ARTICLE

Supporting information

Anthraquinone-based conjugated donor-acceptor (D-A) polymer as a highly efficient photocatalyst for hydrogen peroxide production

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Supporting information List

S-1) Material characterization

A field-emission scanning electron microscope (FESEM, Zeiss SIGMA 300, and Zeiss SUPRA 55-VP) was used to study the morphology of the anthraquinone-based conjugated polymer (ACP). EDAX analysis, the samples were prepared on Pt and Al films. To obtain crystallographic information on the materials, room-temperature X-ray diffraction (XRD) patterns were recorded primarily using a Rigaku MiniFlex diffractometer having the Cu K_α (λ=1.54 Å) line as the X-ray source. To record UV-vis absorption spectra of the materials at room temperature, an Agilent Cary 3500 spectrophotometer was used. Transient Absorption Spectroscopy: The femtosecond transient absorption setup is based on a regenerative amplified Ti: sapphire laser system from coherent (800 nm, 35 fs, 6 mJ/pulse, and 1 kHz repetition rate). X-ray photoelectron spectroscopy (XPS) on a SPECS HSA-3500 with a monochromatic Al Ka X-ray radiation X-ray source and the hemispherical analyzer were used to investigate the elemental states of the sample. The JEOL JNM-ECS400 spectrometer was used to record the nuclear magnetic resonance (NMR) spectrum.

S-2) Photoelectrochemical measurements

Photoelectrochemical (PEC) measurements of ACP photoanodes were conducted in a three-electrode system with a potentiostat (CH Instruments, 660D potentiostat) under simulated AM 1.5 G solar light irradiation, where a Newport Xe lamp with a light intensity of 100 mW/cm^2 was used as the visible-light source. All the photoelectrochemical experiments were performed under visible-light illumination with a light intensity of 100 mW/cm^2. In a standard electrochemical cell, Ag/AgCl (saturated in 1 M aq. KCl) was used as the reference electrode, the as-prepared electrodes were utilized as the working electrode, whereas a Pt wire was used as the counter electrode. Photoreactions were carried out by visible-light irradiation (λ > 420 nm) using a xenon lamp with magnetic stirring at 298 K. The catalyst (10 mg) suspended in pure water (10 ml) was used for the photoreaction. The suspension of the catalyst was purged with oxygen for 45 minutes. The H_2O_2 concentration was measured by using iodometric titration. The concentration was standardized with the commercial H_2O_2 sample, as shown in section S8. The Nyquist plot was obtained using the electrochemical impedance spectroscopy (EIS) technique, measured within the 100-1000 Hz frequency range at E= 0 $V_{Ag/AgCl}$ using DC voltage with an introduction of 5 mV under illuminated conditions. The linear sweep voltammetry (LSV) measurements were carried out at a 50 mV/s scan rate. An aqueous electrolyte containing aq. 0.5M Na_2SO_4 (pH~7) was used. To convert the potential values ($V_{Ag/AgCl}$) measured against the Ag/AgCl reference electrode into potential values (V_{RHE}) against the reversible hydrogen electrode (RHE), the following equation (1) is employed, where $V^0_{Ag/AgCl}$ = 0.1976 V at 298 K in saturated KCl.

$$V_{RHE} = V_{Ag/AgCl} + 0.059 \times pH + V_{Ag/AgCl}^{0}$$

Electron spin resonance (ESR) measurement

Electron spin resonance (ESR) measurements were performed using an ESR spectrometer (Bruker EMX MICRO X spectrometer). 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as a spin-trapping reagent to detect radicals. The measurements were carried out in an H_2O/Isopropanol (1:9, 500 µL), mixture with 2 mg catalyst and 0.1 mmol DMPO within a glass tube (capacity, 4 mL), and the tube was sealed with a rubber septum cap, After ultrasonication (5 min.) and O_2 bubbling (10 min.), a Xe lamp with a filter (λ > 420 nm) was applied as the light source.

Rotating disk electrode (RDE) measurements,

The electron transfer number for the oxygen reduction reaction was measured on a rotating disk electrode (RDE) in O_2 saturated 0.5M $NaSO_4$ (pH~7) solution at room temperature at different rotating speeds after O_2 bubbling for 40 min. The electron transfer number for the oxygen reduction reaction is calculated by the following equation

$$\frac{i}{1} = \frac{1}{JL} + \frac{1}{JK} = \frac{1}{B\omega 1/2} + \frac{1}{JK}$$

Where i is the current intensity, J^L and J^k are the kinetic and diffusion-limiting current densities, ω is the angular velocity, n is the transferred electron number, F is Faraday constant (96485 C mol^{-1}), v is the kinetic viscosity of water (0.01 cm^2 s^{-1}), C is the bulk concentration of O_2 in water (1.26 × 10^{-3} mol cm^{-1}), and D is the diffusion coefficient of O_2 (2.7 × 10^{-5} cm^2 s^{-1}). $B = 0.2nFV^{-1/6}CD^{2/3}$

S-3) Experimental Section

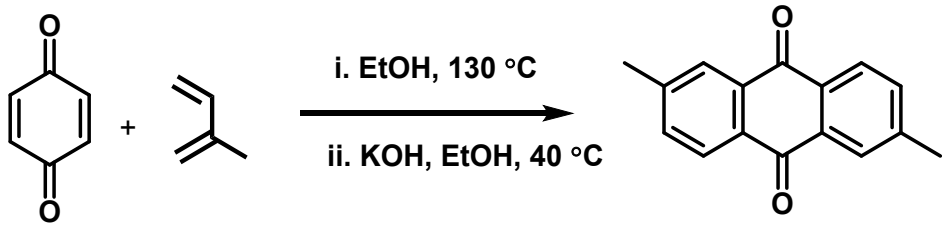
Material: Benzoquinone, isoprene, hydroquinone, absolute ethanol (EtOH), potassium hydroxide (KOH), sulfuryl chloride (SO_2Cl_2), Azobisisobutyronitrile (AIBN), phenol, resorcinol, phloroglucinol, 2-amino phenol, water, potassium iodide (KI), Isopropyl alcohol, Sodium nitrate ($NaNO_3$) were of analytical grade and used without extra purification as received. The polymers were synthesized using deionized (DI) water.

S-3.1) Synthesis of 2,6-dimethyl-9,10-anthraquinone (3)

2,6-Dimethyl-9,10-anthraquinone (3) was synthesized from 1,4-benzoquinone (1) and isoprene (2) using the reported procedure.[1] Benzoquinone (2g, 18.51 mmol), isoprene (5.56 mL), and a small amount of hydroquinone (410 mg) were added to 20 mL absolute ethanol in a 50 mL tube. The reaction tube was sealed and then heated at 130 °C for 8 hours; After 8 hours, the reaction tube was cooled at room temperature, and the entire mixture was transferred and dissolved in ethanolic KOH solution in a round-bottom

flask. The mixture was stirred for the next 10 hours at 40 °C in the presence of air, allowed to cool to room temperature, and then vacuum-filtered to obtain a creamy white solid. This solid was soaked in 100% ethanol and kept in the refrigerator overnight. The solid filter was once more washed with ethanol and water, and dried in the air.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, J = 7.9 Hz, 2H), 8.10 (s, 2H), 7.58 (d, J = 7.9 Hz, 2H), 2.53 (s, 6H).

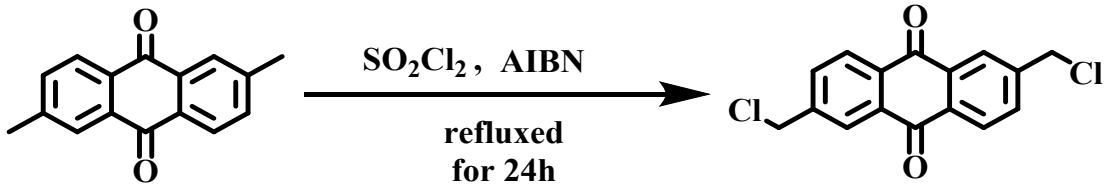


Scheme S1 Synthesis of 2,6-dimethyl-9,10-anthraquinone.

S-3.2) Synthesis of 2,6-bis(chloromethyl)anthraquinone

2,6-Dimethylanthraquinone (3) (3.8 g, 16.09 mmol), sulfuryl chloride (SO_2Cl_2, 50mL), and 2,20-azobis (2-methylpropionitrile) (0.16 g, 0.96 mmol) were added to the round-bottom flask and refluxed for 24 hours. Excess SO_2Cl_2 was removed by vacuum distillation to obtain a milky white solid (Scheme S2).[2] The white solid was filtered and dried, washed multiple times with petroleum ether, and recrystallized from DMF to obtain 3.8 g (78%) of 2,6-bis(chloromethyl)anthraquinone (4).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (m, 4H), 7.85 (d, J = 7.7 Hz, 2H), 4.72 (s, 4H).



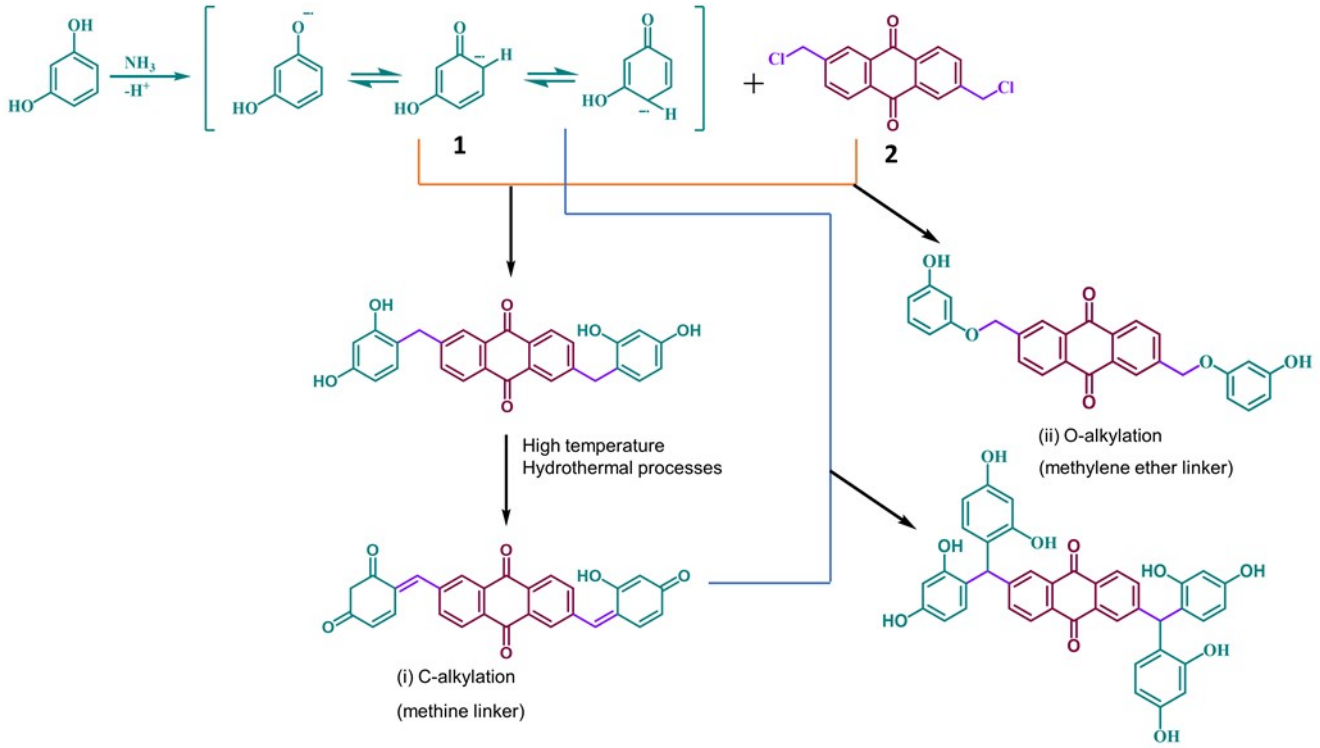
Scheme S2 Synthesis of 2,6 bis chloromethyl anthraquinone.

S-3.3) Synthesis of anthraquinone-based conjugated polymer (ACP)

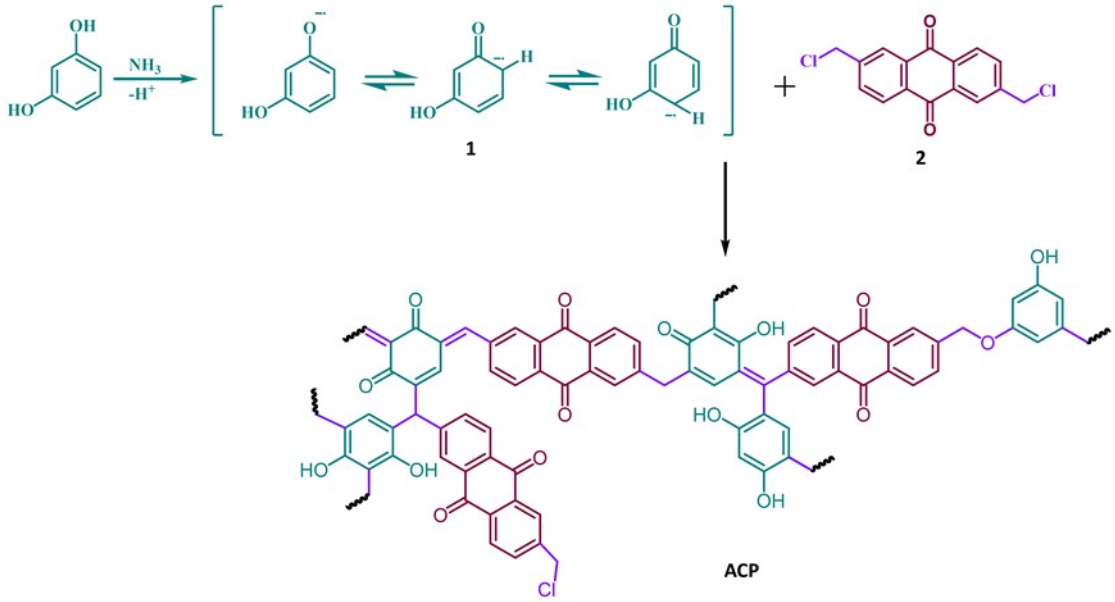
The synthesis of anthraquinone-based conjugated polymer (ACP) is achieved by hydrothermal treatment of resorcinol and 2,6-bis (chloromethyl)anthraquinone. Resorcinol (1 mmol) and 2,6-bis(chloromethyl)anthraquinone (1 mmol) (the mole ratio is 1/1) was added to 8 mL of water and 8 mL ethanol containing NH_3 (200 µL) as a base catalyst, and the mixture was stirred for 5 min. The colloidal suspension was transferred into a stainless steel autoclave with Teflon lining and placed in an oven for 24 hours at 180 °C for hydrothermal treatment, as shown in Scheme 1. The solution was allowed to cool after the reaction was completed. It was filtered by vacuum filtration and washed with ethanol and water. The precipitate was further dried in the air to give brown powder with a 90% yield. Finally, the synthesized photocatalyst was thoroughly characterized and utilized for the photocatalytic generation of H_2O_2. Similarly, different ACP analogs were synthesized using various phenol derivatives such as phenol, phloroglucinol, and 3-aminophenol.

S-3.4) Synthesis mechanism of anthraquinone-based conjugated polymer (ACP).

In the presence of ammonia, resorcinate anions (1) are formed, which react with 2,6-bis(chloromethyl)anthraquinone (2). The reaction can proceed with two pathways with the resonance structure of resorcinate. Firstly, resorcinate anion can react through its C-centered nucleophilic site to form a methylene linker which on high-temperature hydrothermal process affords methine linkage. This effectively forms an anthraquinone-π-conjugated benzenoid-quinoid D-A couple.[3] Further, nucleophilic attack of the resorcinate ion on the highly electrophilic quinone methides leads to methylene-bridge formation (ii). The resorcinate anion can also react through an O-centered nucleophilic site with 2,6-bis(chloromethyl) anthraquinone to create methylene ether linkages. Thus, polycondensation reaction results in crosslinked polymers with extensive quinoid and aromatic forms of resorcinol coupled with anthraquinone units.[3,5]



Scheme S3 Mechanism of various pathways that lead to the polycondensation to form ACP.



Scheme S4 Synthesis of anthraquinone-based conjugated polymer (ACP); the plausible structure of the ACP is derived from the summation of pathways shown in Scheme S3.

S-4) SEM-EDAX of ACP

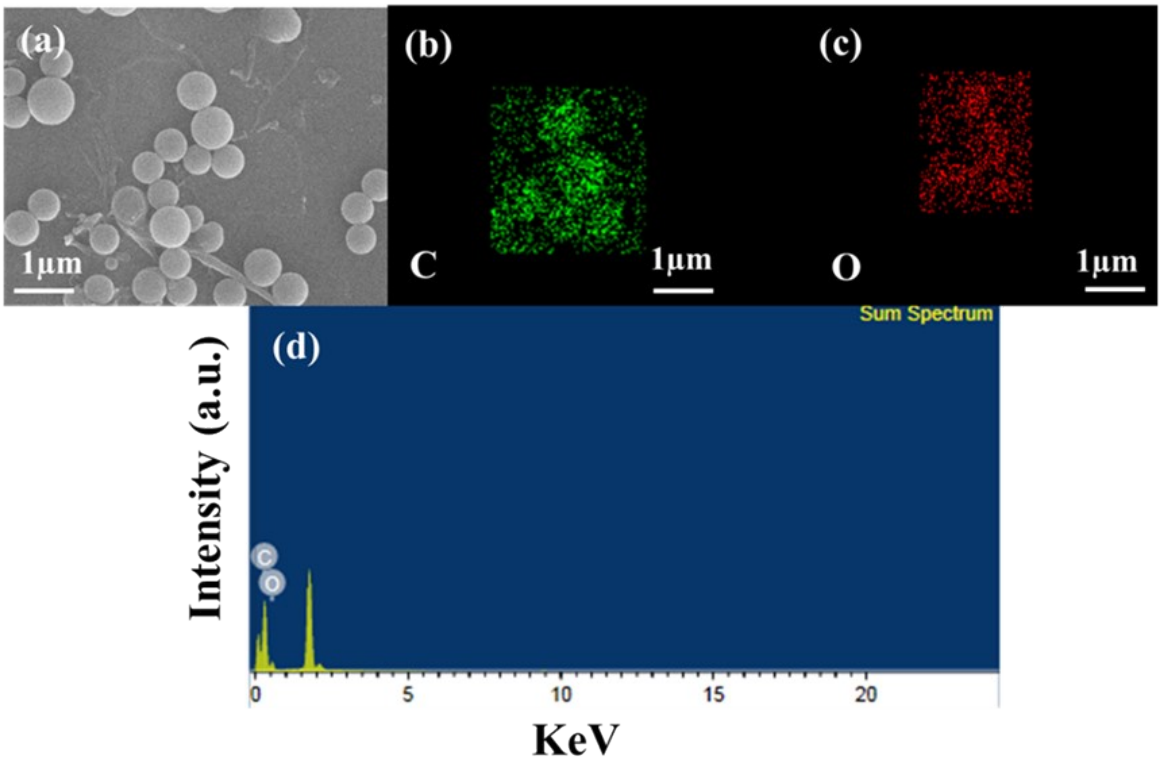


Figure S1. EDAX image of ACP (a) and distribution of carbon, oxygen, (b), (c) and EDAX spectra of ACP (d).

S-5) Brunauer–Emmett–Teller (BET) of ACP

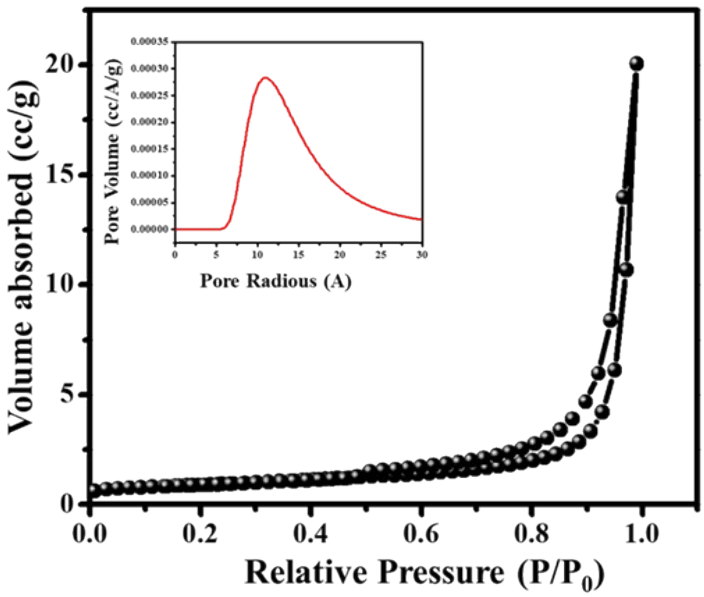


Figure S2 Superimposed BET N_2-adsorption-desorption surface area analysis of ACP is 48 m^2/g.

S-6) Fourier-transform infrared spectroscopy (FT-IR) of ACP

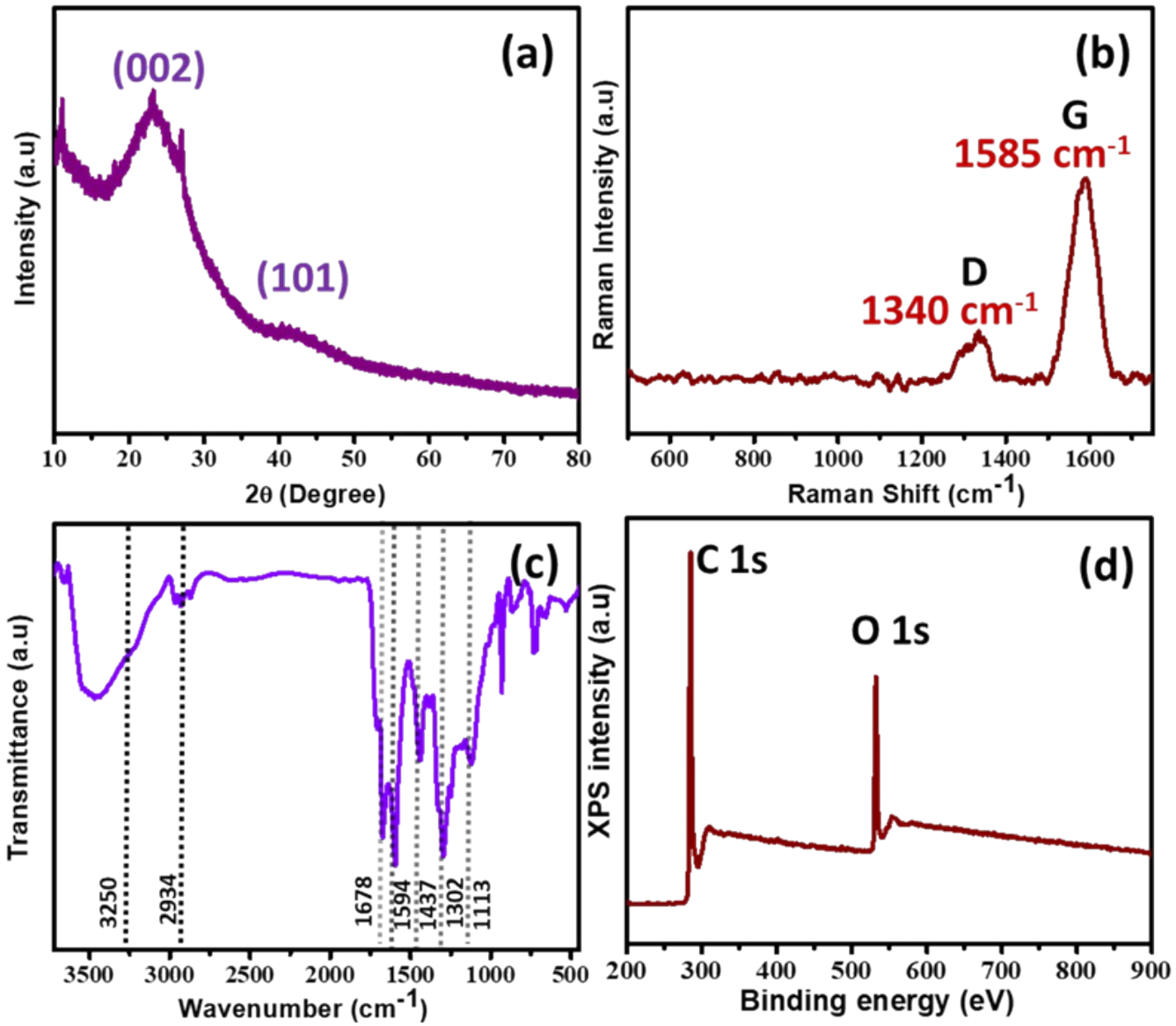


Figure S3 (a) XRD pattern, (b) Raman spectra, and (c) FT-IR of ACP. Characteristics peaks: 3250 cm^{-1} (O-H of resorcinol fragment), 2934 cm^{-1} (C-H of methylene linker), 1678cm^{-1} (C=O of anthraquinone), (1610 cm^{-1}(C=C of aromatic ring), 1450 cm^{-1} (C=C methylene linker), 1290 cm^{-1} (C-H in an aromatic ring), 1050 cm^{-1} (C-O of resorcinol). (d) XPS full survey of ACP.

Table S1 Elemental analysis of atomic (%) of C and O in the polymeric compound by using EDAX and XPS.

Sr. No.	Elements	EDAX atomic (%)	XPS atomic (%)
1	C	79.50	80.10
2	O	20.50	19.90

S-7) H_2O_2 concentration measurements by using the UV-vis absorption spectrometry Iodometric Titration)

Typically, 100ml aq. 0.0029 M ammonium molybdate ($(NH_4)_2MoO_4$) solution containing 1.5 ml H_2SO_4 were prepared in advance. A sample aliquot of 0.5 mL and 1.5 mL of ($(NH_4)_2MoO_4$) solution was mixed with 40 mg of potassium Iodide (KI) before measuring. This give absorbance at 352 nm (Figure S4) corresponds to I_3. The formation of I_3 is given in the reaction below.

$H_2O_2 + 3KI + 2H^+ \rightarrow I_3^- + 2H_2O + 3K \Rightarrow H_2O_2 + 3KI + 2H^+ \rightarrow I_3^- + 2H_2O + 3K^+$ (λ = 352 nm)

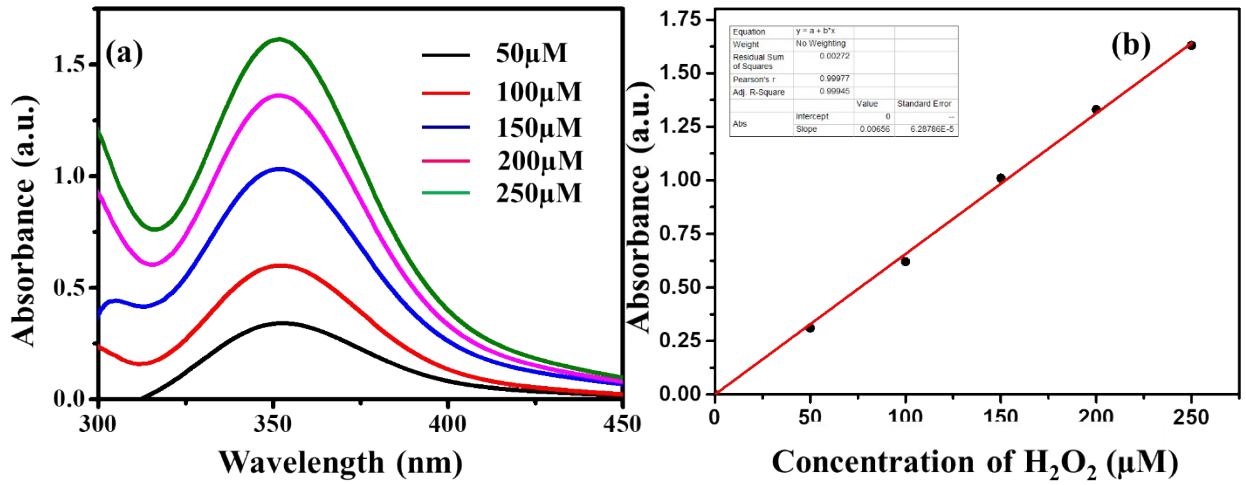


Figure S4 (a) Standard curves for different concentrations of H_2O_2 and (b) the linear relationship of concentration of H_2O_2 vs. UV-vis absorption intensity.

S-8) Photoelectrochemical studies of ACP

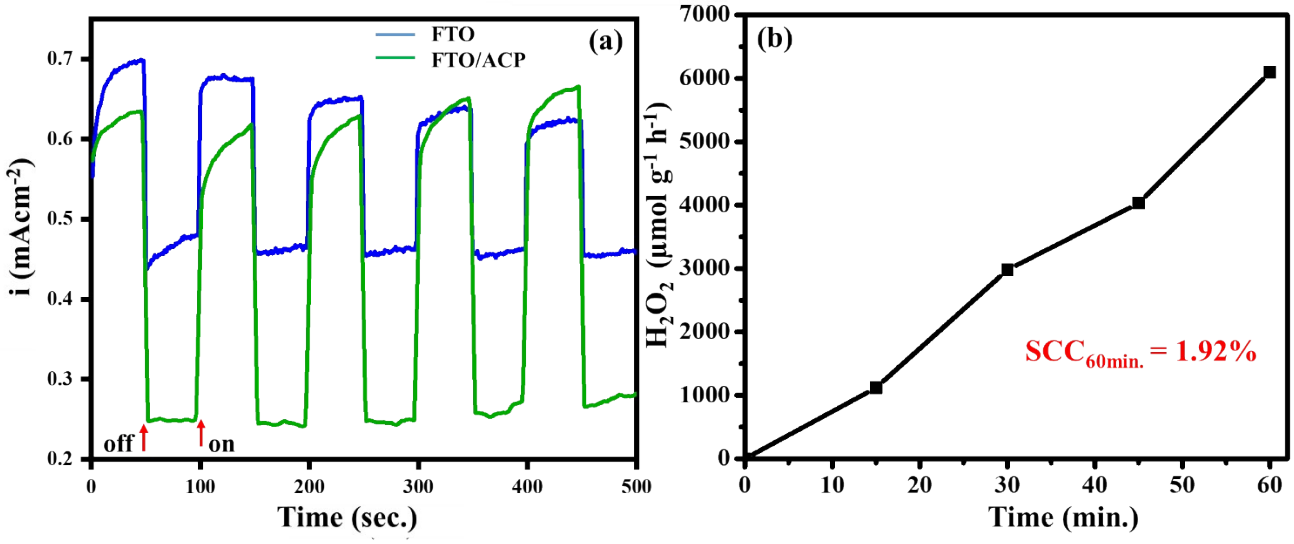


Figure S5 (a) The photo-current properties by light-on/off for FTO and ACP/FTO. (b) The photocatalytic yield of H_2O_2 and SCC efficiency of ACP in 60 min.

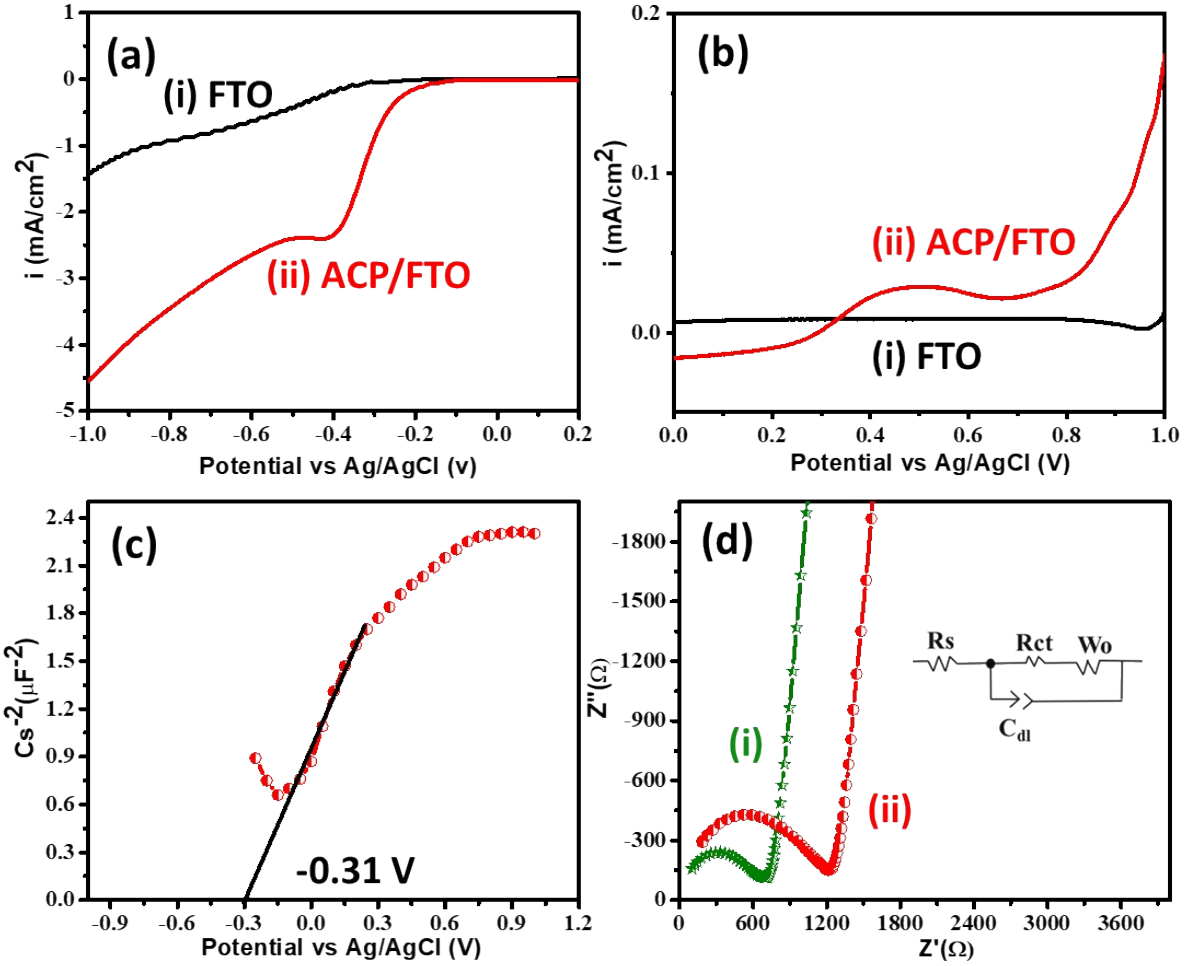


Figure S6 (a) and (b) LSV of FTO, ACP/FTO in 0.5 Na_2SO_4 solutions at a scan rate of 50 mV/s, (c) Mott-Schottky plots in 0.5 Na_2SO_4 solutions (E = 0 V), (d) electrochemical impedance spectroscopy (EIS) for (i) ACP/FTO in the light, (ii) ACP/FTO in dark at E= 0 $V_{Ag/AgCl}$ in the frequency range of 100-1000 Hz.

Rotating disk electrode (RDE) measurements

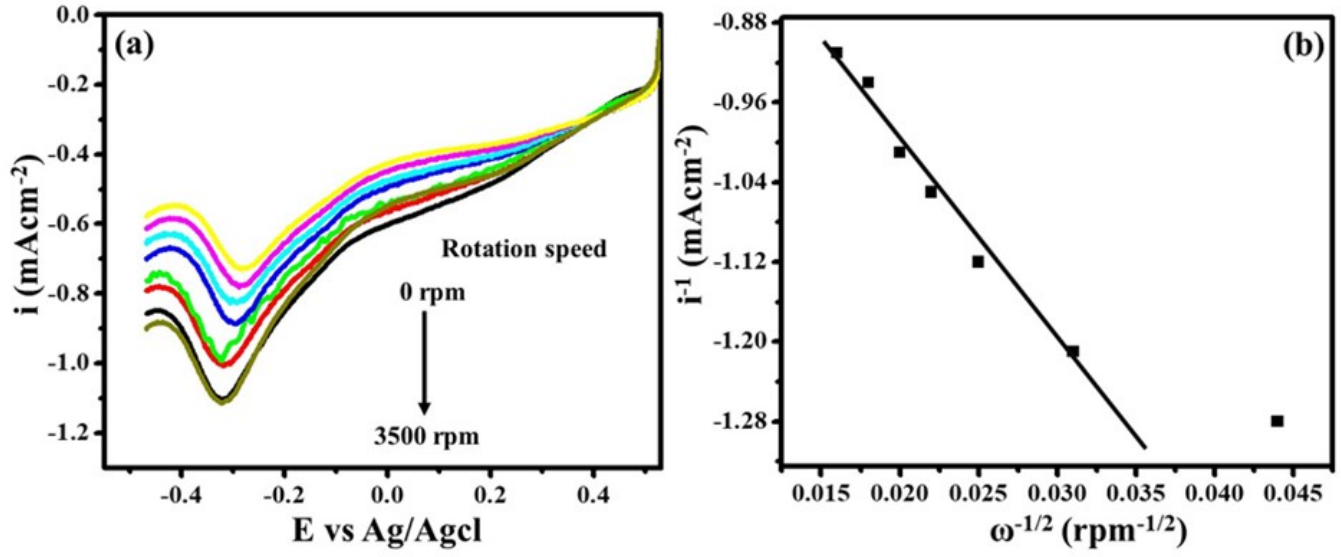


Figure S7 (a) LSV curve of ACP in 0.5 Na_2SO_4 solutions at different rotation speeds (0, 500, 1000, 1500, 2000, 2500, 3000, 3500 rpm) using rotating disc electrode, and (b) Koutecky-Levich plots of ACP.

S-9) SCC Efficiency measurement

To calculate the solar-to-chemical energy conversion (SCC) efficiency, an LED solar simulator was used as the light source (100 mW cm^{-2}). 10 mg catalysts and 10 mL water were added into a round bottom flask and bubbled with O_2 for 45 minutes; the reaction was carried out at 40 °C in a water bath. The SCC efficiency was calculated via the following equation,

$$SCC\ efficiency\ (\%) = \frac{[\Delta G \text{ for } H2O2 \text{ generation (J mol - 1)}][H2O2 \text{ produced (mol)}]}{[\text{total input energy (W)}]\ [\text{reaction time (s)}]} \times 100$$

where the free energy (ΔG) for H_2O_2 formation is 117000 J mol^{-1}, and the irradiated area is 1000 W/m^2 and the irradiated area is 3.14 × 10^{-4} m^2. The total input energy was therefore 9.6 W.

Table S2 Rate of photocatalytic H_2O_2 generation with the polymers produced with various phenolic derivatives

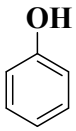
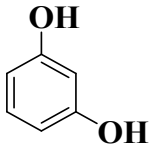
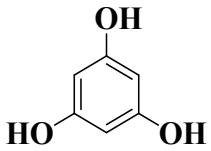
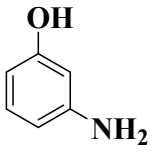
Sr. No.	phenol derivatives	Structure	H_2O_2 (μmol)[a]
1	phenol		1500 μmol g^{-1}
2	Resorcinol		12576 μmol g^{-1}
3	Phloroglucinol		3500 μmol g^{-1}
4	3-Aminophenol		2100 μmol g^{-1}
[a] Reaction conditions: water (10mL), catalyst (10 mg), λ > 420 nm light intensity at 420-700 nm, photoirradiation time (3h).			

Table S3 Comparison of the photocatalytic H_2O_2 production activity of ACP with previously reported organic materials

Sr. No.	Catalysts	Solvent	Light source	Yield of H_2O_2 (μmol g^{-1} h^{-1})	SCC efficiency (%, h^{-1})	Ref.
1)	RF523	H_2O	λ > 420 nm	460	0.5	3
2)	G-C_3N_4-PDI	H_2O	λ > 420 nm	21.1	-	4
3)	RF-acid resins	H_2O	λ > 420 nm	400	0.7	5
4)	(i) TPE-AQ (ii) TPE-AC	H_2O H_2O	λ > 420 nm	909 293		6
5)	DE7-M	H_2O	λ > 420 nm	2216	0.23	7
6)	CNP-S	H_2O	λ > 420 nm	3200		8
7)	CHF-DPDA	H_2O	λ > 420 nm	1725	0.78	9
8)	PM-CDs-30	H_2O	λ > 420 nm	1340	0.21	10
9)	ZIF-8/C_3N_4	H_2O	λ > 420 nm	2641	0.58	11

10)	AQTEE-COP	H_2O	λ > 420 nm	3204	-	[12]
11)	NMT400	H_2O	λ > 420 nm	1695	-	[13]
12)	PQTEE-COP	H_2O	λ > 420 nm	3009	-	[14]
13)	RF-DHAQ	H_2O	λ > 420 nm	1820	1.12	[15]
14)	**ACP**	**H_2O**	**λ > 420 nm**	**6097**	**1. 92**	**This work**

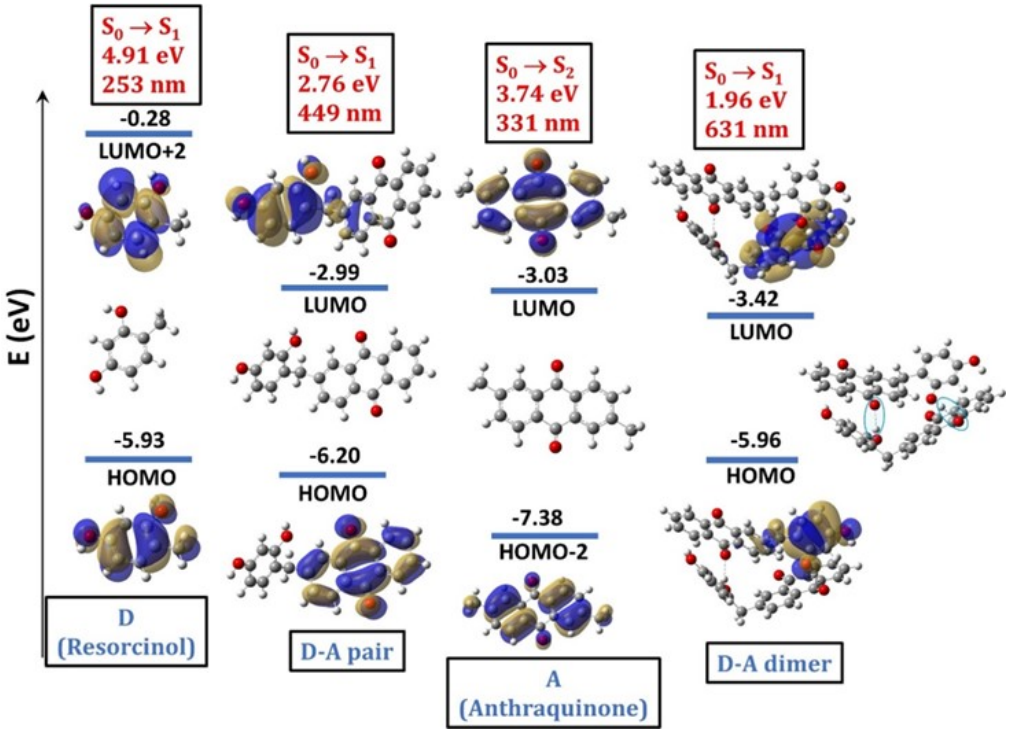


Figure S8 Frontier molecular orbitals of model compounds for donor (resorcinol), acceptor (anthraquinone), donor-acceptor pair and its dimer and their relative energies calculated using DFT-D3 at B3LYP/6-31+G(d).

S-10) ^{1}HNMR

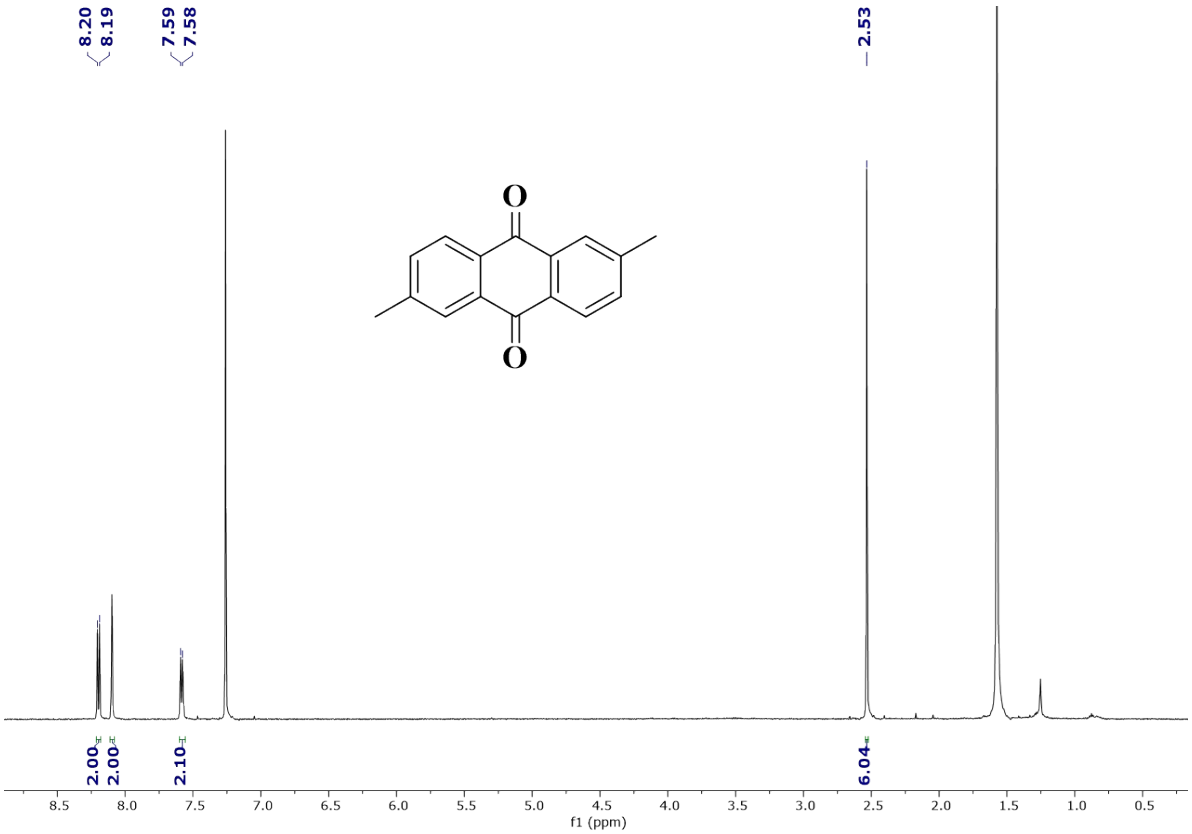


Figure S9 [1]HNMR of 2,6-dimethyl-9,10-anthraquinone

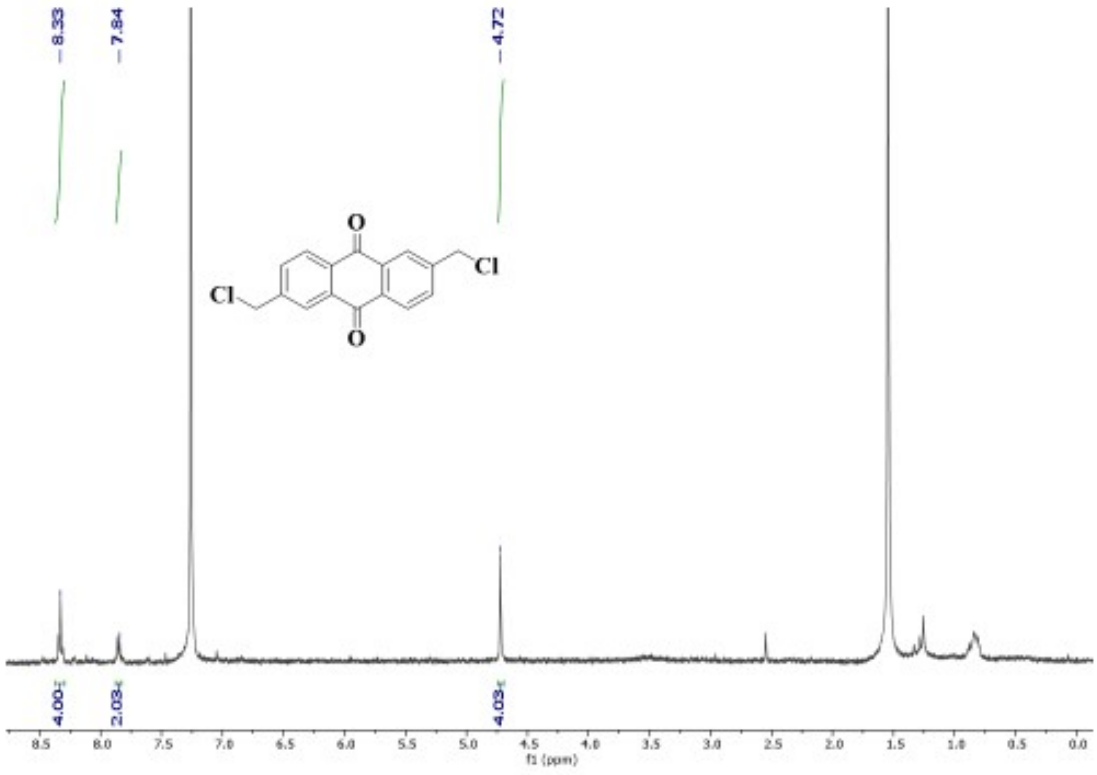


Figure S10 [1]H NMR of 2,6-bis(chloromethyl) anthraquinone.

S-11) Photoluminescence spectra of ACP photocatalyst :

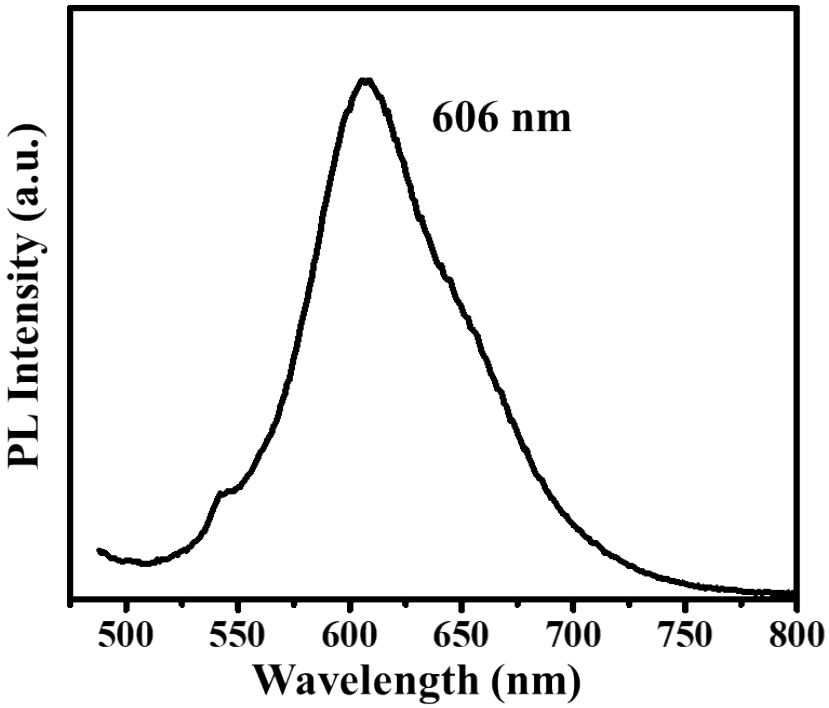
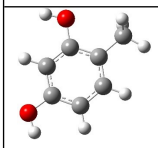
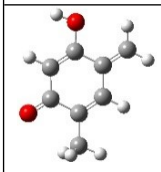
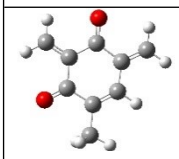
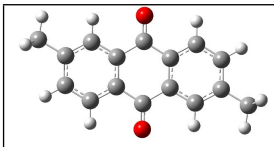
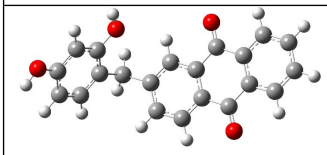
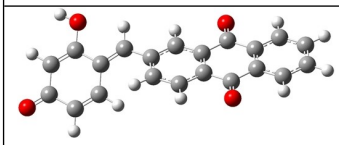
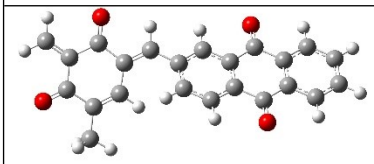
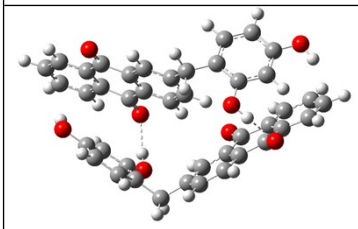
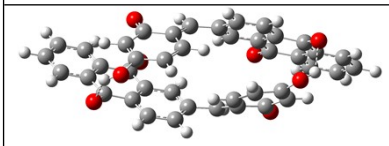


Figure S11 Steady state photoluminescence spectra of ACP photocatalyst

To investigate anthraquinone redox centre advantages. In centres with donor-acceptor semiconductors combined, the steady-state photoluminescence (PL) spectra of ACP have been examined for photoinduced charge separation and transfer to photocatalytic H_2O_2 production. As shown in Figure S12 ACP releases light centered at 606 nm with 490 nm excitation. The PL result of ACP suggested that an enhancement in the hole-electron separation efficiency towards the H_2O_2 production.

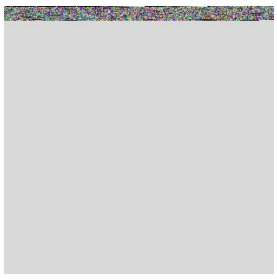
Table S4. The major electronic transitions, related oscillator strength, and orbitals' contributions for the low-lying singlet states of model compounds were calculated from the TD-DFT method at B3LYP/6-31+G(d). The lowest energy transitions are marked in red font

Compound	Transitions	Orbital contribution	E (eV), (λ (nm)	Oscillator strength (*f*)
	$S_0 \rightarrow S_1$	H → L (80%) H-1 → L (20%)	4.91 eV 252 nm	0.0429
	$S_0 \rightarrow S_2$	H-2 → L (99%)	3.6 eV 346 nm	0.0031
	$S_0 \rightarrow S_3$	H → L (93%)	4.37 eV 284 nm	0.4719
	$S_0 \rightarrow S_3$	H → L (97%)	3.49 eV 355 nm	0.0062
	$S_0 \rightarrow S_6$	H → L+1 (79%)	4.25 eV 292 nm	0.2007

	$S_0 \rightarrow S_4$	H-2 → L (79%) H-5 → L (14%)	3.74 eV 331 nm	0.1445
	$S_0 \rightarrow S_4$	H-2 → L (15%) H-5 → L (78%)	4.23 eV 288 nm	0.1624
	$S_0 \rightarrow S_1$	H → L (61%) H-2 → L (30%)	2.85 eV 434 nm	0.1591
	$S_0 \rightarrow S_2$	H → L (33%) H-2 → L (56%)	2.92 eV 425 nm	0.1069
	$S_0 \rightarrow S_1$	H-1→ L (66%) H-1→ L+1 (28%)	2.64 eV 471 nm	0.0028
	$S_0 \rightarrow S_2$	H→ L (73%) H-3 → L (14%)	2.84 eV 436 nm	0.1950
	$S_0 \rightarrow S_1$	H → L (61%) H-2 → L (30%)	2.85 eV 434 nm	0.1591
	$S_0 \rightarrow S_2$	H → L (33%) H-2 → L (56%)	2.92 eV 425 nm	0.1069
	$S_0 \rightarrow S_1$	H → L (99%)	1.96 eV 631 nm	0.0004
	$S_0 \rightarrow S_3$	H-1→ L (99%)	2.13 eV 583 nm	0.0113
	$S_0 \rightarrow S_6$	H-3→ L+1 (69%) H-2→ L+1 (30%)	2.69 eV 461 nm	0.0182
	$S_0 \rightarrow S_1$	H→ L (97%)	2.15 eV 578 nm	0.0017
	$S_0 \rightarrow S_2$	H-1→ L (45%) H→ L+1 (54%)	2.35 eV 529 nm	0.0253
	$S_0 \rightarrow S_3$	H-1→ L (52%) H→ L+1 (44%)	2.52 eV 491 nm	0.1568

Coordinates of model compounds and their structures

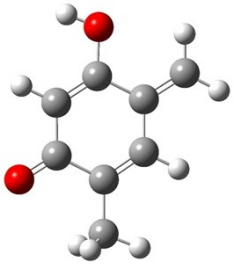
(a) Donor (an aromatic form of resorcinol derivative)



C	2.61809000	-0.83175800	-0.00002900
H	3.10722800	-0.39364300	-0.87895700
H	2.81151400	-1.90969000	-0.00110700
C	1.13615700	-0.55168400	-0.00006300
C	0.17494900	-1.56404700	-0.00007900
C	0.66634600	0.77579100	0.00002500
C	-1.19893700	-1.29543100	-0.00003900

H	0.50729800	-2.59982200	-0.00014400
C	-0.69669800	1.07381700	0.00004400
C	-1.62973800	0.03283800	0.00001600
H	-1.91982000	-2.11038700	-0.00011600
H	-1.05123400	2.10182300	0.00007200
O	1.62141300	1.76262000	0.00003000
H	1.19631900	2.63396800	0.00016700
O	-2.95507500	0.39225000	-0.00000500
H	-3.50987200	-0.40285200	0.00057800
H	3.10684000	-0.39551200	0.88006200

(b) Donor (Quinoidal form of resorcinol)



C	-2.25681800	1.64239800	0.00002100
H	-3.26436100	1.24188500	0.00011400
C	-1.17172200	0.83626100	0.00003100
C	0.18738800	1.37442100	-0.00007600
C	-1.30137900	-0.62755500	0.00015900
C	1.29673400	0.60264900	-0.00008300
H	0.27841600	2.45945500	-0.00016300
C	-0.20905100	-1.42963900	0.00013200
C	1.15002700	-0.88279900	-0.00002800
H	-0.29170500	-2.51406900	0.00020100
O	-2.58300800	-1.08680600	0.00002300
O	2.14145100	-1.61945600	0.00004000
C	2.69553400	1.14713200	-0.00018000
H	3.24873700	0.78906400	0.87611300
H	3.24866600	0.78893500	-0.87646500
H	2.69745400	2.24196800	-0.00025800
H	-2.14453300	2.72318400	-0.00006400
H	-2.58451500	-2.05753700	0.00014800

(b) Donor/Acceptor (Biquinoidal form of resorcinol)

C	2.22755600	-1.96571900	0.00009500
H	3.24117600	-1.57754400	0.00003300
C	1.17424500	-1.12275600	-0.00010100
C	-0.20220200	-1.60130000	-0.00010500
C	1.42442700	0.36009000	-0.00046100
C	-1.30641300	-0.81497700	-0.00004100
H	-0.33172700	-2.68342800	-0.00017200
C	0.21596700	1.24566000	0.00013100
C	-1.16889500	0.66071600	0.00027100
O	2.56034700	0.81891700	-0.00020400
O	-2.16371800	1.38356800	-0.00020300
C	-2.70608000	-1.36062400	-0.00009900
H	-3.25947400	-1.00388600	0.87661200
H	-3.25974400	-1.00303000	-0.87628300
H	-2.70712300	-2.45512500	-0.00061400
H	2.09114000	-3.04405700	0.00029400
C	0.37191600	2.58153000	0.00060800
H	1.36613200	3.01810200	0.00056600
H	-0.49653200	3.23336600	0.00103900

(d) Acceptor (anthraquinone)

C	-2.68598600	0.97684900	0.00034200
C	-3.78182700	0.10979000	0.00021300
C	-3.53563000	-1.27630900	0.00009600
C	-2.23789900	-1.77625400	0.00002500
C	2.68598700	-0.97684400	-0.00051200
C	3.78183000	-0.10978400	-0.00069200
C	3.53563300	1.27631200	-0.00076700
C	2.23790000	1.77625800	-0.00029800
C	-0.23859400	1.45897500	0.00044100
C	0.23859600	-1.45897000	0.00009800
C	-1.37351600	0.48814200	0.00027900
C	-1.14244700	-0.90115800	0.00011700
C	1.37351900	-0.48813800	-0.00004000
C	1.14244900	0.90116400	0.00010000
O	-0.43773700	2.67164100	0.00023900
O	0.43773700	-2.67163600	-0.00067800
H	-2.83117900	2.05326100	0.00051500
H	-4.37662300	-1.96678400	0.00009600

H	-2.04800300	-2.84508600	-0.00004200
H	2.83117900	-2.05325700	-0.00081000
H	4.37662400	1.96678800	-0.00134300
H	2.04800500	2.84509000	-0.00044200
C	-5.19789000	0.63348500	-0.00021800
H	-5.74877000	0.27820000	0.87979800
H	-5.22249900	1.72753200	0.00462700
H	-5.74504100	0.28628400	-0.88581500
C	5.19788300	-0.63350500	0.00097800
H	5.73906300	-0.29944200	0.89532800
H	5.22255800	-1.72737100	-0.01945800
H	5.75464100	-0.26532300	-0.86991400

(e) D-A pair (resorcinol as D and anthraquinone as R)

C	1.04288400	0.65796100	-1.33934600
C	0.06797100	-0.33702000	-1.22917700
C	-1.18754300	-0.05773500	-0.67691400
C	-1.48352900	1.24504500	-0.22574300
C	-0.50817600	2.24509300	-0.33583100
C	0.73698300	1.95180800	-0.88281400
C	-2.19198200	-1.15571400	-0.57368600
C	-2.80912500	1.58074100	0.36215200
C	-3.81862600	0.48394000	0.45955000
C	-3.52438800	-0.82056300	0.01263500
C	-4.49448400	-1.82605500	0.11817500
H	-4.24716500	-2.82320700	-0.23220100
C	-5.74522000	-1.53925700	0.66246600
C	-6.03738600	-0.24271400	1.10704200
C	-5.07807200	0.76349300	1.00586000
H	0.27742700	-1.34856100	-1.55938100
H	-0.74757700	3.24491900	0.01262800
H	1.48837700	2.73493300	-0.95765400
H	-6.49392000	-2.32311800	0.74138100
H	-7.01283300	-0.01995300	1.53140800
H	-5.28305100	1.77441100	1.34390400
O	-3.06768200	2.71668100	0.75364200
O	-1.93621900	-2.29537700	-0.95436600
C	2.41932400	0.34923600	-1.90557400
H	2.35726400	-0.53760400	-2.54523800
H	2.74511200	1.18347500	-2.53837000

C	3.45194200	0.12860100	-0.81612800
C	4.36002000	1.12080800	-0.44158800
C	3.50364700	-1.09189400	-0.11648200
C	5.28773000	0.93476700	0.58749600
H	4.34620700	2.07100700	-0.97104200
C	4.41975600	-1.30478300	0.91361700
C	5.31002700	-0.28680100	1.26591000
H	5.98352300	1.72764800	0.85282400
H	4.45706500	-2.24965600	1.44989500
O	2.61209100	-2.05983500	-0.50321800
H	2.71309400	-2.85155300	0.04710800
O	6.18387700	-0.55982000	2.28681300
H	6.74942500	0.21034200	2.45204800

(f) D-A pair (quinoidal form of resorcinol as D and anthraquinone as R)

C	-0.15167100	1.00384600	-0.17536100
C	0.96790700	0.20054400	-0.45447300
C	0.75411400	-1.16689500	-0.74161100
C	-0.52376400	-1.71152800	-0.70206100
C	-5.42692500	-1.17704100	0.04202100
C	-6.51782000	-0.36501200	0.34779500
C	-6.32873500	0.99973100	0.60419400
C	-5.04902600	1.54981100	0.55416500
C	-2.58887800	1.35609300	0.20139400
C	-2.98786200	-1.52490300	-0.34104400
C	-1.43625100	0.46030900	-0.12153400
C	-1.62883600	-0.91167000	-0.38140000
C	-4.13694100	-0.63292600	-0.01038800
C	-3.94658400	0.74112000	0.24777100
O	-2.41941900	2.55192800	0.41923600
O	-3.15067300	-2.72021100	-0.57053500
H	-0.03283300	2.06555200	0.02112100
H	1.59174900	-1.79038600	-1.03715700
H	-0.69061800	-2.75978800	-0.92910400
H	-5.55169400	-2.23616300	-0.16000700
H	-7.51608700	-0.79252700	0.38716800
H	-7.18018100	1.63146600	0.84250600
H	-4.88078400	2.60420100	0.74929900
C	2.28694200	0.83449100	-0.49764400
H	2.29016400	1.85461600	-0.87346000
C	3.49130700	0.31777700	-0.11119700

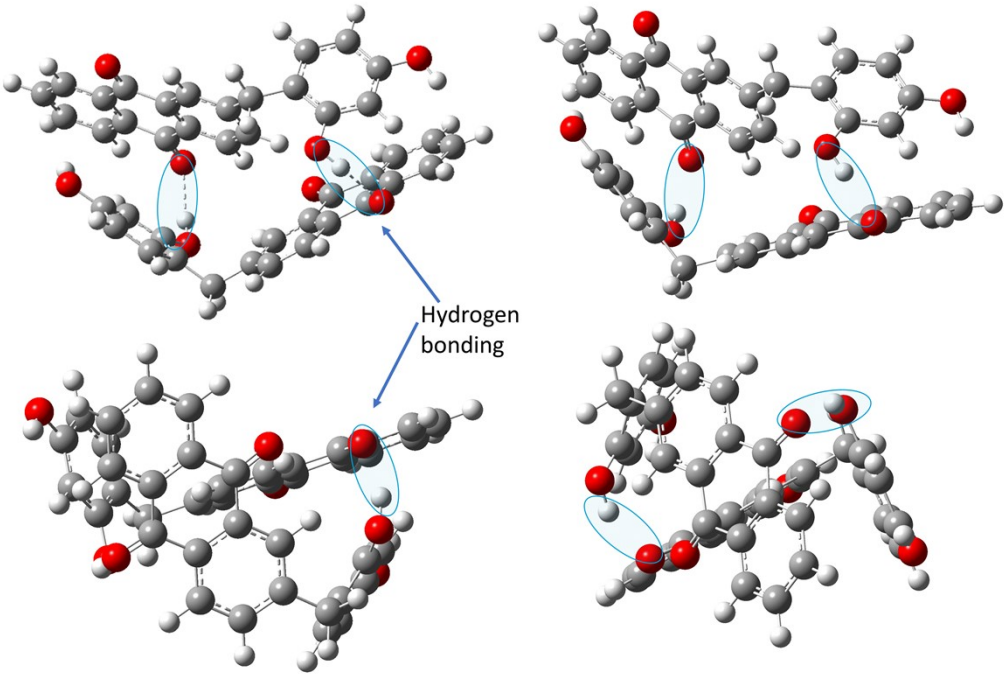
C	3.65771500	-0.95415800	0.58711100
C	4.72127200	1.08689000	-0.35470500
C	4.87029900	-1.43252400	0.93847600
H	2.76202800	-1.49823900	0.86695200
C	5.94681500	0.60617900	-0.02292500
C	6.11211800	-0.69232500	0.63146100
H	4.98544200	-2.36600900	1.48117200
H	6.85551200	1.16582400	-0.23229300
O	7.22342900	-1.14175500	0.93075300
O	4.53061800	2.29239900	-0.96274700
H	5.38447700	2.73572400	-1.09009200

(g) D-A pair (biquinoidal form of resorcinol as D and anthraquinone as R)

C	0.65713900	-1.11403400	-0.11104500
C	-0.47836700	-0.36991300	-0.47682700
C	-0.29419900	0.96750700	-0.89593700
C	0.96986800	1.54453600	-0.90282800
C	5.87734800	1.20744500	-0.07756400
C	6.98474700	0.45646100	0.31301300
C	6.82591700	-0.88029900	0.70276300
C	5.55995000	-1.46348100	0.70113500
C	3.09855400	-1.36555700	0.31849600
C	3.43372300	1.45600200	-0.50596700
C	1.92781600	-0.53575500	-0.10169500
C	2.09033900	0.80782100	-0.49572000
C	4.60101400	0.62958300	-0.08254200
C	4.44112800	-0.71619200	0.31002800
O	2.95550700	-2.53621100	0.65718400
O	3.56924100	2.62722800	-0.84954100
H	0.56102300	-2.15391000	0.18780900
H	-1.14356800	1.53879500	-1.25675900
H	1.11432000	2.56875800	-1.23202000
H	5.97859500	2.24401100	-0.38317500
H	7.97235400	0.90977100	0.31476000
H	7.69020000	-1.46453900	1.00694100
H	5.41510600	-2.49703200	0.99933000
C	-1.78237200	-1.03354400	-0.45776000
H	-1.77626400	-2.09220700	-0.71368500
C	-3.00336800	-0.51595500	-0.14336900
C	-3.22842500	0.81638600	0.39257700

C	-4.19113400	-1.42279900	-0.31530400
C	-4.44338200	1.36725000	0.64664600
H	-2.34533000	1.39804800	0.64430900
C	-5.54318800	-0.80783100	-0.11740100
O	-4.06491100	-2.60227300	-0.62501300
C	-5.68235100	0.60841300	0.36149500
C	-4.61336100	2.74152500	1.22833500
C	-6.64573500	-1.53385400	-0.37464200
O	-6.78775200	1.11776600	0.53736600
H	-5.20355000	3.37411900	0.55480700
H	-5.17250900	2.69655300	2.17056100
H	-3.64627800	3.22022200	1.41138200
H	-6.56000600	-2.56075200	-0.71684900
H	-7.63072500	-1.09621000	-0.24269600

(g) D-A dimer (resorcinol as D and anthraquinone as R)

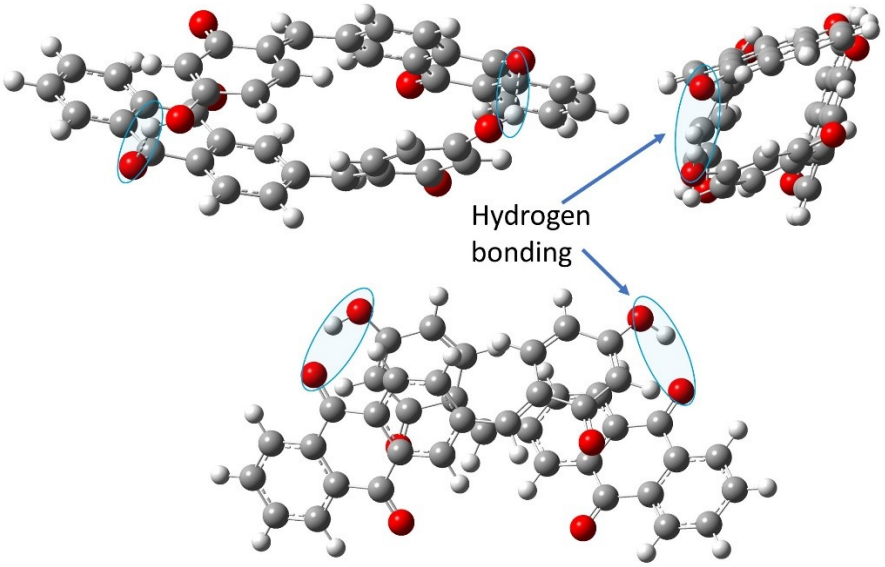


C	-0.32404100	-3.37295100	-0.62885900
C	-0.71457600	-2.69965100	0.53697000
C	-1.95883600	-2.07133800	0.62083200
C	-2.84560000	-2.10925500	-0.47803600
C	-2.44622500	-2.75575700	-1.65378300
C	-1.20261500	-3.37777300	-1.72437900
C	-2.32028800	-1.33476200	1.86514900
C	-4.18211300	-1.48036300	-0.40579000
C	-4.61746800	-0.91410100	0.89816600
C	-3.71290400	-0.80458400	1.97330200
C	-4.12009500	-0.18722400	3.16249600
H	-3.40245600	-0.09708300	3.97183000

C	-5.42176500	0.29407400	3.29207700
C	-6.33015900	0.15969600	2.23330300
C	-5.92703300	-0.43537700	1.03988500
H	-0.04350100	-2.66401900	1.38836600
H	-3.12603800	-2.77611000	-2.49943100
H	-0.91202200	-3.88857300	-2.63940000
H	-5.73285400	0.77174100	4.21698500
H	-7.34862400	0.52312100	2.34339900
H	-6.61211300	-0.54430600	0.20438600
O	-4.91147700	-1.39833100	-1.40317600
O	-1.50488600	-1.16480700	2.76749700
C	1.01411800	-4.08445500	-0.70306100
H	1.16891900	-4.64231100	0.22655600
H	0.98135000	-4.81812600	-1.51690500
C	2.19528800	-3.15630800	-0.93033100
C	2.64793400	-2.84791300	-2.21924000
C	2.88157200	-2.58551900	0.15382500
C	3.73491200	-2.00519900	-2.45020500
H	2.12471400	-3.27569800	-3.07220900
C	4.02182600	-1.79947500	-0.05404100
C	4.42635000	-1.48362200	-1.35319400
H	4.05999000	-1.75625400	-3.45499700
H	4.59055000	-1.44568200	0.79959500
O	2.41790500	-2.84011100	1.41737200
H	2.62447100	-2.08512800	2.00589000
O	5.50112400	-0.67034900	-1.60545300
H	5.82325900	-0.27125400	-0.78123900
C	-3.35185800	1.51627000	-1.97234700
C	-4.57330900	1.77182100	-1.33293200
C	-2.25053100	2.36604700	-1.78432300
C	-4.69765000	2.87168800	-0.48336200
H	-5.40909800	1.09524000	-1.48962200
C	-2.42261900	3.47757200	-0.94795600
C	-3.62227400	3.74500500	-0.29357400
H	-1.57424600	4.13964200	-0.78666300
H	-3.73582000	4.59977700	0.36502200
C	-0.89597900	2.05793800	-2.39007500
C	0.14389300	1.68319700	-1.34703100
H	-0.53095100	2.92042800	-2.96140700
C	1.45320400	2.16522400	-1.43384900
C	-0.18794100	0.84271400	-0.27019700
C	2.41261200	1.82935500	-0.47400400
H	1.75028600	2.81693200	-2.25061700
C	0.75262600	0.49486300	0.69217000
H	-1.20314700	0.46872700	-0.18865900
C	2.06292900	0.98663300	0.60355900

C	3.79070300	2.37543200	-0.61362200
H	0.48108800	-0.14821900	1.52336600
C	3.06143300	0.58942300	1.61710900
C	4.79224600	1.99222200	0.42936700
O	4.10218900	3.11857700	-1.53883600
C	4.43211500	1.17044100	1.51604300
O	2.80124800	-0.23208600	2.50475500
C	6.10814900	2.46014100	0.31822400
C	5.38957800	0.83930900	2.48499600
H	6.36470000	3.08420400	-0.53208700
C	7.05691200	2.12019800	1.28258900
C	6.69529300	1.31451500	2.37126400
H	5.09223800	0.20415300	3.31353200
H	8.07677400	2.48360100	1.18970100
H	7.43346900	1.05480500	3.12520200
H	-0.99459500	1.23174400	-3.10297500
O	-5.86219700	3.14238600	0.19124900
H	-6.48802900	2.41253200	0.06487600
O	-3.19650000	0.43217700	-2.79505800
H	-3.92445000	-0.20243900	-2.65212100

(h) D-A dimer (quinoidal resorcinol as D and anthraquinone as R)



C	1.46153800	-1.04249100	-1.38556300
C	0.77960800	0.03416700	-1.97710100
C	1.53329100	1.14120700	-2.42535900
C	2.90464500	1.19883900	-2.21255400
C	7.05104700	-0.76830300	-0.27036100
C	7.69651800	-1.81612500	0.38240100
C	6.97497500	-2.95506400	0.76504600
C	5.61210900	-3.04637800	0.48895700

C	3.49820000	-2.12460300	-0.44927400
C	5.00819100	0.29595700	-1.21408500
C	2.83467000	-0.98184300	-1.14821100
C	3.56399300	0.15694800	-1.54538000
C	5.68000800	-0.85133800	-0.55184200
C	4.95692700	-2.00144800	-0.17138100
O	2.86374100	-3.12540200	-0.13557000
O	5.61503900	1.34701000	-1.44848200
H	0.91966600	-1.92657000	-1.06206300
H	1.03746800	1.94760400	-2.95662500
H	3.48287400	2.05859800	-2.53560000
H	7.59165200	0.12357800	-0.57126800
H	8.75952800	-1.74741500	0.59719300
H	7.47744000	-3.76830200	1.28174300
H	5.03306100	-3.91486900	0.78550000
C	-0.67770900	-0.04934000	-2.06875100
H	-1.09060100	-1.03598800	-2.27971900
C	-1.59950900	0.92220700	-1.81354400
C	-1.28492400	2.25018300	-1.31351500
C	-3.05679200	0.52200500	-1.91335400
C	-2.25213800	3.07946800	-0.85531700
H	-0.24689000	2.55200500	-1.23655100
C	-4.03064300	1.47474300	-1.42121500
C	-3.63861200	2.65275900	-0.85071400
H	-2.02256600	4.04723600	-0.42034800
H	-5.07257400	1.17364300	-1.44805400
O	-4.47494800	3.48976300	-0.19622900
H	-5.25964200	2.99783700	0.11632100
O	-3.39142200	-0.59029000	-2.34294800
H	5.26002700	2.99800400	-0.11519000
O	4.47506900	3.48963300	0.19715100
C	3.63872800	2.65239500	0.85132400
C	2.25223400	3.07904500	0.85587000
C	4.03075100	1.47426700	1.42159300
C	1.28500900	2.24962700	1.31380200
H	2.02266600	4.04690300	0.42110100
C	3.05688600	0.52136400	1.91338600
H	5.07269200	1.17320700	1.44849600
C	1.59959700	0.92155000	1.81354600
H	0.24696500	2.55142400	1.23682300
O	3.39151600	-0.59103400	2.34270900
C	0.67777500	-0.05003000	2.06852100
C	-0.77953100	0.03360000	1.97685400
H	1.09061600	-1.03672700	2.27936100
C	-1.46157100	-1.04294800	1.38523800
C	-1.53309000	1.14069600	2.42517600

C	-2.83470700	-0.98215900	1.14794500
H	-0.91979000	-1.92705700	1.06167000
C	-2.90444700	1.19846400	2.21242900
H	-1.03716300	1.94702400	2.95645200
C	-3.49838400	-2.12483300	0.44900700
C	-3.56391600	0.15667000	1.54521900
H	-3.48257900	2.05826700	2.53553200
C	-4.95711500	-2.00152900	0.17118800
O	-2.86402000	-3.12564500	0.13515500
C	-5.00810400	0.29583900	1.21395800
C	-5.61242900	-3.04636700	-0.48916300
C	-5.68007300	-0.85137000	0.55173700
O	-5.61487900	1.34689600	1.44856400
C	-6.97530600	-2.95492400	-0.76515600
H	-5.03347500	-3.91489600	-0.78578000
C	-7.05112600	-0.76820600	0.27036000
C	-7.69672900	-1.81594200	-0.38240800
H	-7.47787500	-3.76809500	-1.28185600
H	-7.59163100	0.12371100	0.57133700
H	-8.75974600	-1.74713100	-0.59712800

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