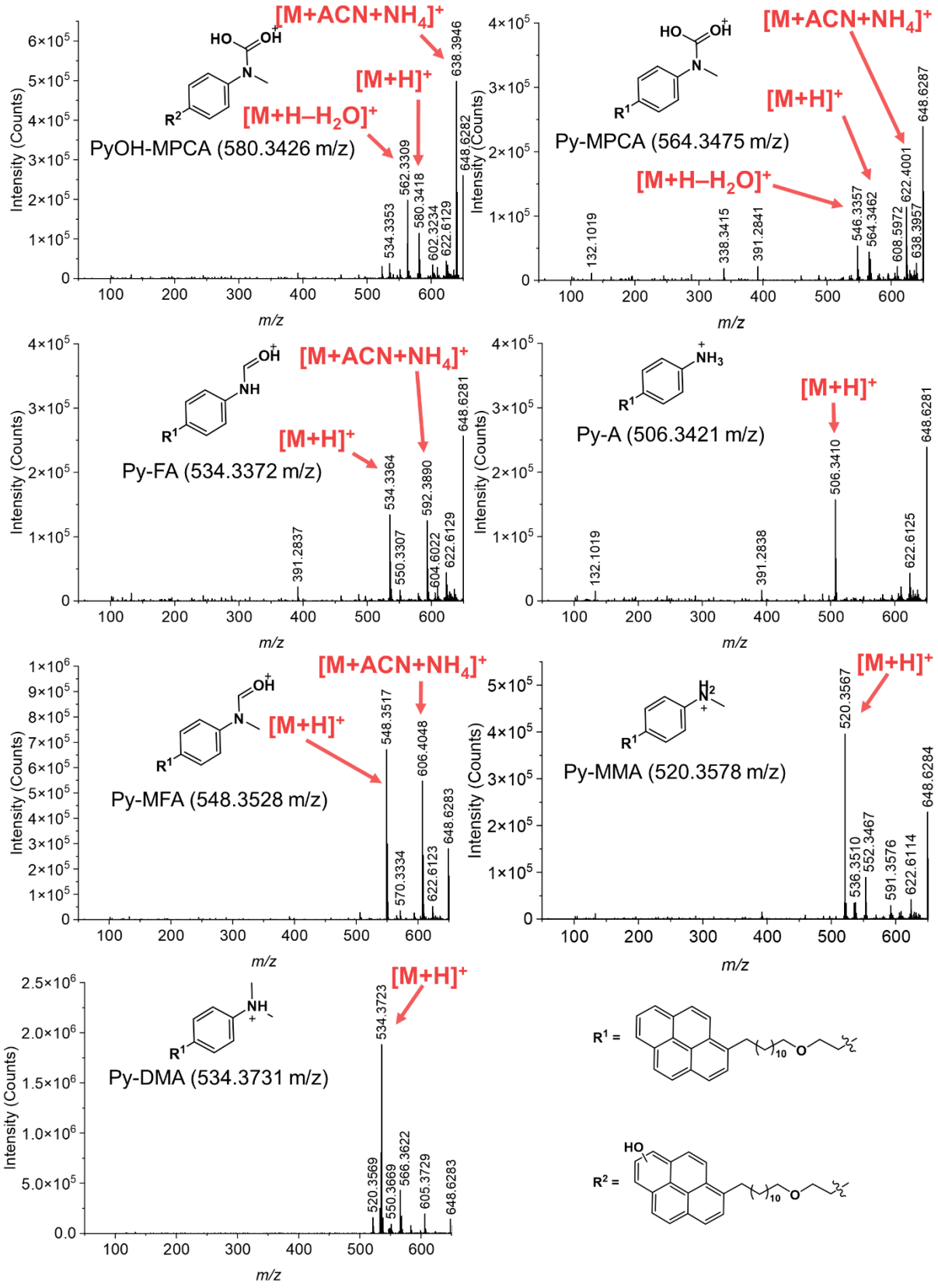

Figure S8. MS spectra of Py-DMA and PD products sharing common functional groups.

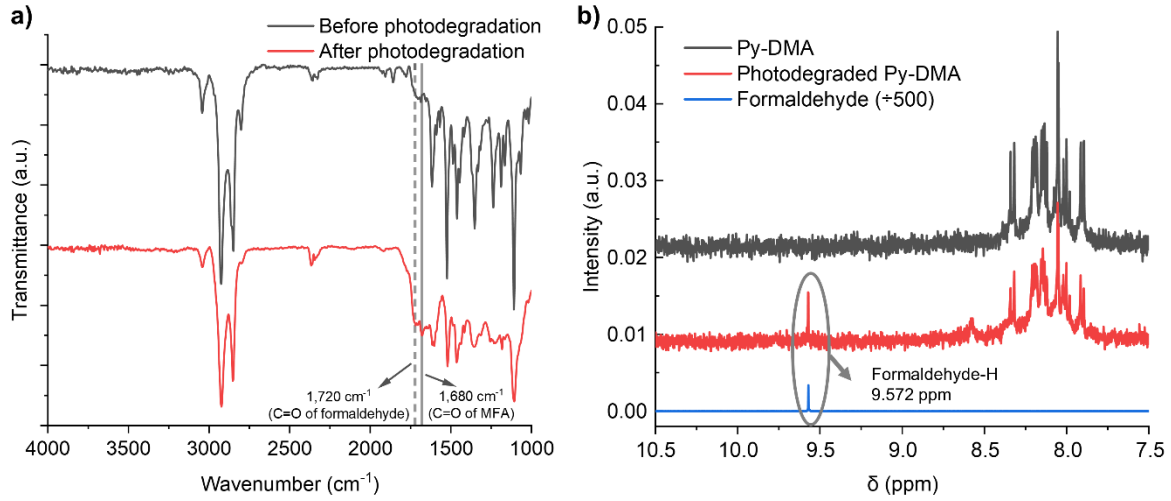

Figure S9. FT-IR and ^{1}H NMR spectra to detect the new functional group in photodegradation product. a) FT-IR spectra of Py-DMA before/after photodegradation. Peaks at 1,680 cm^{-1} and 1,720 cm^{-1} are assigned to C=O stretching of MFA and formaldehyde, respectively. b) ^{1}H NMR spectra of Py-DMA before/after photodegradation and pure formaldehyde solution. Compared to the spectrum of Py-DMA (black), the spectrum of photodegraded Py-DMA (red) has peaks corresponding to formaldehyde-H.

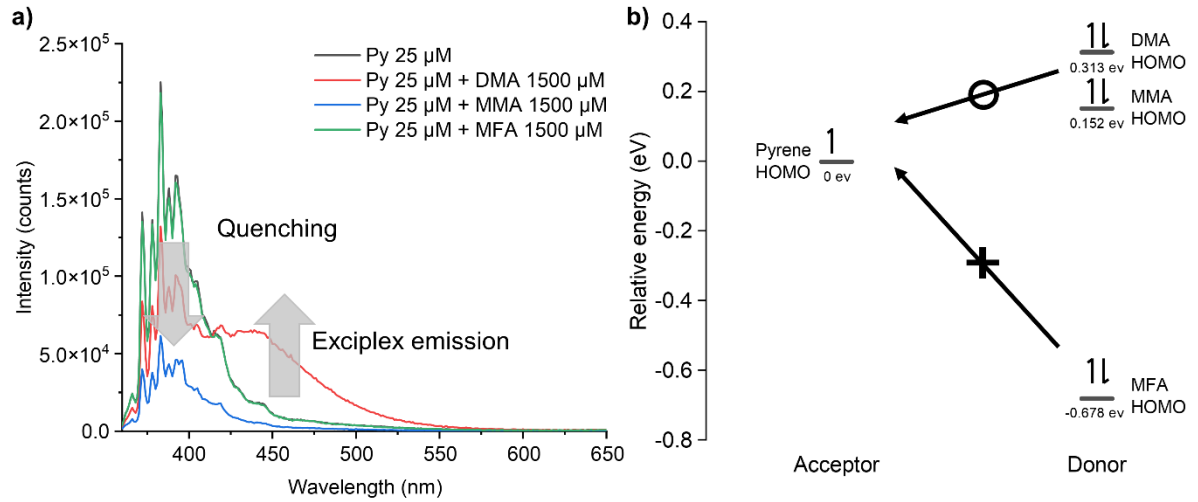

Figure S10. (a) The fluorescence emission spectra of non-linked Py (electron acceptor) and DMA, MMA, MFA (electron donors). Samples were prepared in cyclohexane, where the formation exciplex is more favorable than in ACN, and deoxygenated through Ar-purging. Low oxygen concentration and the use of the non-polar solvent cyclohexane facilitate exciplex formation. Note that the exciplex emission peak is blue-shifted (~ 470 nm) compared to that (~ 550 nm) in Fig. 2b and Fig. S1 due to the lower solvent polarity of cyclohexane than that of ACN. (b) Relative orbital energies for the HOMO levels for various electron donors generated under photodegradation of Py-DMA using B3LYP/6-31G(d) with self-consistent reaction field (SCRF) where ACN is the solvent.

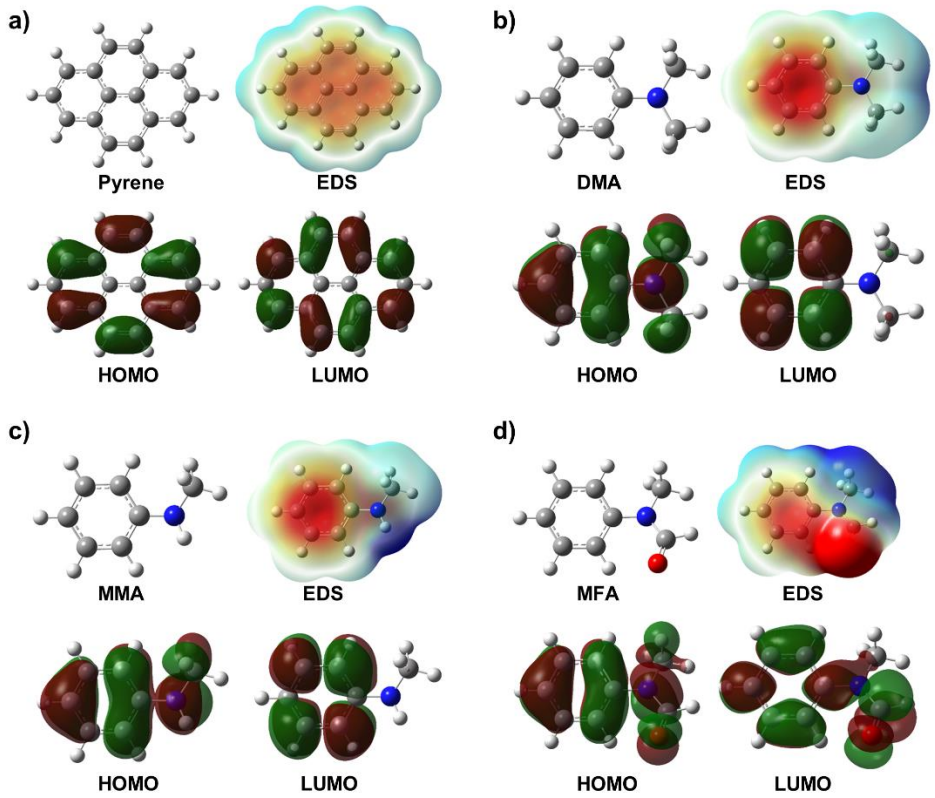

Figure S11. Optimized molecular structure, electron density surface (EDS) mapped with electrostatic potential, HOMO, and LUMO of (a) pyrene, (b) DMA, (c) MMA, and (d) MFA . In EDS, the red color indicates electron-rich region, while the blue color indicates electron-poor region. (B3LYP/6-31G(d), GAUSSIAN16)

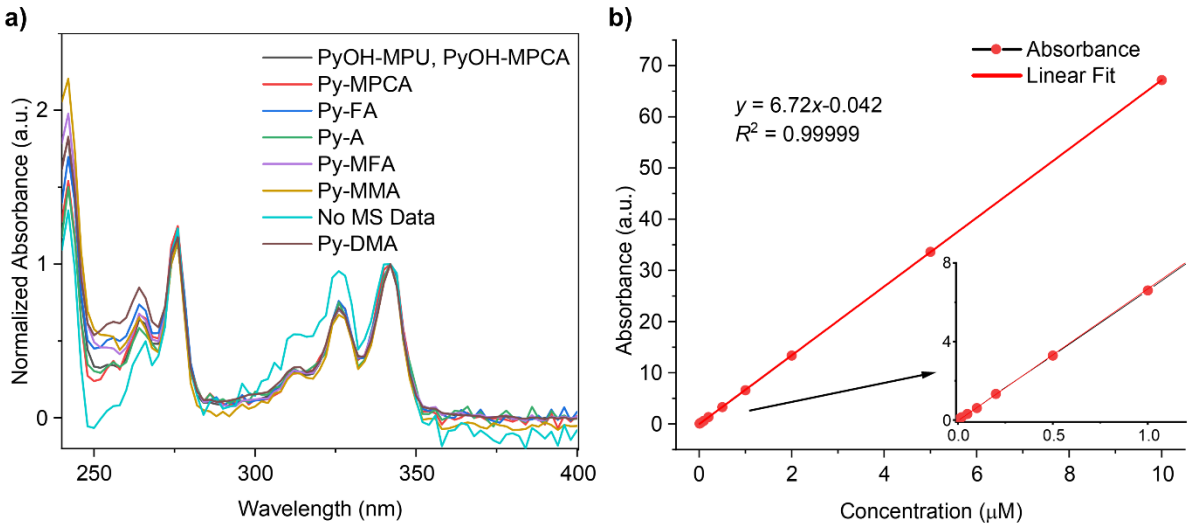

Figure S12. a) The absorption spectra of MS-detected photodegradation products show the same spectrum shape over a range of 275- 350 nm (normalized at 342 nm). This region mainly originates from the acceptor (pyrene) and is relatively less affected by photodegradation. b) An absorbance-concentration plot using Py-DMA solution as a standard in various concentrations from 0.01 μM to 10 μM in ACN. The absorbance area was calculated by integrating the area under the peak of the UV chromatogram (342 nm).

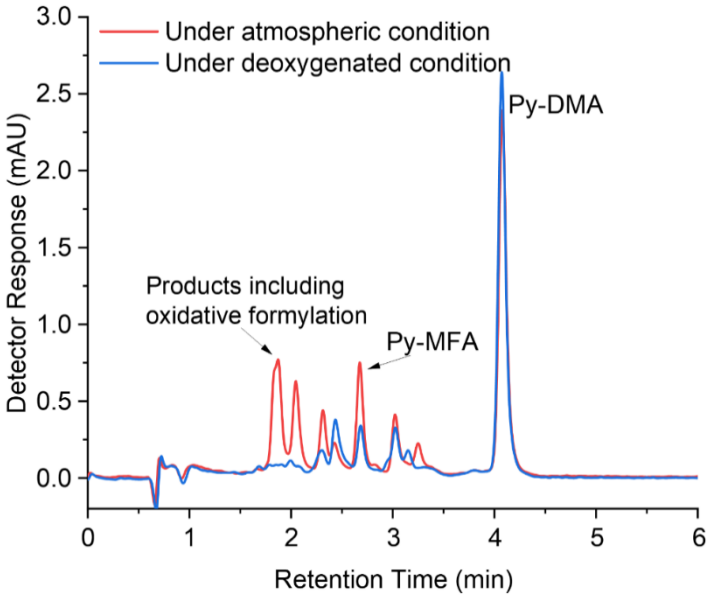

Figure S13. UV chromatograms of Py-DMA after photodegradation under atmospheric and deoxygenated condition. Comparing the UV chromatogram at irradiation time when a similar amount of Py-DMA remained, the amount of Py-MFA is reduced by half under deoxygenated condition. Furthermore, the products containing carbonyl group, related to oxidative formylation, were significantly reduced or, in some cases, undetectable.

Table S1. Cartesian coordinates of the optimized structures for pyrene, DMA, MMA, and MFA calculated by B3LPY/6-31G(d) in GAUSSIAN16

Pyrene

Symbol	X	Y	Z
C	3.525273	0	0.000369
C	2.834402	-1.211767	0.000307
C	1.429596	-1.237082	0.000158
C	0.71371	0	0.000072
C	1.429595	1.237084	0.000133
C	2.8344	1.211768	0.00028
C	0.681219	-2.465813	0.000091
C	-0.71371	0	-0.000074
C	-1.42959	-1.237083	-0.000137
C	-0.68122	-2.465814	-0.00005
C	-2.8344	-1.211768	-0.00028
H	-3.3814	-2.151244	-0.000327
C	-3.52527	-0.000002	-0.000359
C	-2.8344	1.211766	-0.0003
C	-1.4296	1.237083	-0.000158
C	-0.68122	2.465814	-0.000095
C	0.681216	2.465815	0.000043
H	1.230574	3.404037	0.000083
H	-1.23058	3.404036	-0.000158
H	1.230577	-3.404036	0.000154
H	4.611782	0.000002	0.000486
H	3.381403	-2.151242	0.000377
H	3.381404	2.151241	0.000326
H	-1.23058	-3.404036	-0.000103
H	-4.61178	-0.000001	-0.00047
H	-3.38141	2.15124	-0.000363

Table S1. (*continued*)

DMA

Symbol	X	Y	Z
C	1.943939	1.199252	0.016384
C	0.551109	1.209004	-0.03174
C	-0.18528	-0.000007	-0.06979
C	0.551208	-1.209002	-0.03224
C	1.94403	-1.199199	0.015891
C	2.659589	0.00005	0.038752
H	2.472762	2.149246	0.042296
H	0.037308	2.162874	-0.03891
H	0.037451	-2.162889	-0.03998
H	2.472874	-2.149192	0.041325
H	3.744926	0.000137	0.079256
N	-1.57275	-0.00005	-0.15414
C	-2.29564	1.245508	0.059885
H	-3.36485	1.060183	-0.05537
H	-2.12453	1.673561	1.06056
H	-2.00931	1.99819	-0.68336
C	-2.2955	-1.245558	0.060799
H	-3.36486	-1.060084	-0.05275
H	-2.01044	-1.998314	-0.68289
H	-2.1229	-1.673649	1.061189

Table S1. (*continued*)

MMA

Symbol	X	Y	Z
C	1.879499	0.996268	0.045853
C	0.523142	1.300265	-0.00473
C	-0.44619	0.274883	-0.06234
C	-0.00136	-1.062299	-0.0591
C	1.364211	-1.352128	-0.01252
C	2.316849	-0.33376	0.040946
H	2.602558	1.807158	0.091582
H	0.196929	2.338324	-0.00298
H	-0.71863	-1.875523	-0.09434
H	1.680615	-2.392578	-0.0123
H	3.376737	-0.567614	0.080666
N	-1.79234	0.608122	-0.15967
C	-2.83702	-0.365362	0.113488
H	-3.80292	0.143316	0.074473
H	-2.84303	-1.151434	-0.65012
H	-2.73488	-0.848909	1.098083
H	-2.00583	1.543196	0.163038

Table S1. (*continued*)

MFA

Symbol	X	Y	Z
C	2.277154	-1.017824	0.292338
C	0.896733	-1.220244	0.259544
C	0.028509	-0.157931	-0.041831
C	0.574351	1.108347	-0.318754
C	1.955278	1.296263	-0.280026
C	2.81682	0.240372	0.025836
H	2.928357	-1.854385	0.53031
H	0.505833	-2.207367	0.476393
H	-0.07932	1.934837	-0.556394
H	2.358069	2.281482	-0.499452
H	3.891475	0.395809	0.052163
N	-1.37808	-0.393948	-0.097325
C	-1.85054	-1.76431	-0.3231
H	-2.9176	-1.739536	-0.549546
H	-1.32273	-2.20583	-1.172236
H	-1.70117	-2.396312	0.558617
C	-2.32009	0.576025	0.13616
H	-3.3428	0.171181	0.048783
O	-2.11786	1.751696	0.411454