Supporting information

Phenol Hydroxyl-Modified Imine-Based Covalent organic framework for enhanced solar-driven generation of H_2O_2 via Hydrogen Bonds

Contents

1. Experimental protocols and instrument

1.1.Characterizations methods

The powder diffraction patterns were measured by DX-1000 system with Cu Kα radiation source (λ = 1.540598 Å) at a scan rate of 5° min^{-1} in 2θ range from 1.5° to 90°. Nicolet 670 FT-IR spectrophotometer (thermos Nicolet, USA) was used for Fourier transform infrared spectroscopy analyses (FT-IR). Solid-state 13C cross polarization magic angle spinning NMR spectra (13C-CP/MAS NMR) were carried out on Bruker AVANCE III 500 MHz (Bruker, Switzerland) with a standard 4 mm magic angle spinning (MAS) triple resonance probe (the MAS frequency was 10 kHz). X-ray photoelectron spectroscopy (XPS) was conducted on Axis Ultra DLD X-ray photoelectron spectrometer with a monochromatic Al radiation (hν = 15.00 kV) (Kratos Analytical, UK). The porous property and surface area were assessed by The ASAP 2460 Surface Area and Porosity Analyzer. The sample was degassed and evaporated under vacuum at 100 ℃ for one day before N_2 adsorption-desorption at 77 K. Diffuse reflectance ultraviolet-visible (UV-vis, UV3600, Shimadzu, Japan) spectra was performed to measure the light absorption. The morphology was measured by Field emission-scanning electron microscope (SEM, S-4800, Hitachi, Japan). electrochemical workstation was used to test Mott-Schottky measurements, photocurrent, and electrochemical impedance spectroscopy (EIS). The supporting electrolyte for MS measurement and photocurrent was 0.1 M Na_2SO_4 aqueous solution while that for EIS was aqueous solution with 0.1 M KCl, 0.05 M Potassium ferricyanide, and 0.05 M Potassium ferrocyanide. Fluorescence spectroscopy was carried out on F-7100 (Hitachi, Japan).

1.2. Characterization

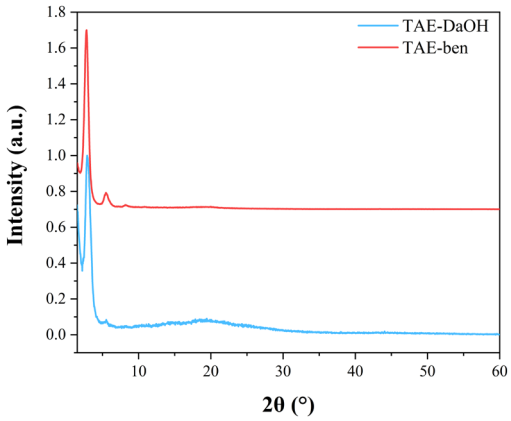

Figure S1. PXRD patterns of TAE-DaOH and TAE-ben.

Both TAE-DaOH and TAE-ben performed identical peak at 2θ of 2.80° corresponding to (100) facet, which were consistent with the simulated eclipsed staking model.

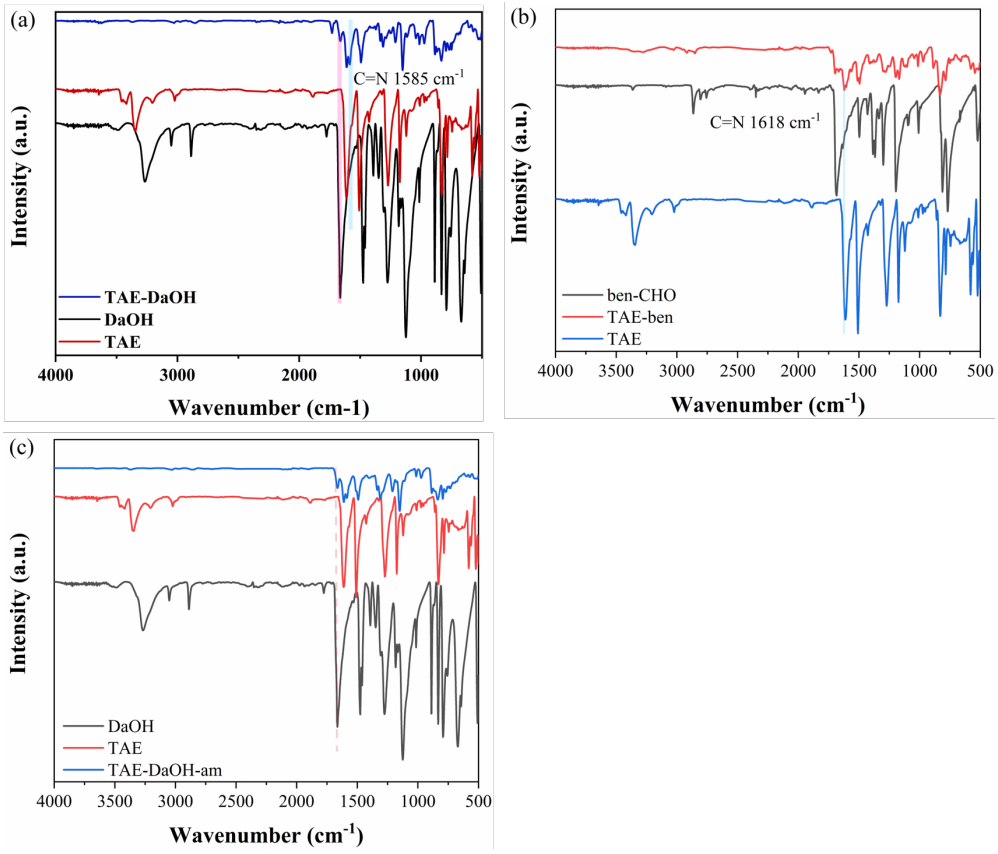

Figure S2. FT-IR of TAE-DaOH and TAE-ben.

As shown in figure S2a and c, the presence of characteristic peak of (C=N) at 1585 cm^{-1} reveal the successful synthesis of TAE-DaOH. The stretching vibrational of C=N was observed at 1620 cm^{-1}, indicating the existence of imine structure in TAE-ben. Furthermore, the absent of characteristic peaks of both NH_2 and C(H)=O suggested highly complete polymerization[1]. Compared with characteristic peak (C=N) of TAE-ben at 1620 cm^{-1}, the characteristic peak of TAE-DaOH redshifted to 1580 cm^{-1}, indicating intramolecular hydrogen bond between phenolic hydroxyl group and imine bond.

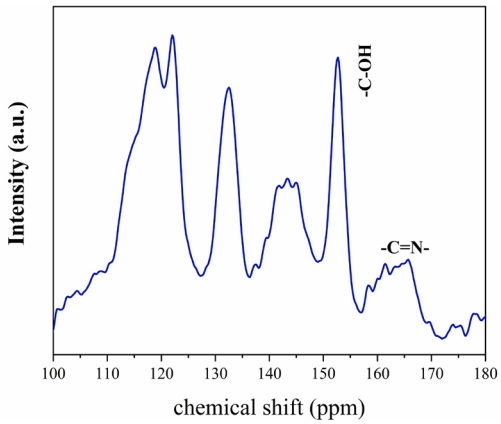

Figure S3. 13C CP-MAS NMR.

The structure of TAE-DaOH was further tested by ^{13}C CP-MAS NMR as shown in figure S3, the present peak at 165 ppm was attributed to carbon of imine while the peak at 151 ppm corresponded to the carbon of phenol[2].

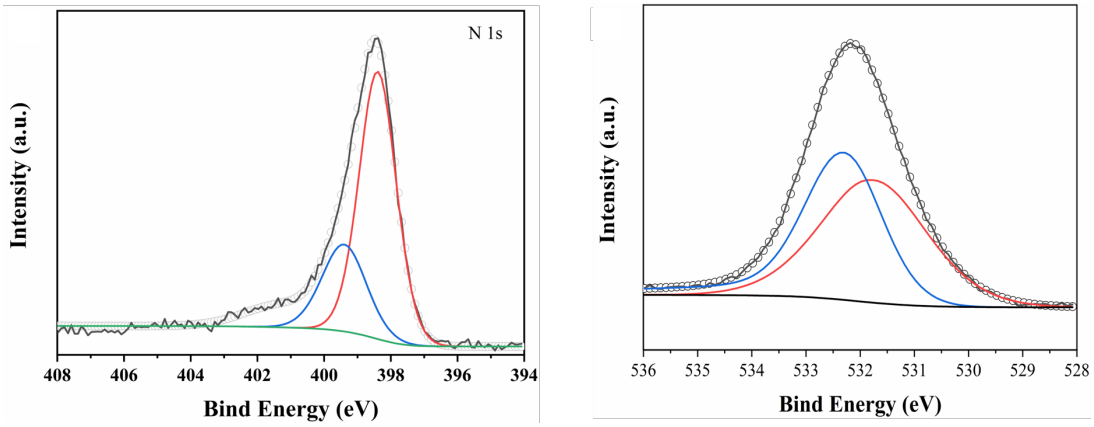

Figure S4. High resolution of XPS pattern, N 1s (left) and O 1s (right).

The state of phenol in TAE-DaOH was further confirmed by XPS (figure S4), the present peak at 532.4 eV in high resolution spectra was assigned to O of phenol (the peak at 531.2 eV was attributed to O of H_2O) [3].

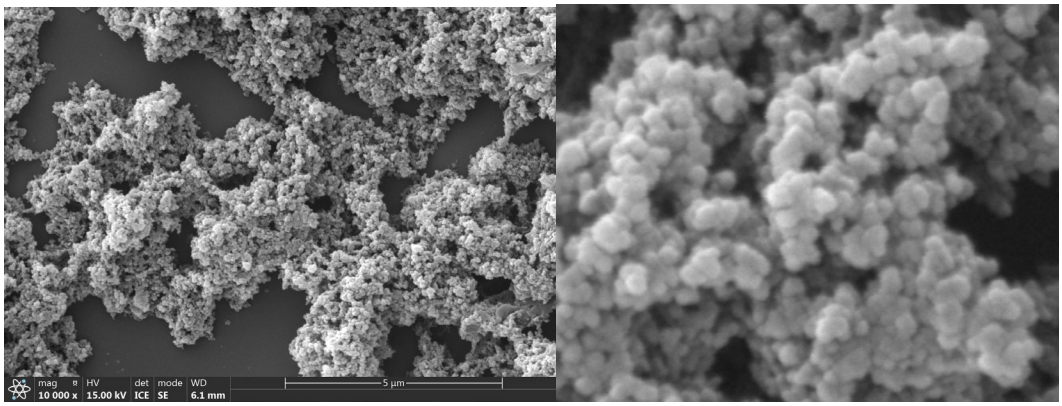

Figure S5. SEM of TAE-DaOH. Proportional scale: 5 µm (left), 3 µm (right).

The prepared TAE-DaOH displayed irregular morphologies with sizes from 20 nm to 30 nm.

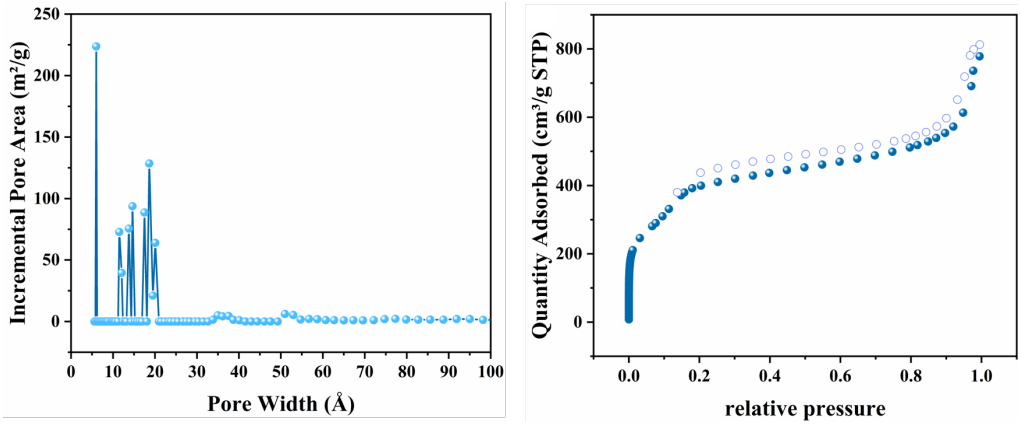

Figure S6. Pore distribution of TAE-DaOH.

According to BET analyze (figure S6), the surface of TAE-DaOH was calculated to be 1217.2 m^2 g^{-1}, the large surface was beneficial for photocatalysis to provide a vast number of reactive sites. In addition, the pore size was evaluated to be 0.60 nm and 1.86 nm, which was fitted with the simulated eclipsed staking model[4].

2. Photochemical properties

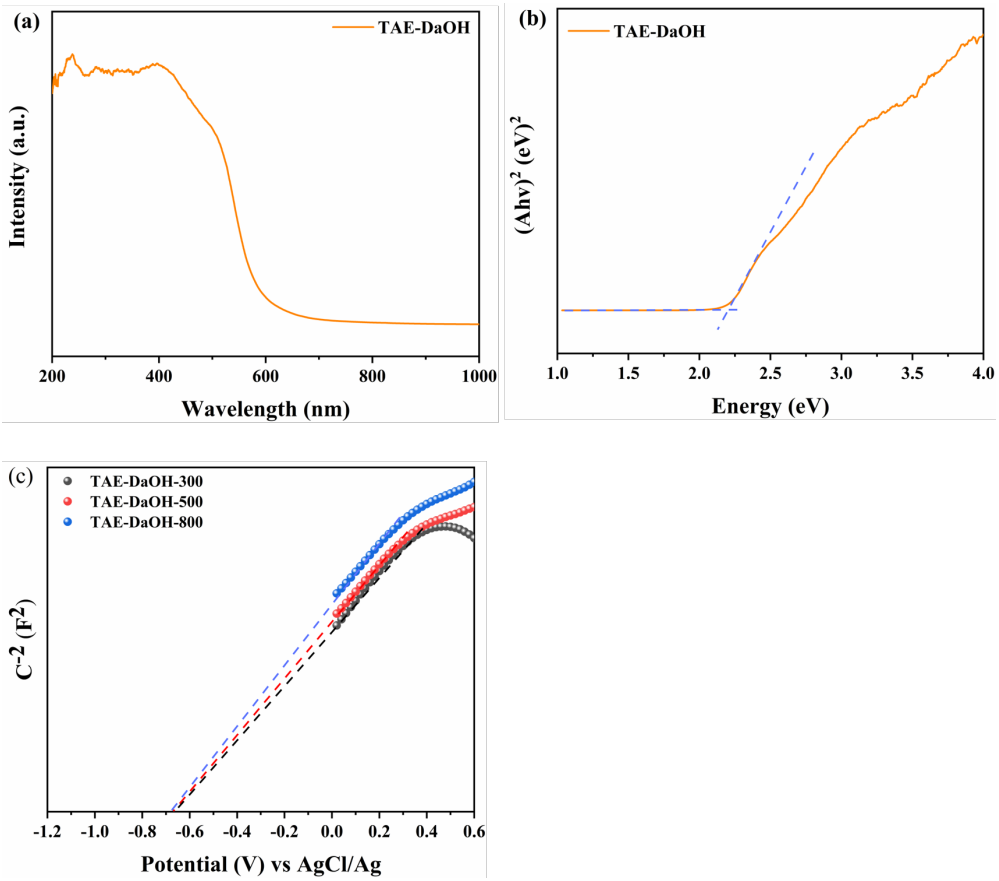

Figure S7. Photochemical properties of TAE-DaOH. (a) UV-vis diffuse reflection, (b) derived band, (c) MS curve.

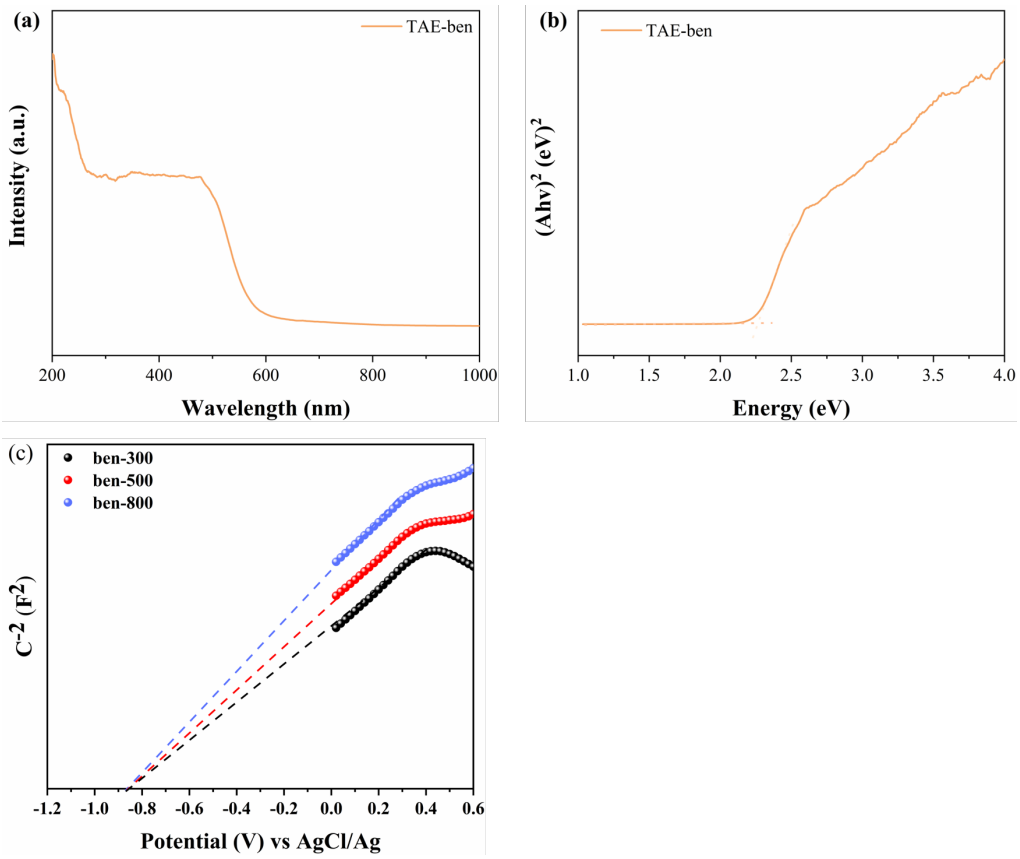

Figure S8. Photochemical properties of TAE-ben. (a) UV-vis diffuse reflection, (b) derived band, (c) MS curve.

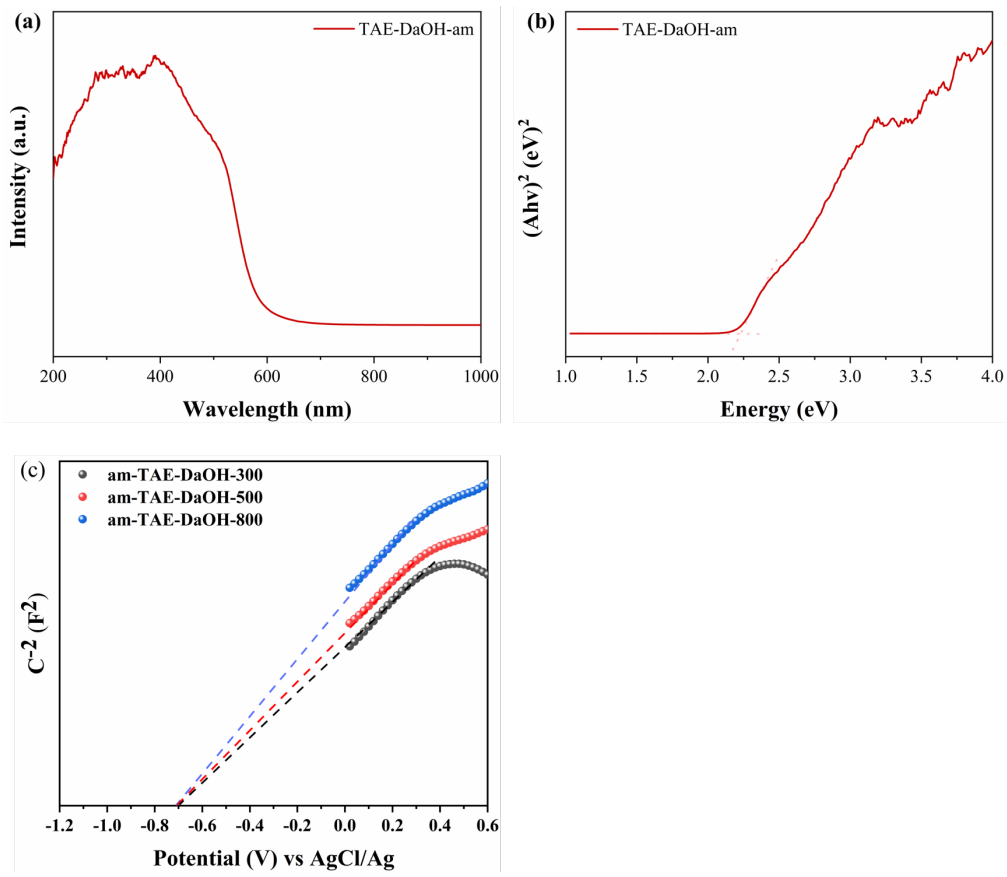

Figure S9. Photochemical properties of TAE-DaOH-am. (a) UV-vis diffuse reflection, (b) derived band, (c) MS curve.

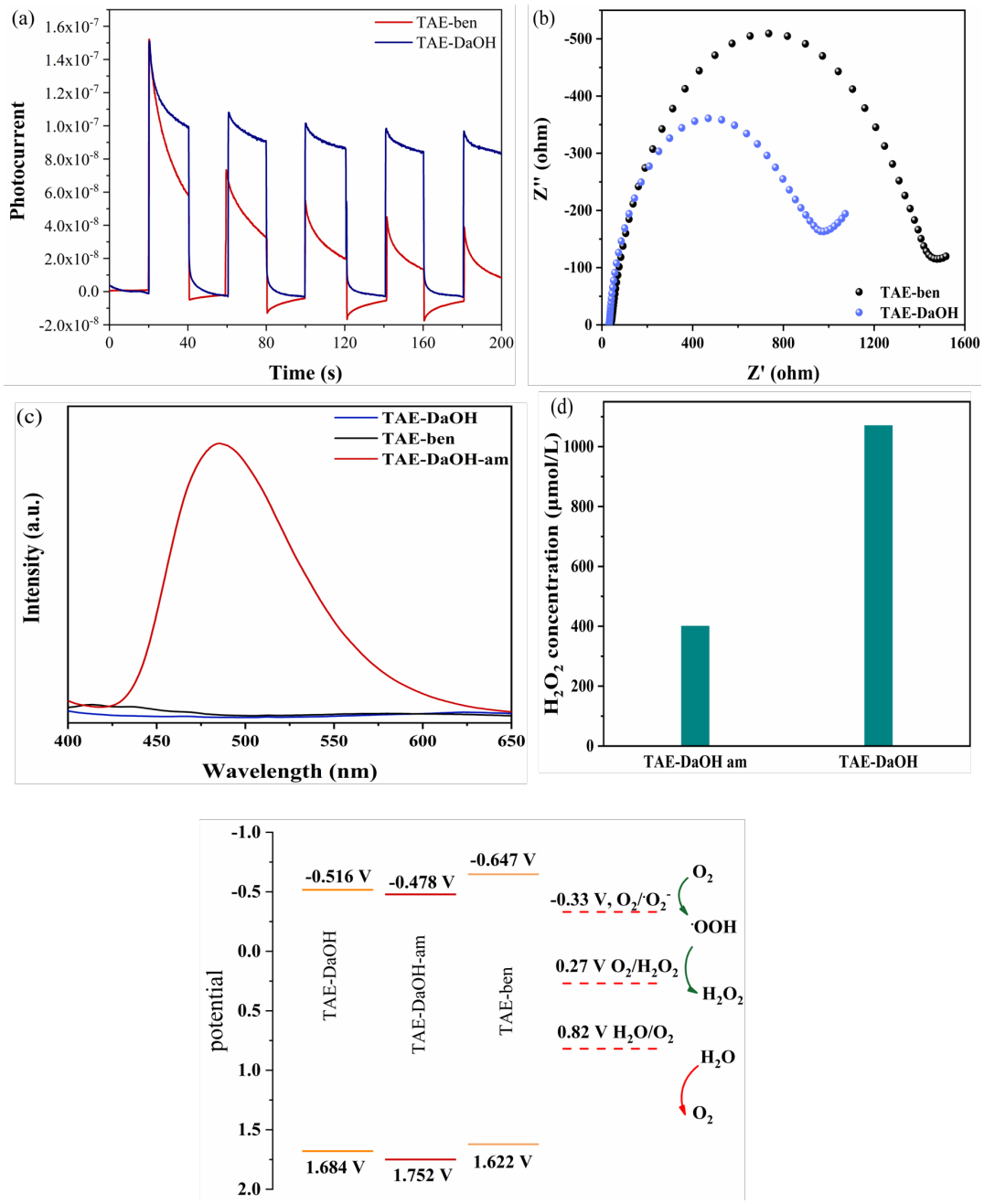

Figure S10. Photochemical property. (a) photocurrent of TAE-DaOH and TAE-ben, (b) EIS of TAE-DaOH and TAE-ben, (c) solid fluorescence of TAE-DaOH, TAE-ben, and TAE-DaOH-am, (d) photocatalytic performance of TAE-DaOH and TAE-dAoH-am, m/V = 1g/L, pH = 7, (e) illustration of bandgaps.

3. Photocatalytic performance

3.1.Dispersion of catalyst in mixture of BA/water.

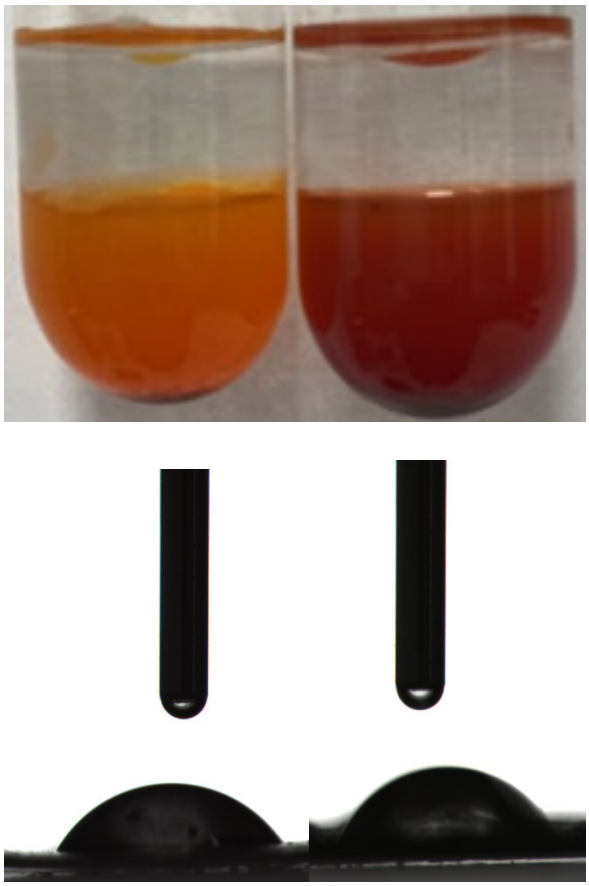

Figure S11. Dispersion of TAE-ben (left) and TAE-DaOH (right) in mixture of BA/water. And contact angle of TAE-ben (left) and TAE-DaOH (right).

3.2.Stability of catalyst

Figure S12. Contrast of TAE-DaOH before and after photocatalysis.

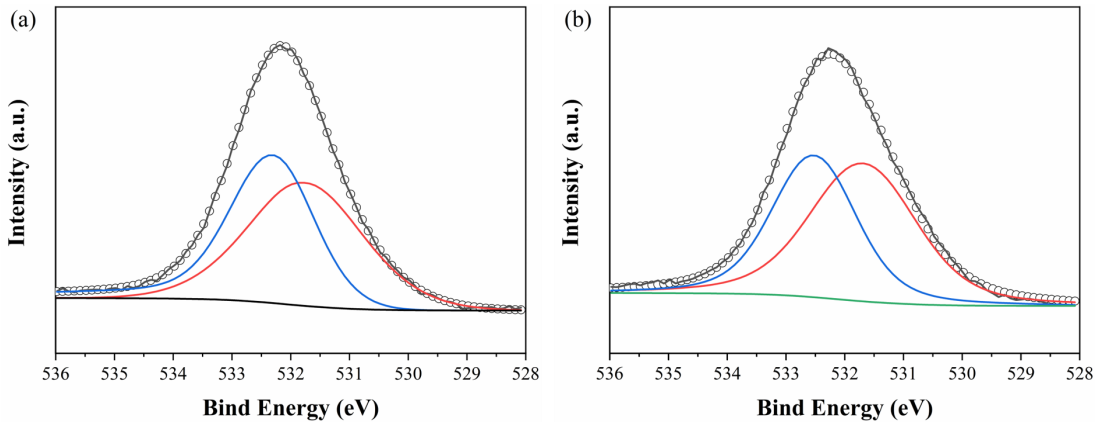

Figure S13. O 1s XPS spectra of TAE-DaOH before and after irradiation.

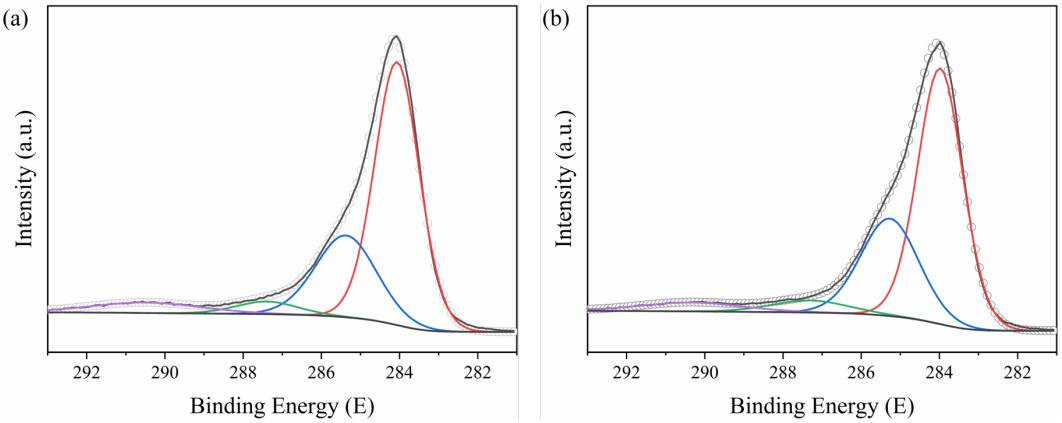

Figure S14. C 1s XPS spectra of TAE-DaOH before and after irradiation

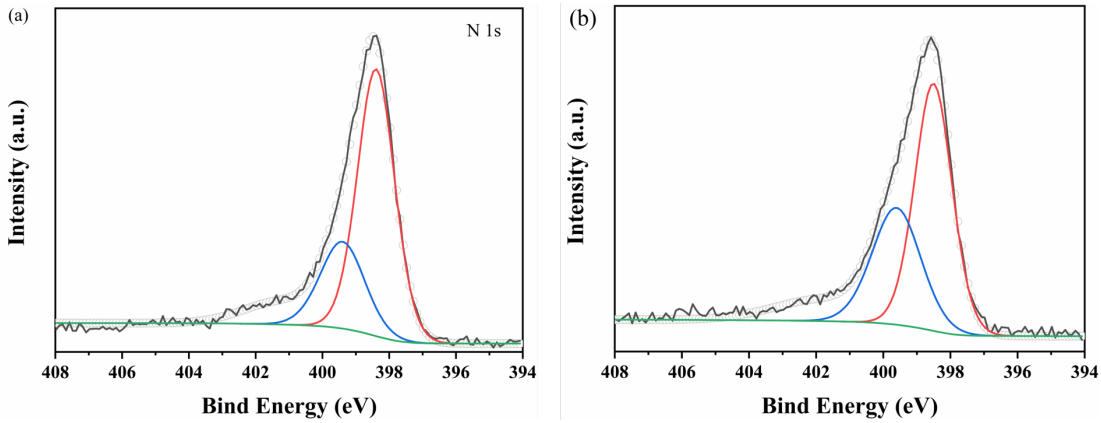

Figure S15. N 1s XPS spectra of TAE-DaOH before and after irradiation.

Experimental condition of figure S11-S16: m/V = 1 g/L, water/BA = 9:1, pH = 7, reaction time per run = 6 h, total runs = 5.

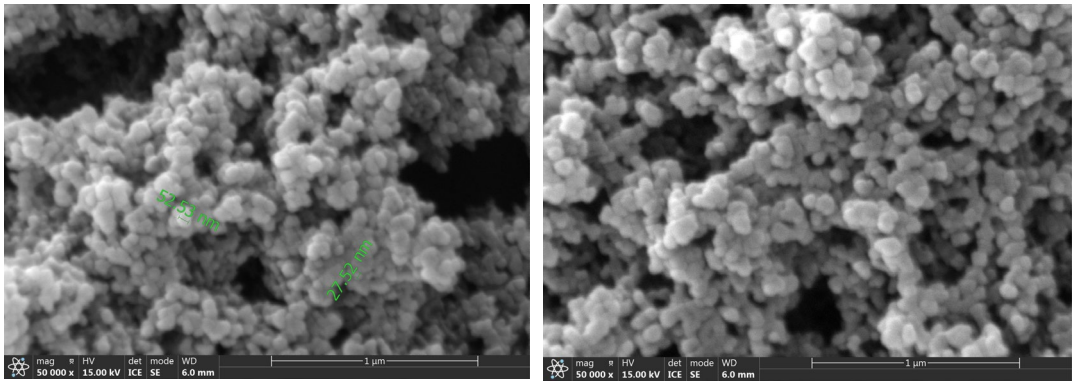

Figure S16. Contrast of SEM of TAE-DaOH after photocatalytic experiment.

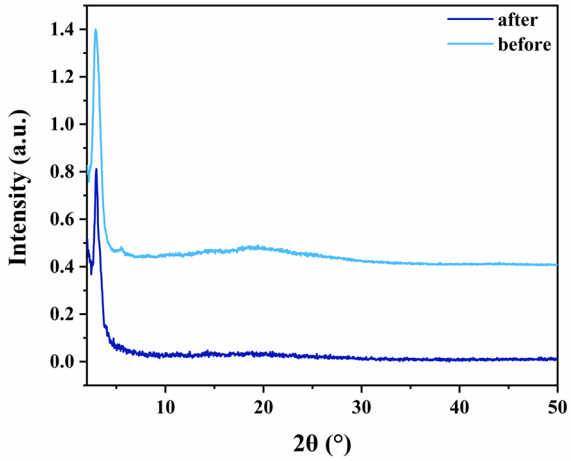

Figure S17. XRD of TAE-DaoH before and after irradiation.

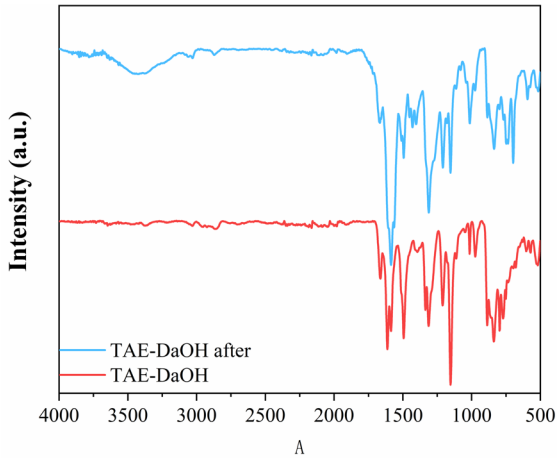

Figure S18. FT-IR of TAE-DaOH before and after irradiation.

3.3.Cycling, pH, and solar experiment

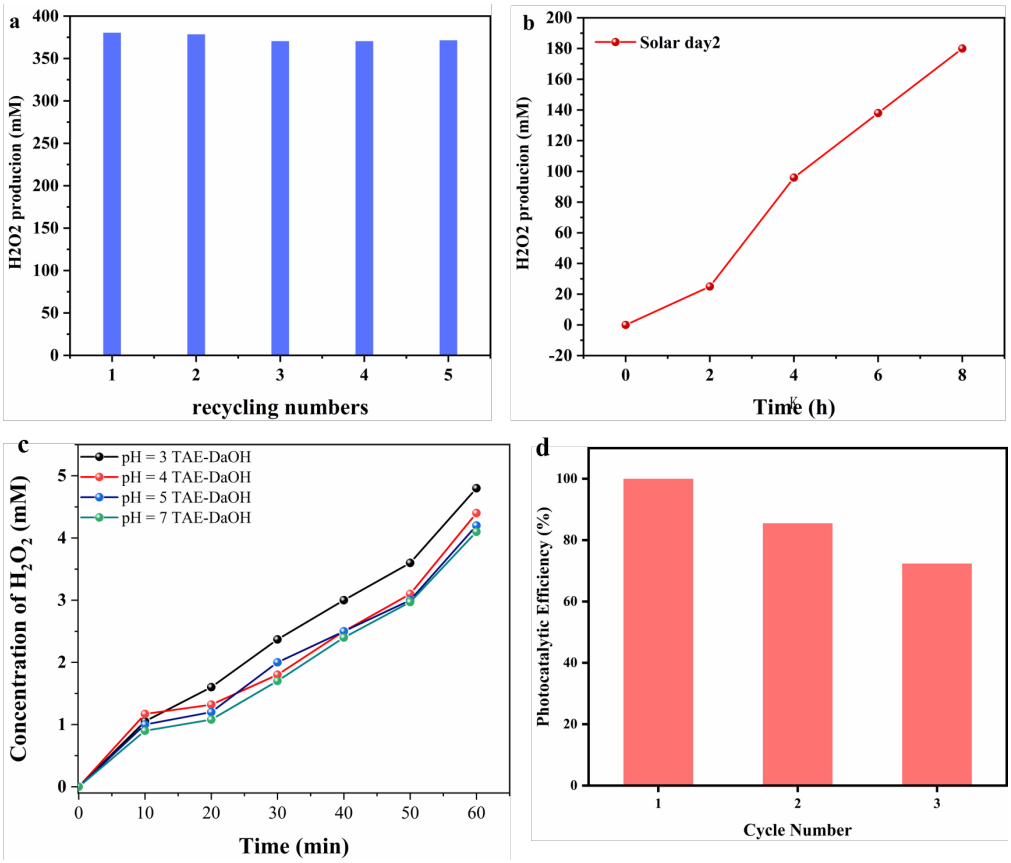

Figure S19. m/V = 1 g/L, water/BA = 5:5, pH = 7 (a) recycling experiment, (b) Solar experiment, (c) pH experiments of TAE-DaOH, (d) recycling experiment of TAE-ben.

4. Mechanism studies

4.1.Reduction reaction of O_2

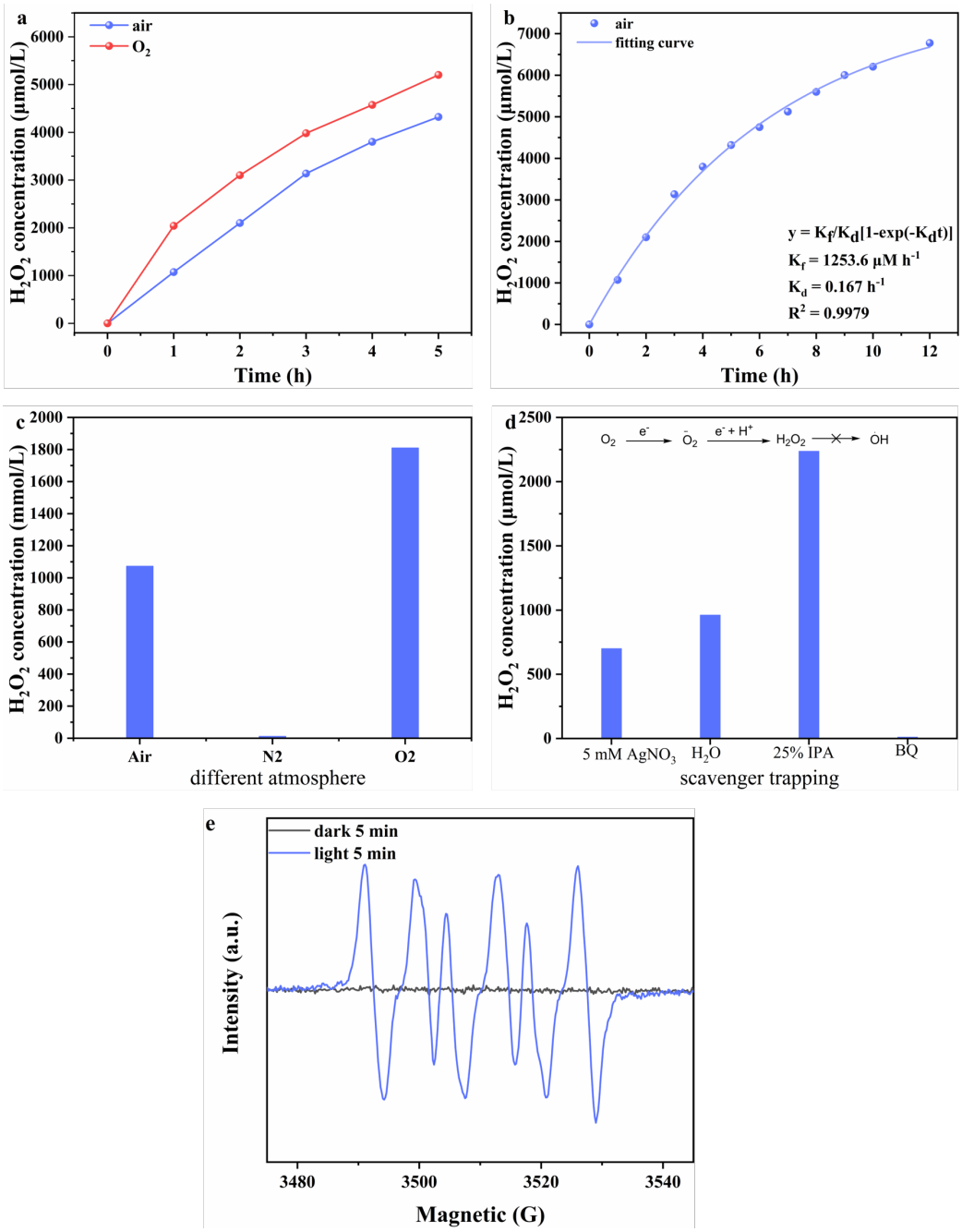

Figure S20. photocatalytic performance for non-sacrificial H_2O_2 production on different condition, m/V = 1g/L, V = 10 mL, pH = 7, light wavelength > 320 nm. (a) kinetic curve under air or oxygen in pure water; (b)fitting curve; (c) Photocatalytic performance of TAE-DaOH under different atmosphere, reaction time = 1 h; (d) scavenger trapping experiments, (e) radical experiment trapped by DMPO.

As shown in figure S19b, the experimental data was well fitted with the overall generation equation as follow:

$[H_2O_2] = (K_f/K_d)[1-\exp(-k_dt)]$

Where K_f and K_d are the composition and decomposition rate constant, respectively. The resulting K_f and K_d were derived to be 1.25 mM h^{-1} and 0.167 h^{-1}, respectively.

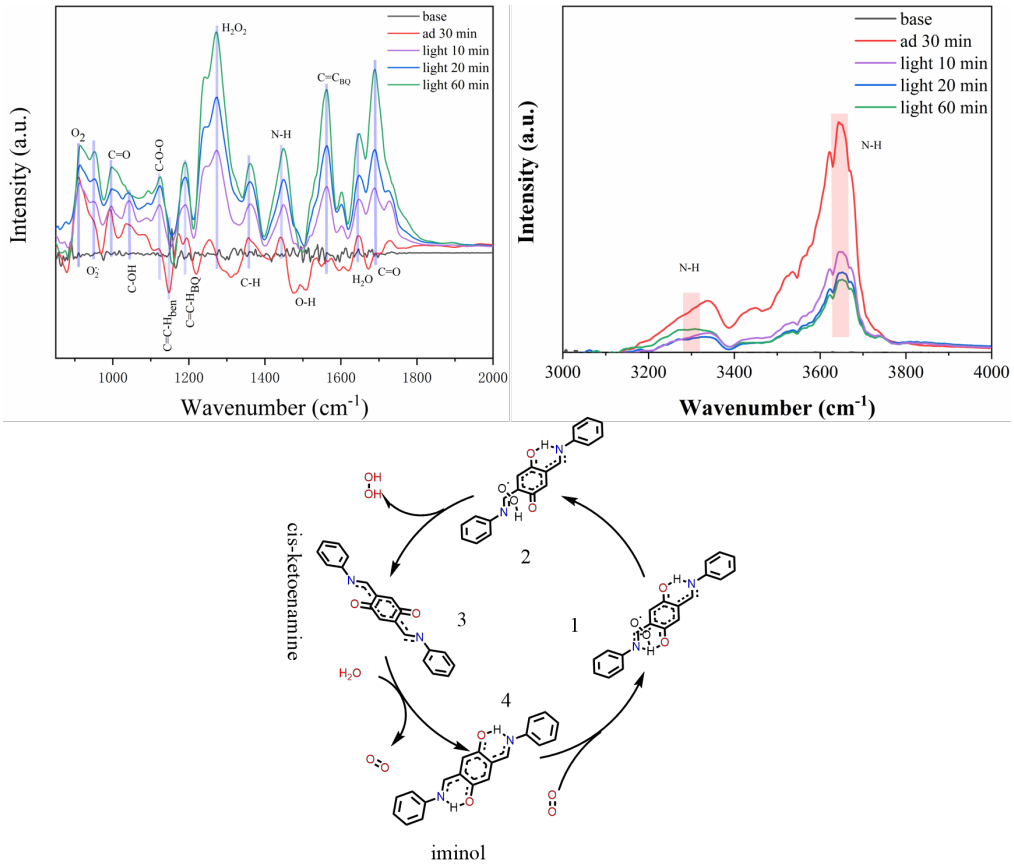

Figure S21. In situ IR of TAE-DaOH.

After adding water, many new peaks were observed, which was attributed to the conversion between iminol and ketoenamine.

4.2.Oxidation of BA

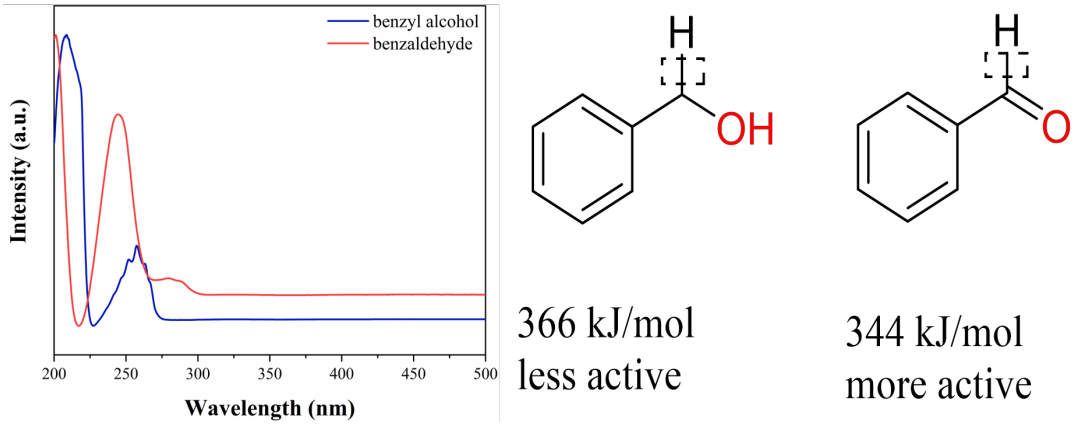

Figure S22. Uv absorption of benzyl alcohol and benzaldehyde.

The UV absorption of benzyl alcohol arranges from 200-300 nm as shown in figure S21, which is low than the wavelength range of Xe lamp. However, the band dissociation energy (BDE) of α-C-H in benzyl alcohol is 366 kJ/mol, suggesting that Benzyl alcohol was excited by light with 326 nm. The generated benzaldehyde (the BDE of PHC(O)-H is 344 kJ/mol) is much more reactive than benzyl alcohol.

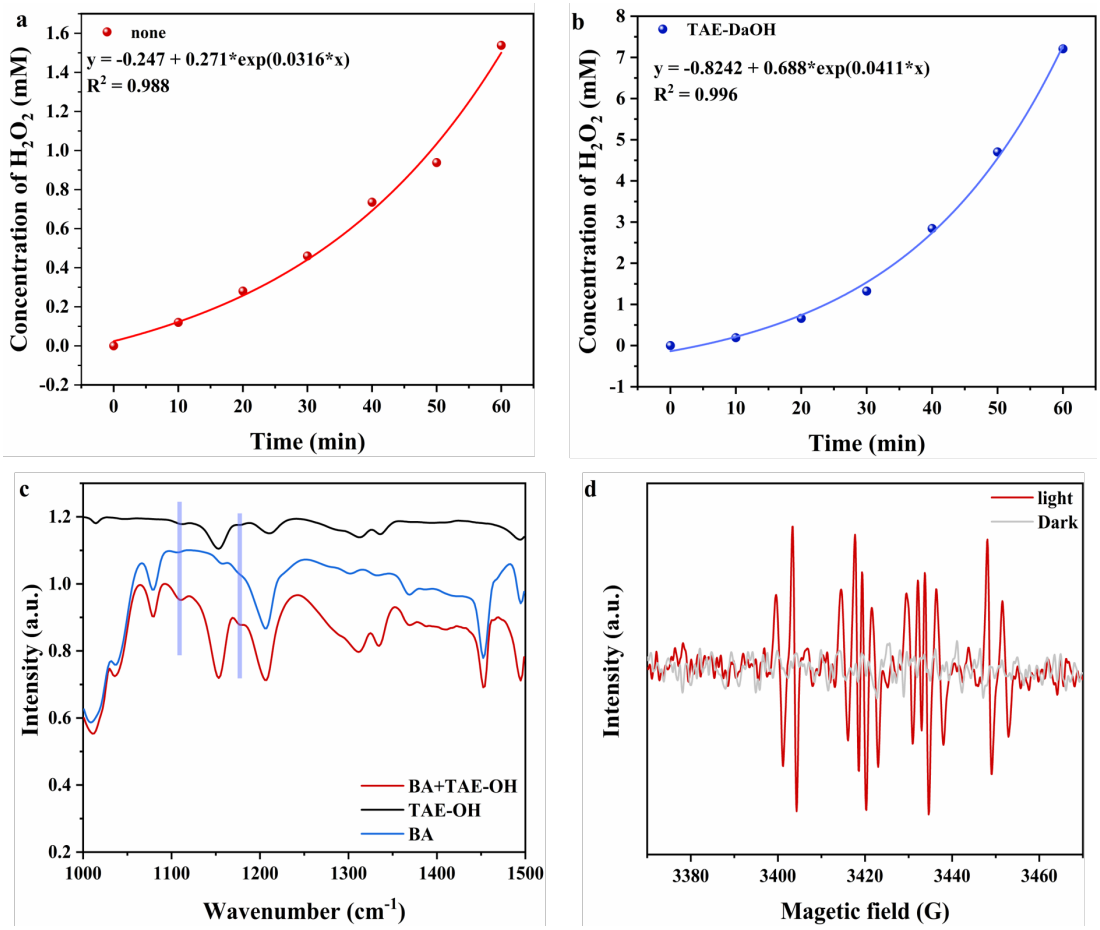

Figure S23. control experiment, V (BA): V (water) = 1:9. (a) generation of H_2O_2 in diphase system without addition of photocatalyst; (b) generation of H_2O_2 in diphase system with adding TAE-DaOH as catalyst; EPR experiment in diphase system without addition of catalyst; (c) FT-IR of TAE-DaOH, benzyl alcohol, and the mixture of them, respectively; (d) EPR detection of the mixture of BA and water, after illumination, characteristic peaks of α-hydroxybenzyl radicals were observed in diphase system without adding catalyst.

the rate of the reaction is expressed as follow[5]:

$$r = d[H_2O_2]/dt = K_1[BA] + K_2[BA][benzaldehyde]$$

$$= K_{1obv} + K_{2obv}[H_2O_2]$$

$$[H_2O_2] = K_{1obv}/K_{2obv}\,[\exp(K_{2obv}t)-1]$$

Where K_{1obv} and K_{2obv} are the non-autocatalytic rate constant and autocatalytic rate

constant, respectively. The resulting K_{1obv} and K_{2obv} are 1.69 mM h^{-1} and 2.47 h^{-1} (figure S22a). As a contrast, the K_{1obv}' and K_{2obv}' is 0.51 mM h^{-1} and 1.81 h^{-1} (K_{1obv}' and K_{2obv}' are the non-autocatalytic rate constant and autocatalytic rate constant in control experiment without adding TAE-DaOH, figure S23b). Furthermore, the concentration of H_2O_2 when TAE-DaOH worked as catalyst was much higher than that without any catalyst in diphase system (figure 3b). Benzyl alcohol was excited by light with 326 nm[6] and reacted with O_2 to generate α-hydroxybenzyl radicals and ·OOH, followed by formation of benzaldehyde and H_2O_2. The result was further confirmed by EPR. After illumination, characteristic peaks of α-hydroxybenzyl radicals were observed in diphase system without adding catalyst (figure S22d). However, the generation of α-hydroxybenzyl radicals from BA is unactive, resulting in low generation of H_2O_2. Intermolecular hydrogen bond between TAE-DaOH and BA can enhance the interaction between holes and BA, leading to fast production of both α-hydroxybenzyl radicals and benzaldehyde[7]. As a result, the generation of H_2O_2 when TAE-DaOH worked as catalyst was much higher than that without catalyst in diphase system.

As shown in figure S23c, redshift was observed. Peaks at 1153 cm^{-1} and 1205 cm^{-1} shifted to 1108 cm^{-1} and 1177 cm^{-1}.

4.3.autocatalysis

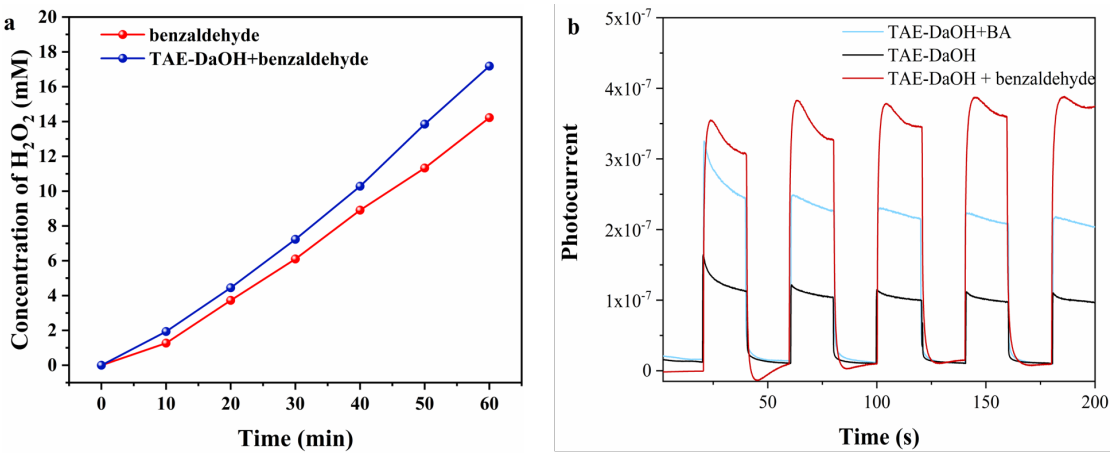

Figure S24. Role of benzaldehyde. (a) control experiment, V (BA): V (water) = 1:9, m/V = 1g/L, (b) photocurrent under different condition.

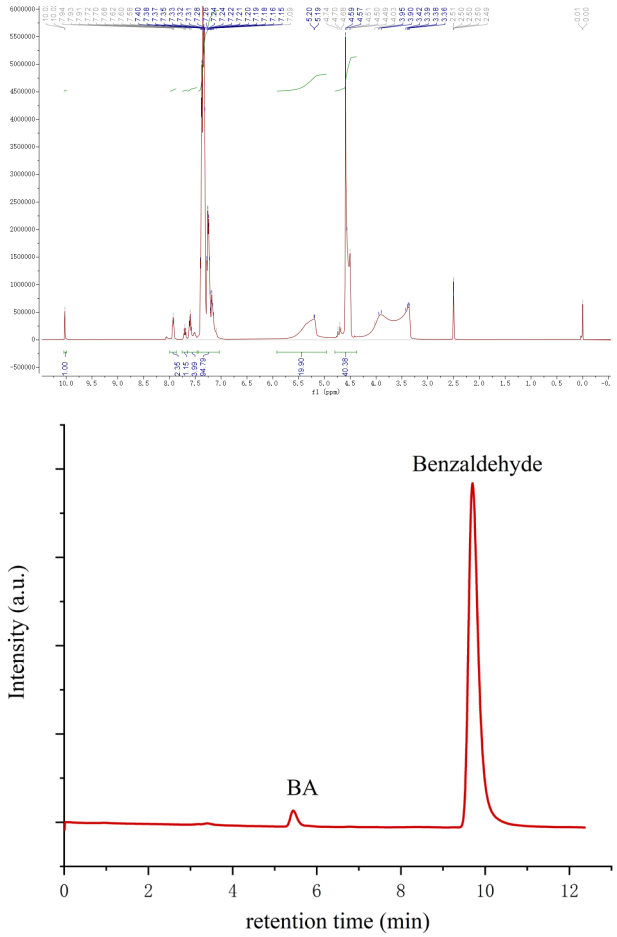

Figure S25. 1H-NMR and HPLC after irradiation. The characteristic peak of benzaldehyde (10.0 ppm) is observed from NMR, demonstrating the generation of benzaldehyde. It is similar in HPLC.

4.4. intramolecular hydrogen bond: suppression both decomposition of H_2O_2 and oxidation of catalysis

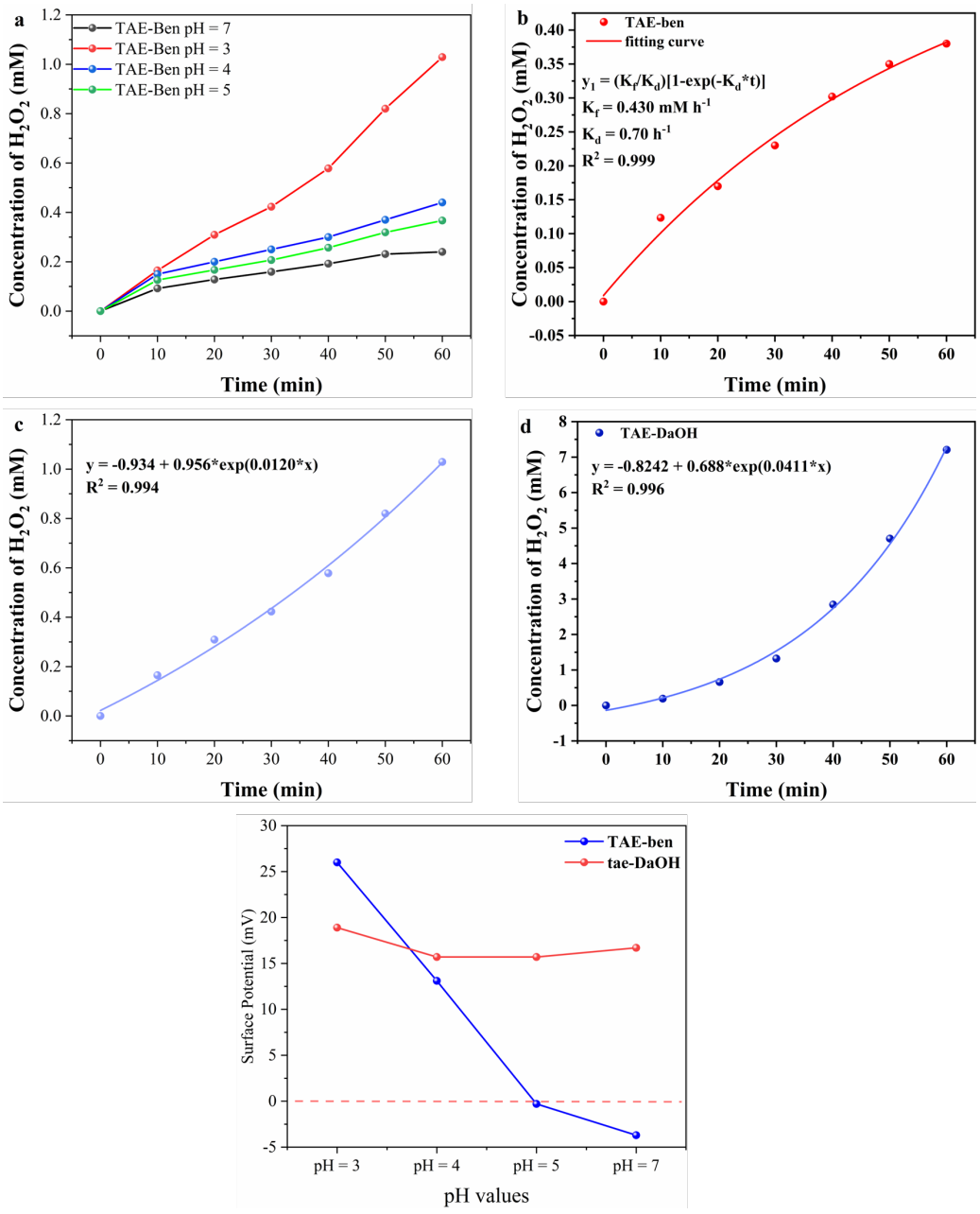

Figure S26. Contrast of reaction curve of TAE-ben. (a) performance of TAE-ben at different pH values, m/V = 1 g/L, BA/water = 1:9, (b), (c), (d) fitting curve of TAE-ben at pH = 7, TAE-ben at

pH = 3, and TAE-DaOH, respectively; (e) surface potential of TAE-ben and TAE-DaOH at different pH values, m/V = 1 g/L.

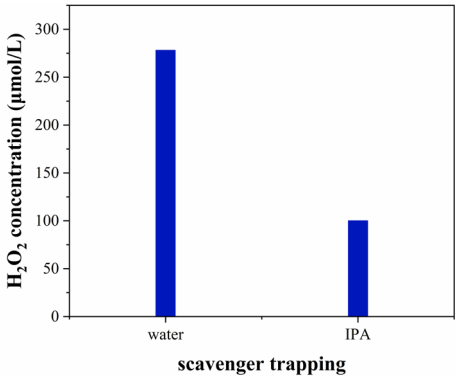

Figure S27. Scavenger trapping experiment. TAE-ben was catalyst, m/V = 1g/L, V(IPA)/V(water) = 1:9.

Figure S28. Contrast of TAE-ben before and after photocatalysis.

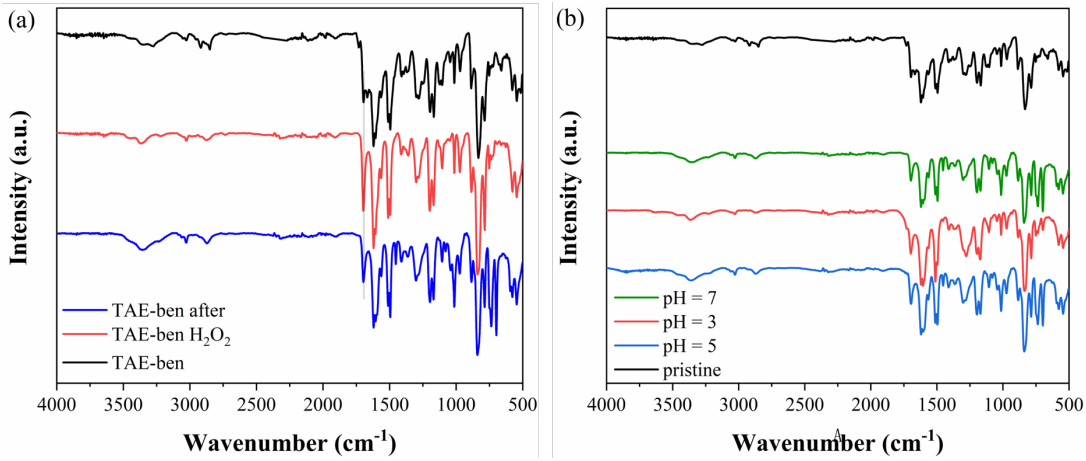

Figure S29. FT-IR of TAE-ben before and after irradiation.

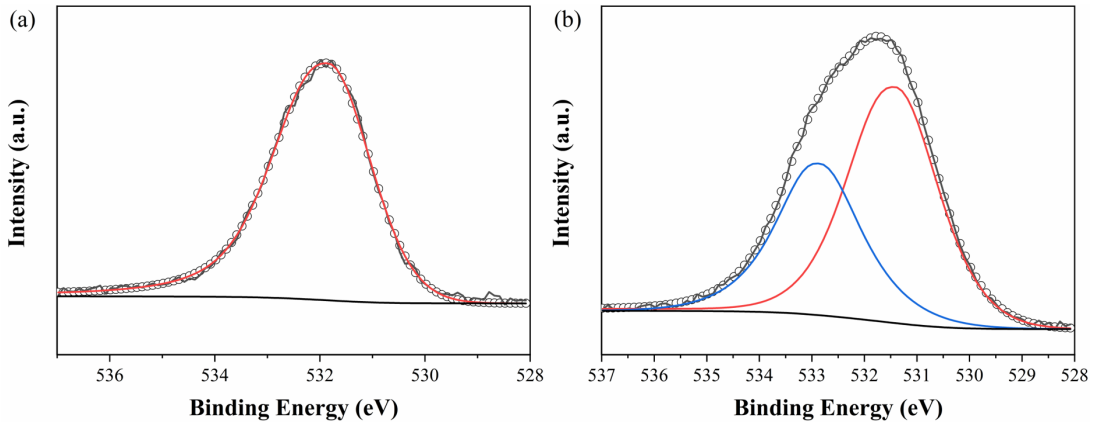

Figure S30. O 1s XPS spectra of TAE-ben before and after irradiation., the peaks at 531. 8 eV (figure a) and 531.5 eV are characteristic one of H2O, while the presence of peak at 532.9 eV is attributed to amide.

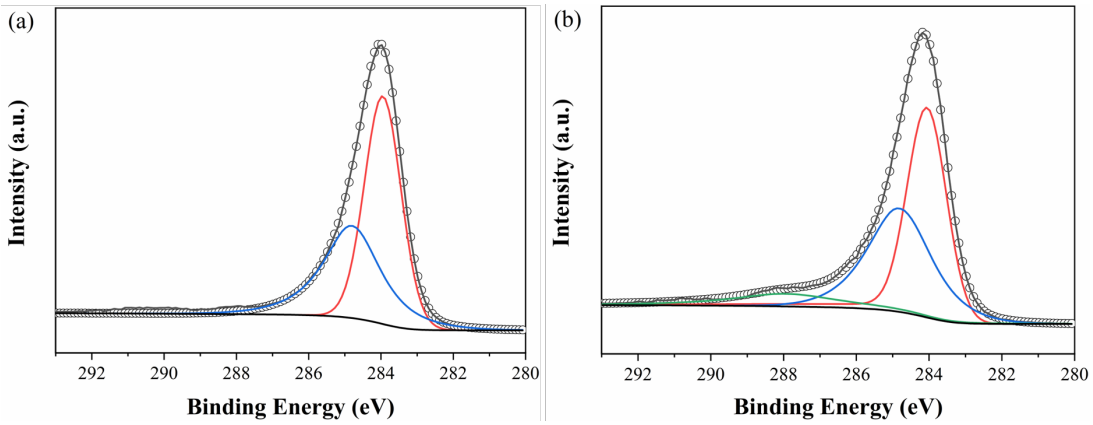

Figure S31. C 1s XPS spectra of TAE-ben before and after irradiation.

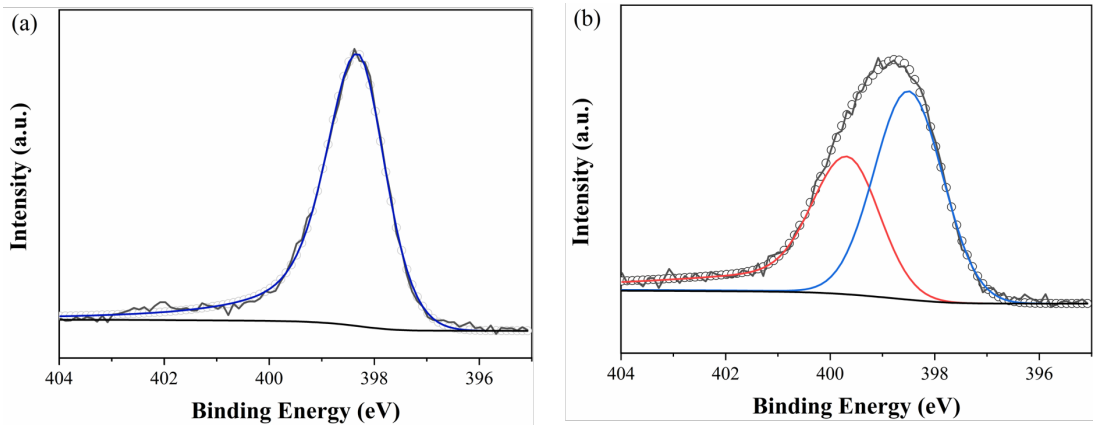

Figure S32. N 1s XPS spectra of TAE-ben before and after irradiation.

Experimental condition of figure S23-S26: m/V = 1 g/L, water/BA = 9:1, pH = 7, reaction time per run = 6 h, total runs = 3, total time = 18 h.

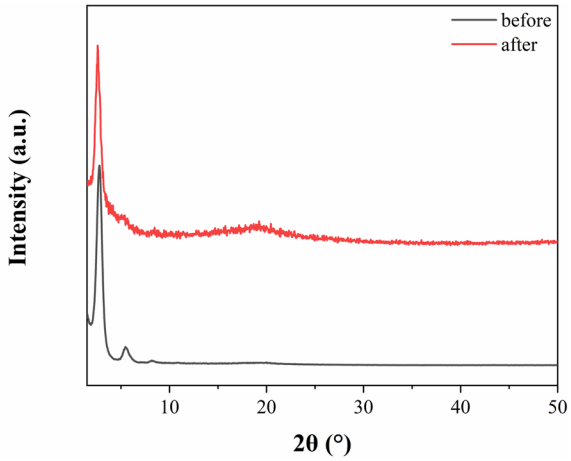

Figure S33. XRD of TAE-ben before and after irradiation.

Figure S34. Photo-reaction vessel with radius 2.25 cm. The radius of stir bar is 0.5 cm.

Figure S35. PLS-SXE 300/300 UV Xe lamp purchased from perfect light company.

5. Comparison with other photocatalysts

Catalyst	Reaction conditions	Rate $\mu mol\ h^{-1}\ g_{cat}^{-1}$	SCC efficiency	Ref
g-C_3N_4	O_2; 90 vol % of ethanol, Xe-lamp 420−500 nm	125	N/A	[8]
g-C_3N_4/PDI/r $GO_{0.05}$	O_2; in the pure water; Xe-lamp λ>420 nm	24.17	0.2	[9]
AQ-augmented g-C_3N_4	O_2; 10 vol % of isopropanol, AM 1.5	361	0.178	[10]
Sb-SAPC15	O_2; in pure water; Xe lamp λ>420 nm	588.1	0.61	[11]
AKMT	O_2; 0.5 g/L (catalyst), 10 vol% ethanol in water; pH=3, AM 1.5G, 298 K	6820	N/A	[12]
Resorcinol-formaldehyde resins	O_2; in the pure water; Xe-lamp λ>420nm	82.5	0.5	[13]
Ni/MIL-125-NH_2	O_2; 20% of benzyl alcohol in acetonitrile; Xe-lamp, λ>420 nm	937	N/A	[14]
MIL-125- R7	O_2; the two-phase system composed of benzyl alcohol (5.0 mL) and water (2.0 mL); Xe-lamp 500 W, λ≥420 nm	800	N/A	[15]
TiO_2	O_2; alcohols (1.75 mmol) in 5 ml water; Hg-lamp λ>280 nm	10.9	N/A	[16]
COF-TfpBpy	O_2; pure water; Xe-lamp λ≥420 nm	2084	0.57	[17]
TPB-DMTP-COF	O_2; three phase system Xe-lamp λ≥420 nm	2882	N/A	[18]
CTF-Ph	O_2; 50 vol% of benzyl alcohol in acetonitrile containing 0.96 wt% of water; AM 1.5G	46933	1.097	[19]
TAE-ben	air; 10 vol% of benzyl alcohol in water; AM 1.5G	280	N/A	This work
TAE-DaOH	air; 50 vol% of benzyl alcohol in water; AM 1.5G	61300	N/A	This work
TAE-DaOH	air; 50 vol% of benzyl alcohol in water; Solar light	26760	N/A	This work

6. Computational part

6.1 Computation Methods:

All density functional theory (DFT) calculations were performed through the Gaussian 09 software. Optimized geometries and harmonic frequencies of all the structures using the PCM implicit solvation (water) model were obtained at the UB3LYP/6-31G(d,p) level of theory with Grimme's D3 dispersion correction (with the Becke-Johnson damping). Normal mode analyses were performed to all optimized structures, to confirm that these structures are corresponding to local minima (no imaginary frequencies) or saddle point (unique imaginary frequency) on the potential energy surface. Each transition state was further verified by the intrinsic reaction coordinate (IRC) calculations.

6.2 The supplementary discussion of oxidation rection of catalyst models by resulted H_2O_2

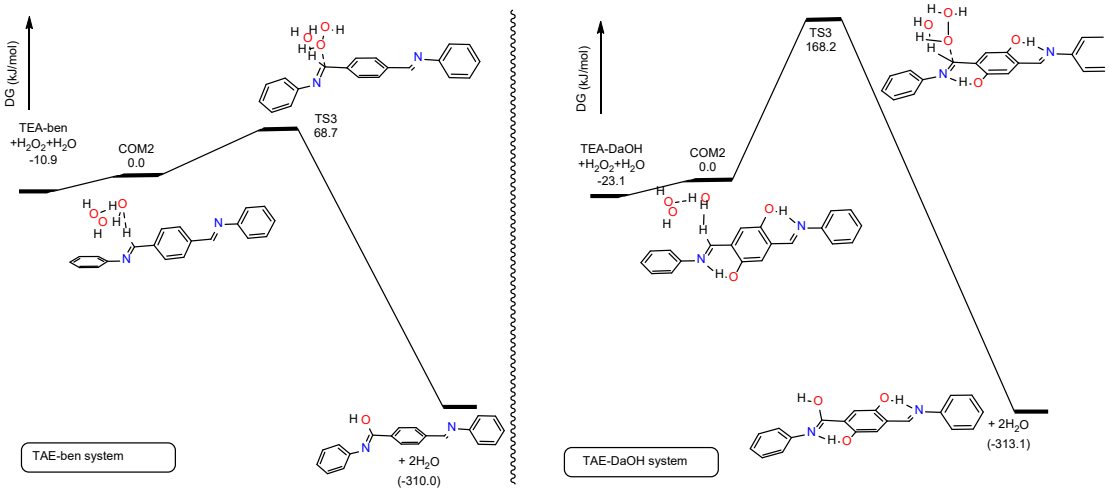

Figure S36. Oxidation mechanism of the TAE-ben and TAE-DaOH and the energy (in kJ/mol) diagram for two systems.

DFT calculation in Figure S35 indicates that TAE-ben catalyst could be oxidized by resulted H_2O_2 with a relatively small energy barrier of 68.7 kJ/mol, while the oxidation of TAE-DaOH is hindered in kinetics with a rather lager barrier of 168.2 kJ/mol. It means that TAE-ben is unstable during the production of H_2O_2 and cannot steadily convert O_2 to H_2O_2, which is in accordance with the observation in the present experiments. In addition, spin contamination $<s^2>$ of 0.983 and the longer O-O bond (2.272 Å) of TS3 in TAE-ben system feature the H_2O_2 moiety of typical diradical properties. For TAE-DaOH system, the H_2O_2 moiety remains the close-shell electron configuration with the shorter O-O bond of 1.908 Å in TS3. The above results imply that the hydrogen-bond in TAE-DaOH stabilizes H2O2 in the reaction and therefore guarantees the high yield of H_2O_2.

6.3 TAE-ben system

Summarized energy of all species of TAE-ben system in Figure 2

species	ZPG(a.u.)	ZPG-corrected Gibbs energy (a.u.)	ΔG(kJ/mol)

TAE	0.259627	-881.088508	
$PhCH_2OH$	0.102128	-346.709719	
O_2	-0.016201	-150.33335	
TAE+ $PhCH_2OH$+ O_2	0.345554	-1378.131577	3.6
IM1	0.376663	-1378.132941	0.0
TS1	0.372594	-1378.060788	189.3
IM2	0.376962	-1378.068293	169.6
TS2	0.370518	-1378.037415	250.7
IM3	0.384472	-1378.169117	-94.9
PhCHO	0.079619	-345.526192	
H_2O_2	0.0041	-151.544838	
TAE+ PhCHO+ O2	0.343346	-1378.159538	-69.8

Summarized energy of all species of TAE-ben system in Figure 3

species	ZPG(a.u.)	ZPG-corrected Gibbs energy (a.u.)	$\Delta G(\mathrm{kJ/mol})$
TAE	0.259627	-881.088508	
H_2O	0.003015	-76.422682	
O_2	-0.016201	-150.33335	
TAE+ H_2O + O_2	0.345554	-1378.131577	3.6
COM_2	0.298893	-1109.051874	0.0
TS3	0.372594	-1378.060788	189.3
Product+$2H_2O$	0.267386	-1109.170151	-310.0

Optimized structures of TAE-ben system

TAE-ben(singlet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.972374	1.212812	0.694549
2	6	0	-5.594660	1.004362	0.677342
3	6	0	-5.062185	-0.114117	0.013279
4	6	0	-5.931848	-1.029094	-0.600497
5	6	0	-7.306912	-0.808184	-0.587801
6	6	0	-7.832743	0.314280	0.057922
7	7	0	-3.684846	-0.396338	-0.039045
8	6	0	-2.802504	0.548213	-0.040650
9	6	0	-1.381454	0.255034	-0.042865
10	6	0	-0.462895	1.317295	-0.045100

11	6	0	0.909895	1.089491	-0.044015
12	6	0	-0.909779	-1.089495	-0.045067
13	6	0	0.463011	-1.317311	-0.046104
14	6	0	1.381576	-0.255048	-0.042724
15	6	0	2.802651	-0.548120	-0.040977
16	7	0	3.684834	0.396591	-0.039878
17	6	0	5.062170	0.114433	0.012667
18	6	0	5.594240	-1.002640	0.679291
19	6	0	5.932156	1.027713	-0.603189
20	6	0	7.307143	0.806294	-0.589911
21	6	0	7.832638	-0.314729	0.058582
22	6	0	6.971881	-1.211501	0.697213
23	1	0	-7.376014	2.074675	1.217037
24	1	0	-7.969492	-1.516036	-1.076088
25	1	0	-8.905139	0.480346	0.077195
26	1	0	-3.090202	1.604571	-0.054981
27	1	0	-0.822956	2.341352	-0.044953
28	8	0	-1.755091	-2.141508	-0.048787
29	1	0	0.823068	-2.341372	-0.047316
30	1	0	3.090618	-1.604441	-0.055142
31	1	0	4.935534	-1.684648	1.206819
32	1	0	5.510287	1.895951	-1.099262
33	1	0	7.969936	1.512773	-1.079906
34	1	0	8.904981	-0.481008	0.078443
35	1	0	7.375105	-2.072297	1.221782
36	1	0	-4.936416	1.687694	1.203790
37	1	0	-5.509517	-1.898293	-1.094462
38	1	0	-2.679435	-1.759633	-0.053909
39	8	0	1.755112	2.141584	-0.046889
40	1	0	2.679505	1.759867	-0.052841

COM1(triplet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.510854	2.231618	-0.302630
2	8	0	-2.980594	2.159364	-1.420591
3	6	0	-7.422815	-1.245653	1.127077
4	6	0	-6.059809	-1.361106	0.860174
5	6	0	-5.482709	-0.608689	-0.176550
6	6	0	-6.293493	0.233088	-0.953583

7	6	0	-7.652472	0.351463	-0.672733
8	6	0	-8.222383	-0.386421	0.368730
9	7	0	-4.117359	-0.677597	-0.506761
10	6	0	-3.215324	-0.863878	0.399287
11	6	0	-1.809697	-0.950853	0.054069
12	6	0	-0.860095	-1.125422	1.074821
13	6	0	0.496383	-1.184081	0.790002
14	6	0	-1.378022	-0.835428	-1.298314
15	6	0	-0.015235	-0.902430	-1.578408
16	6	0	0.931028	-1.068456	-0.558186
17	6	0	2.344424	-1.074981	-0.888530
18	7	0	3.236825	-1.213962	0.034585
19	6	0	4.616655	-1.165873	-0.226275
20	6	0	5.180013	-0.582926	-1.374855
21	6	0	5.462385	-1.703966	0.755613
22	6	0	6.844673	-1.686922	0.583093
23	6	0	7.400164	-1.117210	-0.564922
24	6	0	6.562389	-0.563026	-1.537912
25	1	0	-7.863591	-1.836849	1.923891
26	1	0	-8.268998	1.015290	-1.270841
27	1	0	-9.283749	-0.302503	0.579520
28	1	0	-3.472135	-0.935112	1.461229
29	1	0	-1.184971	-1.197248	2.107972
30	8	0	1.385607	-1.314972	1.810226
31	8	0	-2.249754	-0.650812	-2.308989
32	1	0	0.312737	-0.800549	-2.607874
33	1	0	2.606014	-0.961357	-1.943715
34	1	0	4.545235	-0.115108	-2.117817
35	1	0	5.015853	-2.137524	1.644754
36	1	0	7.487790	-2.112229	1.347167
37	1	0	8.477241	-1.093889	-0.696711
38	1	0	6.989099	-0.101848	-2.423273
39	1	0	-5.449966	-2.053710	1.431192
40	1	0	-5.835532	0.799838	-1.757809
41	1	0	-3.160213	-0.609610	-1.893704
42	1	0	2.301005	-1.311094	1.379422
43	6	0	3.850036	2.136206	0.345834
44	6	0	2.908406	1.982384	1.362547
45	6	0	1.538145	2.040986	1.079879
46	6	0	1.127566	2.236776	-0.242321
47	6	0	2.067489	2.386824	-1.263541
48	6	0	3.432173	2.343139	-0.970909
49	6	0	0.515565	1.912457	2.192559
50	8	0	0.932569	1.076982	3.261481

51	1	0	-0.438338	1.573350	1.763017
52	1	0	0.330911	2.899326	2.636108
53	1	0	1.145908	0.207188	2.874126
54	1	0	4.909555	2.078780	0.575529
55	1	0	3.225175	1.804004	2.385083
56	1	0	0.067329	2.252314	-0.477030
57	1	0	1.733820	2.528405	-2.287342
58	1	0	4.165111	2.457603	-1.763526

TS1(triplet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.637312	0.053520	1.961058
2	8	0	-1.904241	0.215981	1.658360
3	6	0	8.017756	1.608359	-0.502948
4	6	0	6.704284	1.159821	-0.618754
5	6	0	6.316243	-0.033547	0.013086
6	6	0	7.263339	-0.779420	0.730696
7	6	0	8.571660	-0.317463	0.851182
8	6	0	8.952801	0.877995	0.236267
9	7	0	5.011679	-0.556653	-0.061608
10	6	0	3.975617	0.194657	-0.218088
11	6	0	2.647727	-0.393214	-0.334252
12	6	0	1.547083	0.415118	-0.529994
13	6	0	0.212990	-0.115062	-0.670398
14	6	0	2.472370	-1.822652	-0.255963
15	6	0	1.181603	-2.372114	-0.331142
16	6	0	0.061617	-1.564829	-0.466947
17	6	0	-1.252047	-2.170382	-0.456844
18	7	0	-2.295297	-1.505550	-0.075894
19	6	0	-3.615048	-2.003906	-0.046864
20	6	0	-3.954731	-3.361323	-0.151254
21	6	0	-4.618315	-1.035344	0.104127
22	6	0	-5.956217	-1.418421	0.129634
23	6	0	-6.299154	-2.767428	0.016218
24	6	0	-5.295888	-3.733249	-0.121295
25	1	0	8.315146	2.525830	-1.000887
26	1	0	9.295505	-0.894015	1.418243
27	1	0	9.975258	1.231990	0.320175
28	1	0	4.041594	1.285449	-0.256232

29	1	0	1.658589	1.492047	-0.609525
30	8	0	-0.752628	0.613722	-1.012034
31	8	0	3.509732	-2.635166	-0.091402
32	1	0	1.080467	-3.447646	-0.227657
33	1	0	-1.332926	-3.211992	-0.770387
34	1	0	-3.187967	-4.123259	-0.236125
35	1	0	-4.343646	0.010442	0.181758
36	1	0	-6.725316	-0.660739	0.237732
37	1	0	-7.341264	-3.069296	0.040518
38	1	0	-5.560112	-4.783013	-0.197568
39	1	0	5.993913	1.714343	-1.222758
40	1	0	6.952253	-1.707723	1.198667
41	1	0	4.335030	-2.045817	-0.036889
42	1	0	-2.101502	-0.496415	0.691331
43	6	0	-4.867128	2.492210	-1.367328
44	6	0	-3.533020	2.813448	-1.103005
45	6	0	-3.078068	2.943282	0.212097
46	6	0	-3.982792	2.735694	1.262314
47	6	0	-5.317879	2.426173	1.002824
48	6	0	-5.766714	2.305284	-0.316403
49	6	0	-1.638942	3.327130	0.515395
50	8	0	-0.776279	3.285390	-0.605000
51	1	0	-1.272631	2.685825	1.328908
52	1	0	-1.619998	4.359192	0.890083
53	1	0	-0.704991	2.337713	-0.856954
54	1	0	-5.204036	2.390696	-2.395093
55	1	0	-2.829096	2.965918	-1.913931
56	1	0	-3.636531	2.813981	2.289657
57	1	0	-6.006843	2.269607	1.827800
58	1	0	-6.804631	2.059832	-0.520378

IM2(triplet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.080515	0.748253	2.075665
2	8	0	-2.949079	0.548228	1.090280
3	6	0	7.788502	1.337712	-0.735268
4	6	0	6.473152	0.881291	-0.760514
5	6	0	6.104997	-0.227391	0.020033
6	6	0	7.072276	-0.884578	0.795060

7	6	0	8.382839	-0.414399	0.822850
8	6	0	8.744712	0.698556	0.059591
9	7	0	4.799097	-0.751514	0.048153
10	6	0	3.755738	-0.030314	-0.186146
11	6	0	2.433508	-0.639547	-0.183669
12	6	0	1.309642	0.115321	-0.437701
13	6	0	-0.019563	-0.446288	-0.441795
14	6	0	2.280313	-2.045410	0.091803
15	6	0	0.991806	-2.620477	0.100933
16	6	0	-0.148789	-1.876580	-0.143678
17	6	0	-1.426933	-2.577483	-0.105415
18	7	0	-2.568857	-1.998375	-0.212831
19	6	0	-3.743419	-2.768129	-0.207446
20	6	0	-3.834755	-4.042536	-0.796731
21	6	0	-4.885715	-2.196179	0.378994
22	6	0	-6.082585	-2.906092	0.418362
23	6	0	-6.166571	-4.178010	-0.156515
24	6	0	-5.042510	-4.736807	-0.770944
25	1	0	8.070805	2.188825	-1.346781
26	1	0	9.122954	-0.920743	1.434125
27	1	0	9.768513	1.058279	0.072474
28	1	0	3.812211	1.044142	-0.378189
29	1	0	1.387329	1.179835	-0.636801
30	8	0	-1.013670	0.292196	-0.712633
31	8	0	3.325422	-2.811429	0.343180
32	1	0	0.919795	-3.682426	0.313257
33	1	0	-1.346690	-3.660727	0.051732
34	1	0	-2.973851	-4.466755	-1.303324
35	1	0	-4.802377	-1.205523	0.813045
36	1	0	-6.955122	-2.463030	0.888526
37	1	0	-7.104875	-4.723337	-0.139386
38	1	0	-5.108524	-5.714103	-1.239282
39	1	0	5.745853	1.361887	-1.406159
40	1	0	6.776055	-1.749447	1.379676
41	1	0	4.148971	-2.204195	0.295047
42	1	0	-2.401701	0.192535	0.327266
43	6	0	-4.020568	4.749803	-1.284970
44	6	0	-2.706637	4.302887	-1.133350
45	6	0	-2.245322	3.857733	0.110131
46	6	0	-3.125056	3.858652	1.198966
47	6	0	-4.437086	4.310705	1.052380
48	6	0	-4.889310	4.759333	-0.191281
49	6	0	-0.806051	3.410983	0.285733
50	8	0	-0.215964	2.928712	-0.913743

51	1	0	-0.756651	2.655393	1.081795
52	1	0	-0.197144	4.263917	0.611515
53	1	0	-0.584374	2.030899	-1.044030
54	1	0	-4.366694	5.089917	-2.256986
55	1	0	-2.027572	4.282292	-1.979306
56	1	0	-2.785662	3.480534	2.159331
57	1	0	-5.110152	4.301360	1.904960
58	1	0	-5.912014	5.105498	-0.308245

TS2(triplet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.707222	-1.233721	1.701722
2	8	0	1.900538	-0.517354	1.905487
3	6	0	-8.036433	-1.381090	-0.604653
4	6	0	-6.713763	-0.957818	-0.708382
5	6	0	-6.265225	0.125568	0.065624
6	6	0	-7.162191	0.792035	0.913738
7	6	0	-8.480595	0.355539	1.018991
8	6	0	-8.921410	-0.733037	0.262049
9	7	0	-4.946673	0.615913	0.015550
10	6	0	-3.942417	-0.129286	-0.300024
11	6	0	-2.603925	0.438212	-0.379862
12	6	0	-1.529847	-0.346567	-0.744201
13	6	0	-0.195277	0.184763	-0.872253
14	6	0	-2.385605	1.831841	-0.085609
15	6	0	-1.077968	2.361511	-0.121924
16	6	0	0.011344	1.574222	-0.442482
17	6	0	1.352271	2.137950	-0.339639
18	7	0	2.366891	1.395882	-0.061636
19	6	0	3.676482	1.899444	0.007708
20	6	0	4.100705	3.100064	-0.591550
21	6	0	4.612279	1.097335	0.683041
22	6	0	5.938560	1.505800	0.793124
23	6	0	6.351608	2.708750	0.215569
24	6	0	5.429943	3.497758	-0.481686
25	1	0	-8.380577	-2.212810	-1.211200
26	1	0	-9.165538	0.869216	1.685972
27	1	0	-9.951564	-1.066386	0.335624
28	1	0	-4.044200	-1.198362	-0.504274

29	1	0	-1.668889	-1.395716	-0.984481
30	8	0	0.730926	-0.499170	-1.383801
31	8	0	-3.388401	2.626096	0.251844
32	1	0	-0.946915	3.401941	0.158314
33	1	0	1.432097	3.224349	-0.452939
34	1	0	3.404982	3.704329	-1.163976
35	1	0	4.286027	0.154143	1.106871
36	1	0	6.651149	0.877430	1.317914
37	1	0	7.387419	3.023946	0.291996
38	1	0	5.752809	4.421530	-0.951698
39	1	0	-6.043632	-1.444255	-1.409195
40	1	0	-6.804994	1.637718	1.492303
41	1	0	-4.231049	2.049411	0.246797
42	1	0	1.991124	0.037435	1.084949
43	6	0	4.755037	-1.998275	-1.314482
44	6	0	3.407391	-2.334165	-1.201197
45	6	0	2.895100	-2.827269	0.010706
46	6	0	3.769022	-2.968065	1.105451
47	6	0	5.115451	-2.635477	0.988524
48	6	0	5.614795	-2.145945	-0.223000
49	6	0	1.459794	-3.151905	0.186946
50	8	0	0.630462	-3.112625	-0.917574
51	1	0	1.061087	-2.218993	1.011150
52	1	0	1.280406	-4.064142	0.764069
53	1	0	0.647676	-2.186617	-1.268178
54	1	0	5.137421	-1.622131	-2.258752
55	1	0	2.746352	-2.223299	-2.052715
56	1	0	3.380919	-3.337231	2.050747
57	1	0	5.776767	-2.752943	1.841748
58	1	0	6.662857	-1.878313	-0.313045

IM3(singlet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.490491	0.292499	2.452923
2	8	0	-3.540041	0.208539	1.444559
3	6	0	7.770864	1.548062	-0.628300
4	6	0	6.469761	1.049427	-0.626793
5	6	0	6.196134	-0.194923	-0.033250
6	6	0	7.247764	-0.938137	0.525135

7	6	0	8.543781	-0.428141	0.528801
8	6	0	8.810349	0.817520	-0.046112
9	7	0	4.911686	-0.768119	0.000611
10	6	0	3.846502	-0.037511	0.046416
11	6	0	2.525299	-0.636100	0.030974
12	6	0	1.390435	0.188943	0.088650
13	6	0	0.102633	-0.335077	0.074200
14	6	0	2.357534	-2.045042	-0.035389
15	6	0	1.064600	-2.562140	-0.060801
16	6	0	-0.076229	-1.741035	-0.008039
17	6	0	-1.354707	-2.441050	-0.100138
18	7	0	-2.538286	-1.949476	0.033974
19	6	0	-3.642563	-2.804370	-0.198013
20	6	0	-3.656321	-3.755392	-1.232651
21	6	0	-4.779435	-2.652813	0.612766
22	6	0	-5.889801	-3.471008	0.419081
23	6	0	-5.893989	-4.429808	-0.598044
24	6	0	-4.777147	-4.561487	-1.426336
25	1	0	7.975484	2.506111	-1.096250
26	1	0	9.347561	-1.006051	0.974199
27	1	0	9.822228	1.209958	-0.053368
28	1	0	3.896930	1.054102	0.113034
29	1	0	1.520183	1.265792	0.134386
30	8	0	-0.986530	0.477555	0.135815
31	8	0	3.406754	-2.888900	-0.081233
32	1	0	0.945312	-3.638538	-0.129278
33	1	0	-1.243423	-3.511666	-0.306726
34	1	0	-2.806093	-3.836206	-1.902065
35	1	0	-4.770401	-1.898299	1.391665
36	1	0	-6.757853	-3.355292	1.060934
37	1	0	-6.765494	-5.057846	-0.753361
38	1	0	-4.780770	-5.286649	-2.234432
39	1	0	5.675329	1.606905	-1.111953
40	1	0	7.026175	-1.905623	0.964164
41	1	0	4.228043	-2.317140	-0.053764
42	1	0	-3.152135	-0.487887	0.845458
43	6	0	-4.555182	3.333047	0.130653
44	6	0	-3.185490	3.125208	0.027928
45	6	0	-2.345686	4.189864	-0.346860
46	6	0	-2.895238	5.455318	-0.616148
47	6	0	-4.269334	5.655729	-0.518487
48	6	0	-5.098073	4.594097	-0.144347
49	6	0	-0.896050	4.035436	-0.457435
50	8	0	-0.257495	2.996485	-0.284596

51	1	0	-1.740185	0.552903	1.881950
52	1	0	-0.344901	4.955732	-0.719829
53	1	0	-0.722909	1.422040	-0.017956
54	1	0	-5.195968	2.510622	0.430258
55	1	0	-2.787335	2.143666	0.249442
56	1	0	-2.240217	6.273936	-0.900771
57	1	0	-4.693924	6.631652	-0.728731
58	1	0	-6.169464	4.749829	-0.063626

COM2(singlet state)

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.437086	1.858126	1.284287
2	1	0	-4.841866	0.971551	1.326843
3	8	0	-5.067310	2.373237	0.080724
4	1	0	-5.582741	3.113171	0.442705
5	6	0	7.674414	2.516145	-0.755636
6	6	0	6.284064	2.454103	-0.704644
7	6	0	5.617672	1.237177	-0.924820
8	6	0	6.370939	0.092817	-1.243604
9	6	0	7.761536	0.166161	-1.310221
10	6	0	8.419703	1.372597	-1.058634
11	7	0	4.212767	1.243135	-0.861425
12	6	0	3.593978	0.221656	-0.391787
13	6	0	2.132169	0.138775	-0.353007
14	6	0	1.321835	1.174311	-0.850786
15	6	0	-0.060784	1.065804	-0.800142
16	6	0	1.525618	-1.005986	0.196396
17	6	0	0.143317	-1.117698	0.247366
18	6	0	-0.664045	-0.081908	-0.251258
19	6	0	-2.126038	-0.151808	-0.222358
20	7	0	-2.764871	-1.127485	0.316339
21	6	0	-4.169237	-1.113998	0.240825
22	6	0	-4.904265	-1.411085	1.402816
23	6	0	-4.858944	-0.835346	-0.952079
24	6	0	-6.252948	-0.830928	-0.972071
25	6	0	-6.979235	-1.091595	0.191856
26	6	0	-6.299083	-1.379751	1.379384
27	1	0	8.177669	3.459913	-0.568460
28	1	0	8.332405	-0.721045	-1.567604

29	1	0	9.502527	1.424941	-1.112978
30	1	0	4.131264	-0.642748	0.020647
31	1	0	1.798533	2.053264	-1.270456
32	1	0	-0.330739	-1.997485	0.668381
33	1	0	-3.637605	2.769173	-1.050253
34	1	0	-4.365253	-1.641832	2.316052
35	1	0	-4.295164	-0.639755	-1.858440
36	1	0	-6.773219	-0.617315	-1.900805
37	1	0	-8.064123	-1.079266	0.173899
38	1	0	-6.854457	-1.587774	2.288657
39	1	0	5.692145	3.335736	-0.480317
40	1	0	5.863248	-0.839359	-1.470063
41	8	0	-2.890333	2.857732	-1.672244
42	1	0	-3.158567	2.322175	-2.429767
43	1	0	-2.642001	0.701835	-0.673691
44	1	0	-0.699719	1.860924	-1.175976
45	1	0	2.150840	-1.807212	0.580417

TS3(singlet state with <S**2>= 0.7249)

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.712699	1.289240	0.871502
2	1	0	-3.684919	1.318332	0.896974
3	8	0	-2.810963	3.182322	0.787461
4	1	0	-1.842064	3.248577	0.778704
5	6	0	7.457038	2.331125	-1.386249
6	6	0	6.066789	2.286790	-1.316694
7	6	0	5.400100	1.057535	-1.183876
8	6	0	6.152484	-0.130635	-1.169766
9	6	0	7.543037	-0.079879	-1.257320
10	6	0	8.201761	1.148121	-1.356843
11	7	0	3.994956	1.080748	-1.121143
12	6	0	3.379401	0.239159	-0.373869
13	6	0	1.916845	0.168576	-0.310082
14	6	0	1.153346	1.049028	-1.092295
15	6	0	-0.237344	1.000329	-1.053262
16	6	0	1.260666	-0.762073	0.516252
17	6	0	-0.125600	-0.807527	0.559357
18	6	0	-0.881570	0.071999	-0.227285
19	6	0	-2.371683	0.081909	-0.189722

20	7	0	-3.000592	-0.899507	0.515059
21	6	0	-4.338176	-1.129653	0.276090
22	6	0	-4.904084	-2.232606	0.962390
23	6	0	-5.174655	-0.357484	-0.577845
24	6	0	-6.507794	-0.708973	-0.740639
25	6	0	-7.042501	-1.821311	-0.077146
26	6	0	-6.233860	-2.581895	0.775116
27	1	0	7.960642	3.289144	-1.473467
28	1	0	8.113288	-1.004056	-1.255872
29	1	0	9.284448	1.182442	-1.426276
30	1	0	3.919316	-0.468473	0.269599
31	1	0	1.654755	1.769285	-1.732364
32	1	0	-0.641601	-1.520802	1.191718
33	1	0	-3.218567	2.870003	-0.898728
34	1	0	-4.257961	-2.801244	1.622578
35	1	0	-4.791069	0.521812	-1.088851
36	1	0	-7.142125	-0.111565	-1.387922
37	1	0	-8.085633	-2.085711	-0.217095
38	1	0	-6.647314	-3.439439	1.295999
39	1	0	5.475556	3.196420	-1.348161
40	1	0	5.643905	-1.088384	-1.123700
41	8	0	-3.423709	2.510021	-1.795594
42	1	0	-4.166244	3.038349	-2.113474
43	1	0	-2.809078	0.451282	-1.117722
44	1	0	-0.833221	1.681785	-1.653863
45	1	0	1.859634	-1.439270	1.115016

TAE-DaOH system

Summarized energy of all species of TAE-DaOH system in Figure 3

species	ZPG(a.u.)	ZPG-corrected Gibbs energy (a.u.)	ΔG(kJ/mol)
TAE-DaOH	0.265292	-1031.558635	
$PhCH_2OH$	0.102128	-346.709719	
O_2	-0.016201	-150.33335	
TAE-DaOH+ $PhCH_2OH$+ O_2	0.351219	-1528.601704	-6.1
IM1	0.385281	-1528.599384	0
TS1	0.381904	1528.551321	125.9
IM2	0.382927	-1528.552011	124.3
TS2	0.383422	-1528.533138	173.8
IM3		-1528.617036	-46.3
PhCHO	0.079619	-345.526192	

H_2O_2	0.0041	-151.544838	
TAE-DaOH+ PhCHO+ O_2	0.349011	-1528.629665	-79.4

Summarized energy of all species of TAE-DaOH system in Figure 4

species	ZPG	ZPG-corrected Gibbs nergy(a.u)	$\Delta G(\mathrm{kJ/mol})$
TAE-DaOH	0.265292	-1031.558635	
H_2O	0.003015	-76.422682	
O2	-0.016201	-150.33335	
TAE-DaOH+ H_2O + O_2	0.272407	-1259.526155	-23.1
COM2	0.306604	-1259.517352	0.0
TS3	0.309368	-1259.453119	168.5
Product +2H^2O	0.274951	-1259.636619	-313.1

Optimized structures of TAE-DaOH system

TAE-DaOH

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.972374	1.212812	0.694549
2	6	0	-5.594660	1.004362	0.677342
3	6	0	-5.062185	-0.114117	0.013279
4	6	0	-5.931848	-1.029094	-0.600497
5	6	0	-7.306912	-0.808184	-0.587801
6	6	0	-7.832743	0.314280	0.057922
7	7	0	-3.684846	-0.396338	-0.039045
8	6	0	-2.802504	0.548213	-0.040650
9	6	0	-1.381454	0.255034	-0.042865
10	6	0	-0.462895	1.317295	-0.045100
11	6	0	0.909895	1.089491	-0.044015
12	6	0	-0.909779	-1.089495	-0.045067
13	6	0	0.463011	-1.317311	-0.046104
14	6	0	1.381576	-0.255048	-0.042724
15	6	0	2.802651	-0.548120	-0.040977
16	7	0	3.684834	0.396591	-0.039878
17	6	0	5.062170	0.114433	0.012667
18	6	0	5.594240	-1.002640	0.679291
19	6	0	5.932156	1.027713	-0.603189

20	6	0	7.307143	0.806294	-0.589911
21	6	0	7.832638	-0.314729	0.058582
22	6	0	6.971881	-1.211501	0.697213
23	1	0	-7.376014	2.074675	1.217037
24	1	0	-7.969492	-1.516036	-1.076088
25	1	0	-8.905139	0.480346	0.077195
26	1	0	-3.090202	1.604571	-0.054981
27	1	0	-0.822956	2.341352	-0.044953
28	8	0	-1.755091	-2.141508	-0.048787
29	1	0	0.823068	-2.341372	-0.047316
30	1	0	3.090618	-1.604441	-0.055142
31	1	0	4.935534	-1.684648	1.206819
32	1	0	5.510287	1.895951	-1.099262
33	1	0	7.969936	1.512773	-1.079906
34	1	0	8.904981	-0.481008	0.078443
35	1	0	7.375105	-2.072297	1.221782
36	1	0	-4.936416	1.687694	1.203790
37	1	0	-5.509517	-1.898293	-1.094462
38	1	0	-2.679435	-1.759633	-0.053909
39	8	0	1.755112	2.141584	-0.046889
40	1	0	2.679505	1.759867	-0.052841

COM1(triplet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.510854	2.231618	-0.302630
2	8	0	-2.980594	2.159364	-1.420591
3	6	0	-7.422815	-1.245653	1.127077
4	6	0	-6.059809	-1.361106	0.860174
5	6	0	-5.482709	-0.608689	-0.176550
6	6	0	-6.293493	0.233088	-0.953583
7	6	0	-7.652472	0.351463	-0.672733
8	6	0	-8.222383	-0.386421	0.368730
9	7	0	-4.117359	-0.677597	-0.506761
10	6	0	-3.215324	-0.863878	0.399287
11	6	0	-1.809697	-0.950853	0.054069
12	6	0	-0.860095	-1.125422	1.074821
13	6	0	0.496383	-1.184081	0.790002
14	6	0	-1.378022	-0.835428	-1.298314
15	6	0	-0.015235	-0.902430	-1.578408

16	6	0	0.931028	-1.068456	-0.558186
17	6	0	2.344424	-1.074981	-0.888530
18	7	0	3.236825	-1.213962	0.034585
19	6	0	4.616655	-1.165873	-0.226275
20	6	0	5.180013	-0.582926	-1.374855
21	6	0	5.462385	-1.703966	0.755613
22	6	0	6.844673	-1.686922	0.583093
23	6	0	7.400164	-1.117210	-0.564922
24	6	0	6.562389	-0.563026	-1.537912
25	1	0	-7.863591	-1.836849	1.923891
26	1	0	-8.268998	1.015290	-1.270841
27	1	0	-9.283749	-0.302503	0.579520
28	1	0	-3.472135	-0.935112	1.461229
29	1	0	-1.184971	-1.197248	2.107972
30	8	0	1.385607	-1.314972	1.810226
31	8	0	-2.249754	-0.650812	-2.308989
32	1	0	0.312737	-0.800549	-2.607874
33	1	0	2.606014	-0.961357	-1.943715
34	1	0	4.545235	-0.115108	-2.117817
35	1	0	5.015853	-2.137524	1.644754
36	1	0	7.487790	-2.112229	1.347167
37	1	0	8.477241	-1.093889	-0.696711
38	1	0	6.989099	-0.101848	-2.423273
39	1	0	-5.449966	-2.053710	1.431192
40	1	0	-5.835532	0.799838	-1.757809
41	1	0	-3.160213	-0.609610	-1.893704
42	1	0	2.301005	-1.311094	1.379422
43	6	0	3.850036	2.136206	0.345834
44	6	0	2.908406	1.982384	1.362547
45	6	0	1.538145	2.040986	1.079879
46	6	0	1.127566	2.236776	-0.242321
47	6	0	2.067489	2.386824	-1.263541
48	6	0	3.432173	2.343139	-0.970909
49	6	0	0.515565	1.912457	2.192559
50	8	0	0.932569	1.076982	3.261481
51	1	0	-0.438338	1.573350	1.763017
52	1	0	0.330911	2.899326	2.636108
53	1	0	1.145908	0.207188	2.874126
54	1	0	4.909555	2.078780	0.575529
55	1	0	3.225175	1.804004	2.385083
56	1	0	0.067329	2.252314	-0.477030
57	1	0	1.733820	2.528405	-2.287342
58	1	0	4.165111	2.457603	-1.763526

TS1(triplet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.637312	0.053520	1.961058
2	8	0	-1.904241	0.215981	1.658360
3	6	0	8.017756	1.608359	-0.502948
4	6	0	6.704284	1.159821	-0.618754
5	6	0	6.316243	-0.033547	0.013086
6	6	0	7.263339	-0.779420	0.730696
7	6	0	8.571660	-0.317463	0.851182
8	6	0	8.952801	0.877995	0.236267
9	7	0	5.011679	-0.556653	-0.061608
10	6	0	3.975617	0.194657	-0.218088
11	6	0	2.647727	-0.393214	-0.334252
12	6	0	1.547083	0.415118	-0.529994
13	6	0	0.212990	-0.115062	-0.670398
14	6	0	2.472370	-1.822652	-0.255963
15	6	0	1.181603	-2.372114	-0.331142
16	6	0	0.061617	-1.564829	-0.466947
17	6	0	-1.252047	-2.170382	-0.456844
18	7	0	-2.295297	-1.505550	-0.075894
19	6	0	-3.615048	-2.003906	-0.046864
20	6	0	-3.954731	-3.361323	-0.151254
21	6	0	-4.618315	-1.035344	0.104127
22	6	0	-5.956217	-1.418421	0.129634
23	6	0	-6.299154	-2.767428	0.016218
24	6	0	-5.295888	-3.733249	-0.121295
25	1	0	8.315146	2.525830	-1.000887
26	1	0	9.295505	-0.894015	1.418243
27	1	0	9.975258	1.231990	0.320175
28	1	0	4.041594	1.285449	-0.256232
29	1	0	1.658589	1.492047	-0.609525
30	8	0	-0.752628	0.613722	-1.012034
31	8	0	3.509732	-2.635166	-0.091402
32	1	0	1.080467	-3.447646	-0.227657
33	1	0	-1.332926	-3.211992	-0.770387
34	1	0	-3.187967	-4.123259	-0.236125
35	1	0	-4.343646	0.010442	0.181758
36	1	0	-6.725316	-0.660739	0.237732
37	1	0	-7.341264	-3.069296	0.040518
38	1	0	-5.560112	-4.783013	-0.197568

39	1	0	5.993913	1.714343	-1.222758
40	1	0	6.952253	-1.707723	1.198667
41	1	0	4.335030	-2.045817	-0.036889
42	1	0	-2.101502	-0.496415	0.691331
43	6	0	-4.867128	2.492210	-1.367328
44	6	0	-3.533020	2.813448	-1.103005
45	6	0	-3.078068	2.943282	0.212097
46	6	0	-3.982792	2.735694	1.262314
47	6	0	-5.317879	2.426173	1.002824
48	6	0	-5.766714	2.305284	-0.316403
49	6	0	-1.638942	3.327130	0.515395
50	8	0	-0.776279	3.285390	-0.605000
51	1	0	-1.272631	2.685825	1.328908
52	1	0	-1.619998	4.359192	0.890083
53	1	0	-0.704991	2.337713	-0.856954
54	1	0	-5.204036	2.390696	-2.395093
55	1	0	-2.829096	2.965918	-1.913931
56	1	0	-3.636531	2.813981	2.289657
57	1	0	-6.006843	2.269607	1.827800
58	1	0	-6.804631	2.059832	-0.520378

IM2(triplet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.080515	0.748253	2.075665
2	8	0	-2.949079	0.548228	1.090280
3	6	0	7.788502	1.337712	-0.735268
4	6	0	6.473152	0.881291	-0.760514
5	6	0	6.104997	-0.227391	0.020033
6	6	0	7.072276	-0.884578	0.795060
7	6	0	8.382839	-0.414399	0.822850
8	6	0	8.744712	0.698556	0.059591
9	7	0	4.799097	-0.751514	0.048153
10	6	0	3.755738	-0.030314	-0.186146
11	6	0	2.433508	-0.639547	-0.183669
12	6	0	1.309642	0.115321	-0.437701
13	6	0	-0.019563	-0.446288	-0.441795
14	6	0	2.280313	-2.045410	0.091803
15	6	0	0.991806	-2.620477	0.100933
16	6	0	-0.148789	-1.876580	-0.143678
17	6	0	-1.426933	-2.577483	-0.105415

18	7	0	-2.568857	-1.998375	-0.212831
19	6	0	-3.743419	-2.768129	-0.207446
20	6	0	-3.834755	-4.042536	-0.796731
21	6	0	-4.885715	-2.196179	0.378994
22	6	0	-6.082585	-2.906092	0.418362
23	6	0	-6.166571	-4.178010	-0.156515
24	6	0	-5.042510	-4.736807	-0.770944
25	1	0	8.070805	2.188825	-1.346781
26	1	0	9.122954	-0.920743	1.434125
27	1	0	9.768513	1.058279	0.072474
28	1	0	3.812211	1.044142	-0.378189
29	1	0	1.387329	1.179835	-0.636801
30	8	0	-1.013670	0.292196	-0.712633
31	8	0	3.325422	-2.811429	0.343180
32	1	0	0.919795	-3.682426	0.313257
33	1	0	-1.346690	-3.660727	0.051732
34	1	0	-2.973851	-4.466755	-1.303324
35	1	0	-4.802377	-1.205523	0.813045
36	1	0	-6.955122	-2.463030	0.888526
37	1	0	-7.104875	-4.723337	-0.139386
38	1	0	-5.108524	-5.714103	-1.239282
39	1	0	5.745853	1.361887	-1.406159
40	1	0	6.776055	-1.749447	1.379676
41	1	0	4.148971	-2.204195	0.295047
42	1	0	-2.401701	0.192535	0.327266
43	6	0	-4.020568	4.749803	-1.284970
44	6	0	-2.706637	4.302887	-1.133350
45	6	0	-2.245322	3.857733	0.110131
46	6	0	-3.125056	3.858652	1.198966
47	6	0	-4.437086	4.310705	1.052380
48	6	0	-4.889310	4.759333	-0.191281
49	6	0	-0.806051	3.410983	0.285733
50	8	0	-0.215964	2.928712	-0.913743
51	1	0	-0.756651	2.655393	1.081795
52	1	0	-0.197144	4.263917	0.611515
53	1	0	-0.584374	2.030899	-1.044030
54	1	0	-4.366694	5.089917	-2.256986
55	1	0	-2.027572	4.282292	-1.979306
56	1	0	-2.785662	3.480534	2.159331
57	1	0	-5.110152	4.301360	1.904960
58	1	0	-5.912014	5.105498	-0.308245

TS2(triplet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.707222	-1.233721	1.701722
2	8	0	1.900538	-0.517354	1.905487
3	6	0	-8.036433	-1.381090	-0.604653
4	6	0	-6.713763	-0.957818	-0.708382
5	6	0	-6.265225	0.125568	0.065624
6	6	0	-7.162191	0.792035	0.913738
7	6	0	-8.480595	0.355539	1.018991
8	6	0	-8.921410	-0.733037	0.262049
9	7	0	-4.946673	0.615913	0.015550
10	6	0	-3.942417	-0.129286	-0.300024
11	6	0	-2.603925	0.438212	-0.379862
12	6	0	-1.529847	-0.346567	-0.744201
13	6	0	-0.195277	0.184763	-0.872253
14	6	0	-2.385605	1.831841	-0.085609
15	6	0	-1.077968	2.361511	-0.121924
16	6	0	0.011344	1.574222	-0.442482
17	6	0	1.352271	2.137950	-0.339639
18	7	0	2.366891	1.395882	-0.061636
19	6	0	3.676482	1.899444	0.007708
20	6	0	4.100705	3.100064	-0.591550
21	6	0	4.612279	1.097335	0.683041
22	6	0	5.938560	1.505800	0.793124
23	6	0	6.351608	2.708750	0.215569
24	6	0	5.429943	3.497758	-0.481686
25	1	0	-8.380577	-2.212810	-1.211200
26	1	0	-9.165538	0.869216	1.685972
27	1	0	-9.951564	-1.066386	0.335624
28	1	0	-4.044200	-1.198362	-0.504274
29	1	0	-1.668889	-1.395716	-0.984481
30	8	0	0.730926	-0.499170	-1.383801
31	8	0	-3.388401	2.626096	0.251844
32	1	0	-0.946915	3.401941	0.158314
33	1	0	1.432097	3.224349	-0.452939
34	1	0	3.404982	3.704329	-1.163976
35	1	0	4.286027	0.154143	1.106871
36	1	0	6.651149	0.877430	1.317914
37	1	0	7.387419	3.023946	0.291996
38	1	0	5.752809	4.421530	-0.951698
39	1	0	-6.043632	-1.444255	-1.409195
40	1	0	-6.804994	1.637718	1.492303

41	1	0	-4.231049	2.049411	0.246797
42	1	0	1.991124	0.037435	1.084949
43	6	0	4.755037	-1.998275	-1.314482
44	6	0	3.407391	-2.334165	-1.201197
45	6	0	2.895100	-2.827269	0.010706
46	6	0	3.769022	-2.968065	1.105451
47	6	0	5.115451	-2.635477	0.988524
48	6	0	5.614795	-2.145945	-0.223000
49	6	0	1.459794	-3.151905	0.186946
50	8	0	0.630462	-3.112625	-0.917574
51	1	0	1.061087	-2.218993	1.011150
52	1	0	1.280406	-4.064142	0.764069
53	1	0	0.647676	-2.186617	-1.268178
54	1	0	5.137421	-1.622131	-2.258752
55	1	0	2.746352	-2.223299	-2.052715
56	1	0	3.380919	-3.337231	2.050747
57	1	0	5.776767	-2.752943	1.841748
58	1	0	6.662857	-1.878313	-0.313045

IM3(singlet state)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.490491	0.292499	2.452923
2	8	0	-3.540041	0.208539	1.444559
3	6	0	7.770864	1.548062	-0.628300
4	6	0	6.469761	1.049427	-0.626793
5	6	0	6.196134	-0.194923	-0.033250
6	6	0	7.247764	-0.938137	0.525135
7	6	0	8.543781	-0.428141	0.528801
8	6	0	8.810349	0.817520	-0.046112
9	7	0	4.911686	-0.768119	0.000611
10	6	0	3.846502	-0.037511	0.046416
11	6	0	2.525299	-0.636100	0.030974
12	6	0	1.390435	0.188943	0.088650
13	6	0	0.102633	-0.335077	0.074200
14	6	0	2.357534	-2.045042	-0.035389
15	6	0	1.064600	-2.562140	-0.060801
16	6	0	-0.076229	-1.741035	-0.008039
17	6	0	-1.354707	-2.441050	-0.100138
18	7	0	-2.538286	-1.949476	0.033974
19	6	0	-3.642563	-2.804370	-0.198013

20	6	0	-3.656321	-3.755392	-1.232651
21	6	0	-4.779435	-2.652813	0.612766
22	6	0	-5.889801	-3.471008	0.419081
23	6	0	-5.893989	-4.429808	-0.598044
24	6	0	-4.777147	-4.561487	-1.426336
25	1	0	7.975484	2.506111	-1.096250
26	1	0	9.347561	-1.006051	0.974199
27	1	0	9.822228	1.209958	-0.053368
28	1	0	3.896930	1.054102	0.113034
29	1	0	1.520183	1.265792	0.134386
30	8	0	-0.986530	0.477555	0.135815
31	8	0	3.406754	-2.888900	-0.081233
32	1	0	0.945312	-3.638538	-0.129278
33	1	0	-1.243423	-3.511666	-0.306726
34	1	0	-2.806093	-3.836206	-1.902065
35	1	0	-4.770401	-1.898299	1.391665
36	1	0	-6.757853	-3.355292	1.060934
37	1	0	-6.765494	-5.057846	-0.753361
38	1	0	-4.780770	-5.286649	-2.234432
39	1	0	5.675329	1.606905	-1.111953
40	1	0	7.026175	-1.905623	0.964164
41	1	0	4.228043	-2.317140	-0.053764
42	1	0	-3.152135	-0.487887	0.845458
43	6	0	-4.555182	3.333047	0.130653
44	6	0	-3.185490	3.125208	0.027928
45	6	0	-2.345686	4.189864	-0.346860
46	6	0	-2.895238	5.455318	-0.616148
47	6	0	-4.269334	5.655729	-0.518487
48	6	0	-5.098073	4.594097	-0.144347
49	6	0	-0.896050	4.035436	-0.457435
50	8	0	-0.257495	2.996485	-0.284596
51	1	0	-1.740185	0.552903	1.881950
52	1	0	-0.344901	4.955732	-0.719829
53	1	0	-0.722909	1.422040	-0.017956
54	1	0	-5.195968	2.510622	0.430258
55	1	0	-2.787335	2.143666	0.249442
56	1	0	-2.240217	6.273936	-0.900771
57	1	0	-4.693924	6.631652	-0.728731
58	1	0	-6.169464	4.749829	-0.063626

COM2(singlet state)

Input orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	8	0	-4.622770	2.230584	1.189660
2	1	0	-5.073367	1.387546	0.992278
3	8	0	-5.017176	2.992634	0.016109
4	1	0	-5.517802	3.718246	0.424418
5	6	0	7.689681	2.328822	-0.924842
6	6	0	6.305535	2.276281	-0.779266
7	6	0	5.603955	1.102444	-1.096080
8	6	0	6.306533	-0.004903	-1.601852
9	6	0	7.690235	0.059018	-1.754332
10	6	0	8.388088	1.220065	-1.411018
11	7	0	4.207836	1.116999	-0.923270
12	6	0	3.552985	0.040782	-0.633142
13	6	0	2.107930	0.045316	-0.504822
14	6	0	1.356935	1.241138	-0.693316
15	6	0	-0.027754	1.195427	-0.558764
16	6	0	1.446143	-1.152928	-0.186670
17	6	0	0.062314	-1.202402	-0.054727
18	6	0	-0.686458	-0.005176	-0.245376
19	6	0	-2.131814	0.005722	-0.117435
20	7	0	-2.787062	-1.074691	0.164263
21	6	0	-4.190408	-1.070213	0.239999
22	6	0	-4.799521	-1.946542	1.151184
23	6	0	-4.998582	-0.251366	-0.571014
24	6	0	-6.387333	-0.282411	-0.432414
25	6	0	-6.985610	-1.134353	0.500381
26	6	0	-6.186052	-1.969286	1.285684
27	1	0	8.223213	3.237939	-0.665263
28	1	0	8.223967	-0.797921	-2.153778
29	1	0	9.465406	1.264875	-1.534935
30	1	0	4.062420	-0.912678	-0.458188
31	1	0	-3.380543	3.273789	-0.793510
32	1	0	-4.168582	-2.587037	1.758804
33	1	0	-4.542112	0.391413	-1.316060
34	1	0	-6.999997	0.355343	-1.061661
35	1	0	-8.065500	-1.156515	0.603453
36	1	0	-6.643973	-2.640837	2.005069
37	1	0	5.749603	3.130698	-0.406645
38	1	0	5.768725	-0.897625	-1.903762
39	1	0	-0.616121	2.096814	-0.705938
40	1	0	2.019572	-2.063284	-0.041932
41	8	0	-2.512374	3.266804	-1.238789
42	1	0	-2.682132	2.814628	-2.074974

43	1	0	-2.626610	0.971809	-0.250953
44	8	0	-0.533330	-2.374987	0.251827
45	1	0	-1.513817	-2.186462	0.303147
46	8	0	1.952283	2.415413	-0.995825
47	1	0	2.933741	2.231428	-1.037063

TS3(singlet state with <S**>=0.000)

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.666071	1.202781	1.176128
2	1	0	-3.636071	1.269370	1.235052
3	8	0	-2.662496	3.103318	1.341311
4	1	0	-1.691651	3.119602	1.301328
5	6	0	7.458332	2.382388	-1.372769
6	6	0	6.069927	2.342391	-1.268922
7	6	0	5.404165	1.112987	-1.145269
8	6	0	6.148423	-0.078887	-1.169894
9	6	0	7.536625	-0.031036	-1.283932
10	6	0	8.197781	1.196357	-1.378503
11	7	0	4.000957	1.143107	-1.041699
12	6	0	3.355099	0.238061	-0.382196
13	6	0	1.905811	0.239976	-0.317217
14	6	0	1.145718	1.241858	-0.980152
15	6	0	-0.246328	1.195910	-0.888889
16	6	0	1.246325	-0.764248	0.411489
17	6	0	-0.142000	-0.804342	0.507080
18	6	0	-0.892309	0.190843	-0.164050
19	6	0	-2.377698	0.261876	-0.083080
20	7	0	-3.033685	-0.845985	0.408659
21	6	0	-4.370200	-1.020351	0.144155
22	6	0	-4.953119	-2.217168	0.631939
23	6	0	-5.188892	-0.097332	-0.564190
24	6	0	-6.526276	-0.393863	-0.785499
25	6	0	-7.080739	-1.594559	-0.322065
26	6	0	-6.287408	-2.504378	0.387338
27	1	0	7.963460	3.339720	-1.456170
28	1	0	8.102839	-0.957068	-1.310223
29	1	0	9.278805	1.227405	-1.470248
30	1	0	3.875220	-0.555260	0.165049
31	1	0	-3.153019	3.103914	-0.356259
32	1	0	-4.321407	-2.904164	1.184892

33	1	0	-4.787655	0.850003	-0.913576
34	1	0	-7.148540	0.315908	-1.321000
35	1	0	-8.127542	-1.813671	-0.505069
36	1	0	-6.716960	-3.431211	0.753023
37	1	0	5.482870	3.255264	-1.267012
38	1	0	5.640209	-1.036875	-1.131803
39	1	0	-0.835552	1.958291	-1.389617
40	1	0	1.825930	-1.529908	0.917957
41	8	0	-3.402255	2.899483	-1.289415
42	1	0	-4.186209	3.435182	-1.462740
43	1	0	-2.813459	0.802872	-0.922327
44	8	0	-0.717907	-1.796110	1.231767
45	1	0	-1.699456	-1.692827	1.125202
46	8	0	1.728848	2.229979	-1.689493
47	1	0	2.715922	2.079238	-1.620085

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