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Supporting Information for:

A consecutive-photoreduction-based multicolor photochromic gel and its color recovery through heat-induced solation

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General Methods

Materials:

Disodium anthraquinone-2,6-disulfonate (AQDS), sodium anthraquinone-2-sulfonate monohydrate (AQS), and ι-carrageenan were purchased from Tokyo Chemical Industry Co. (TCI). Indigo carmine (IC), agar, and methylcellulose 25 were purchased from FUJIFILM Wako Pure Chemical Co. Triethanolamine (TEOA) was purchased from Sigma-Aldrich. All reagents were used without further purification.

Sample preparation:

IC (200 μM), AQDS (400 μM), and TEOA (10 mM) were dissolved in Milli-Q water to prepare the solution samples. For the ι-carrageenan samples, ι-carrageenan (typically, 0.2 wt% for sol preparation and 2 wt% for gel preparation) was added to the solution and dissolved by heating at ~60°C. The sol was then cooled at approximately 10°C to obtain the gel. Although cooling to room temperature was enough for the gelation, a refrigerator (~10°C) was used to keep a constant temperature. Bubbling for the gel samples was conducted in the sol state at ~60°C.

The aqueous agar and methylcellulose samples containing AQS were prepared in the following ways for the measurements in Fig.S11. For the methylcellulose sol, methylcellulose 25 (2 wt%) was added to aqueous AQS, stirred at ~60°C, and finally dissolved by cooling at ~10°C. For the agar gel, agar (0.4 wt%) was added to aqueous AQS and dissolved by heating at ~60°C. The sol was then cooled at ~10°C to obtain the gel.

Photoreduction and air-oxidation:

Photoirradiation for photoreduction of the sample in the cuvette was conducted by a 365-nm LED light source (a UV-LED controller CL-1501 (Asahi Spectra) and a 365-nm LED CL-H1-365-9-1-B (Asahi Spectra) equipped with a rod lens RLQL80-1 (Asahi Spectra)). The light intensity was basically set to 3.9 mW cm^{-2}.

For the solution samples, air-oxidation was conducted by shaking the cuvette. For the gel samples, air-oxidation was conducted by air bubbling in the sol state heated at ~60°C. In cyclability measurements of the photoreduction (Fig. S8), air bubbling was conducted to oxidize the reduced form of AQDS and to saturate the sample with air.

UV-Vis (absorption or optical density) spectroscopy:

UV-Vis spectra were measured on a UV-3600 spectrometer (SHIMADZU) at room temperature. The 1.0-mm quartz cuvette was used.

Measurements of the time evolution of absorption:

Absorbance changes over time were traced using an OCEAN FX spectrometer (Ocean Optics) as a detector and a DH-2000-BAL deuterium-halogen light source (Ocean Optics) as a probe light. To suppress the effect of probe light on photoreaction, the light sources were controlled by a home-made MATLAB code in the

following ways: The probe light and the 365-nm LED light (a UV-LED controller CL-1501 (Asahi Spectra) and a 365-nm LED CL-H1-365-9-1-B (Asahi Spectra) equipped with a rod lens RLQL80-1 (Asahi Spectra)) were alternatingly irradiated for 0.1 and 2 s, respectively. The spectral data were acquired during the probe light irradiation. The 1.0-mm quartz cuvette was used.

Multicolor photopatterning:

The photomasks were made of polyester film. The transmittance of each part of the photomask was measured by a UV-3600 spectrometer (SHIMADZU). The gel sample was prepared in a glass petri dish with the inner diameter of 7 cm.

Coloration stability in the AQDS-IC aqueous solution and hydrogel after UV light irradiation

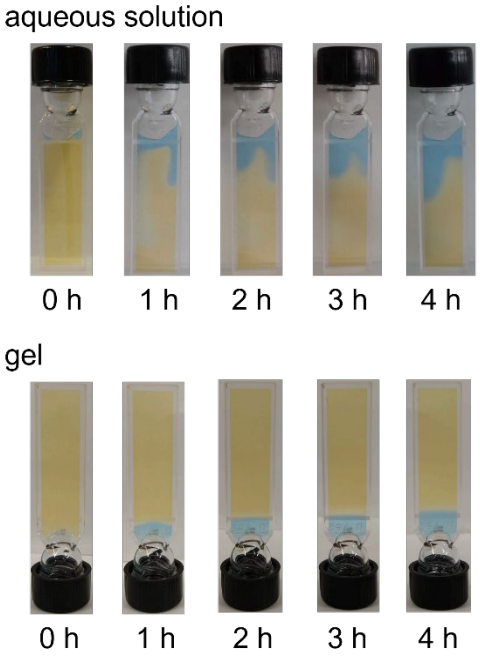

Fig. S1 Photographs of (top) the AQDS-IC aqueous solution and (bottom) 2wt% ι-carrageenan hydrogel (200 μM IC, 400 μM AQDS, 10 mM TEOA; 1.0 mm cuvette) after 365-nm light irradiation.

Absorption spectral changes of the AQDS-IC hydrogel

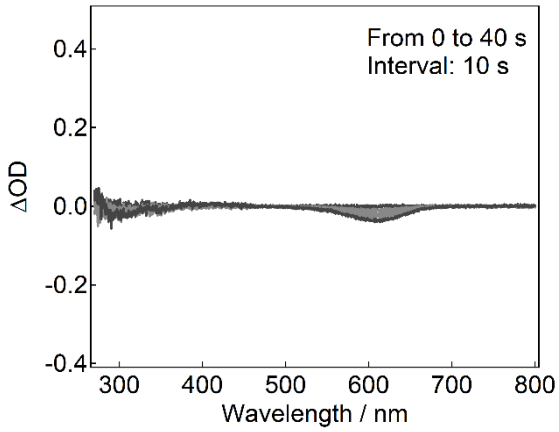

Fig. S2 Absorption spectral changes in the range of 0–40 s of the AQDS-IC hydrogel (200 μM IC, 400 μM AQDS, 10 mM TEOA, 2wt% ι-carrageenan; 1.0 mm cuvette) under 365-nm light irradiation (3.9 mW cm^{-2}). This data is correspondent with the absorption changes shown in Fig.2c.

Photoinduced color changes in the AQDS-IC aqueous solution and hydrogel

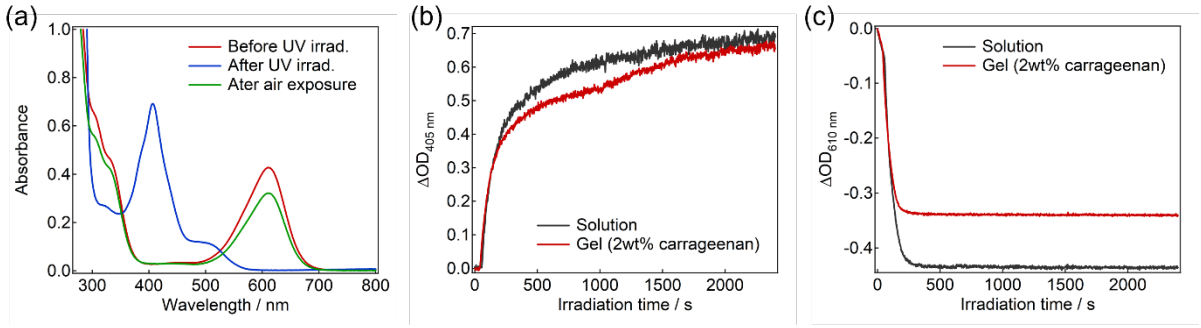

Fig. S3 (a) Absorption spectra of the AQDS-IC aqueous solution (200 μM IC, 400 μM AQDS, 10 mM TEOA; 1.0 mm cuvette) before and after 365-nm light irradiation (3.9 mW cm^{-2}) and air exposure. (b,c) The absorption changes at 405 and 610 nm under the 365-nm light irradiation. The absorption changes in the hydrogel (shown in Fig.3c) were overlaid for comparison.

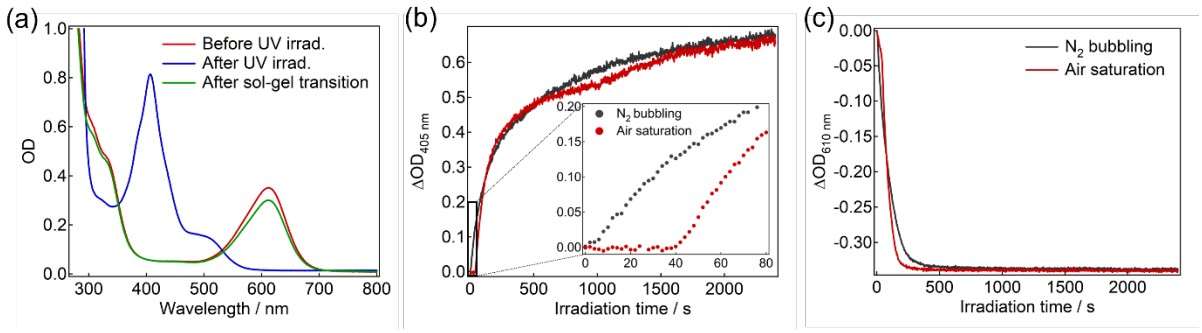

Fig. S4 (a) Absorption spectra of the N_2-bubbled AQDS-IC hydrogel (200 μM IC, 400 μM AQDS, 10 mM TEOA; 1.0 mm cuvette) before and after 365-nm light irradiation (3.9 mW cm^{-2}) and after the sol–gel transition. (b,c) The absorption changes at 405 and 610 nm under the 365-nm light irradiation. The absorption changes in the air-saturated hydrogel (shown in Fig.3c) were overlaid for comparison.

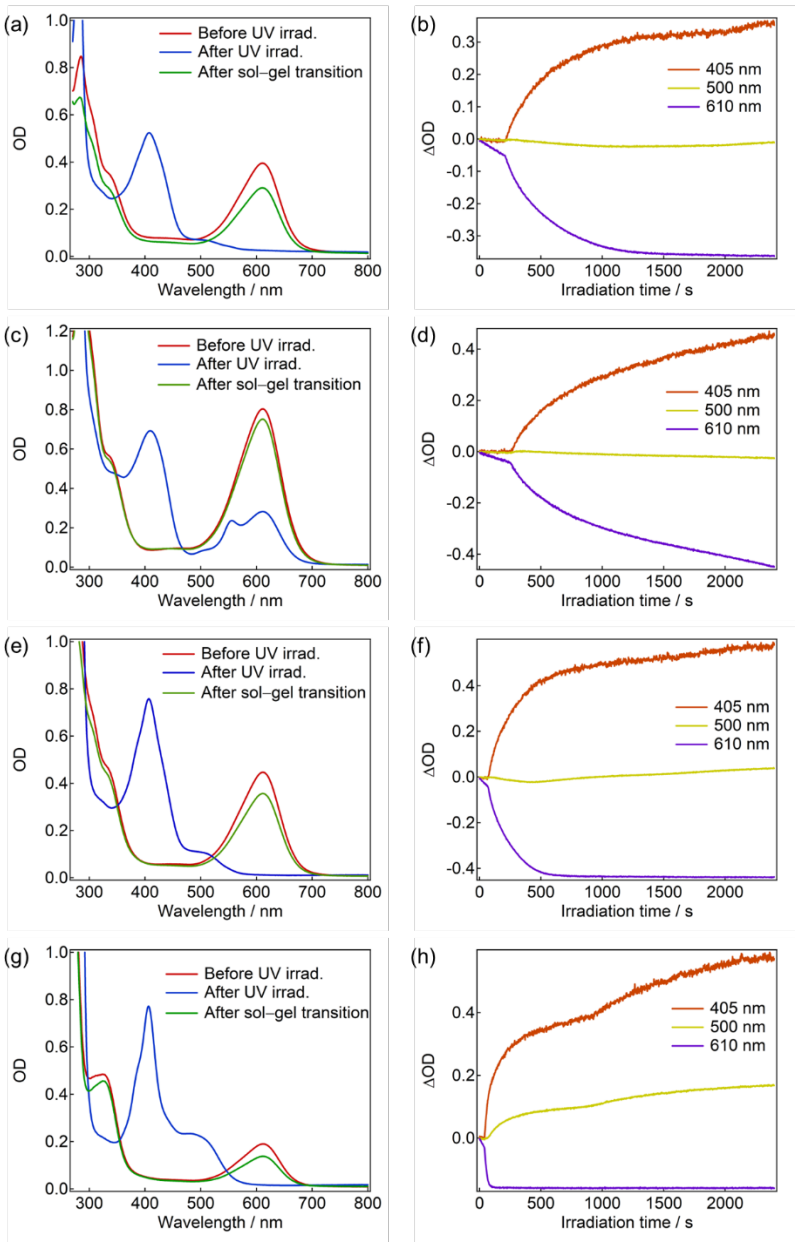

Fig. S5 (a,c,e,g) Absorption spectra of the AQDS-IC hydrogels with different concentrations of AQDS and IC (10 mM TEOA; 1.0 mm cuvette) before and after 365-nm light irradiation (3.9 mW cm^{-2}) and after the sol–gel transition. (b,d,f,h) The absorption changes at 405, 500, and 610 nm under the 365-nm light irradiation. (a,b) 300 μM IC, 100 μM AQDS; (c,d) 500 μM IC, 100 μM AQDS; (e,f) 300 μM IC, 300 μM AQDS; (g,h) 100 μM IC, 500 μM AQDS.

The coloration dynamics were investigated in the hydrogels containing various concentrations of AQDS and IC (Fig. S5). The decrease in the AQDS concentration extended the induction period caused by the dissolved oxygen, because the oxygen consumption is induced by the excitation of AQDS. The increase in the IC concentration also prevented the photoexcitation of AQDS to give some extension of the induction period.

The larger IC/AQDS ratios slowed down the reduction of IC. Notably, in the hydrogel of 500 μM IC and 100 μM AQDS, a distinctive absorption peak at ~555 nm was observed after photoirradiation (Fig.

S5c). This peak would be attributed to the IC radical anion,[1] which is an intermediate in the two-electron reduction. As a result of the slow reduction of IC, the IC radical anion would be transiently detected in this light irradiation condition. In contrast, the smaller IC/AQDS ratio led to a shorter induction period and faster depletion of IC (Fig. S5h).

The best concentration condition would depend on the application, but we selected 200 μM IC and 400 μM AQDS as the basic condition in this study, based on the balance between the color change amount and dynamics.

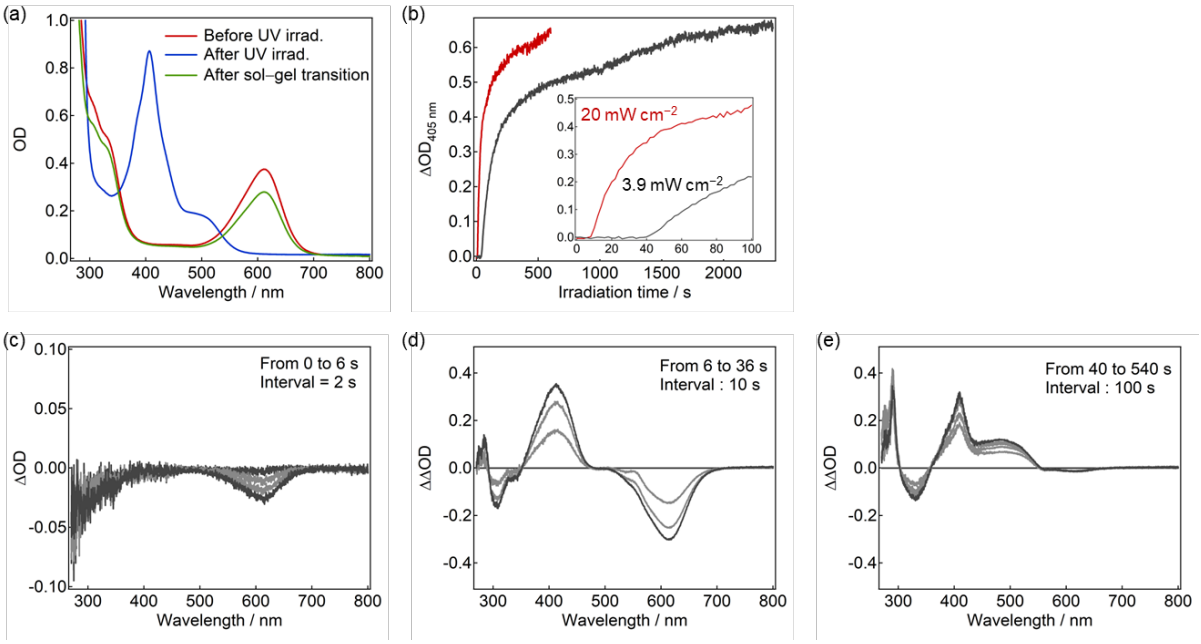

Fig. S6 (a) Absorption spectra of the AQDS-IC hydrogel (200 μM IC, 400 μM AQDS, 10 mM TEOA, 2wt% ι-carrageenan; 1.0 mm cuvette) before and after 365-nm light irradiation (20 mW cm^{-2}) and after the sol–gel transition. (b, red) The absorption change at 405 nm under the 365-nm light irradiation (black: The absorption changes under the light intensity of 3.9 mW cm^{-2} (shown in Fig.3c) for comparison). (c–e) Absorption spectral changes of the hydrogel under the 365-nm light; (c) 0–6 s, (d) 6–36 s, (e) 40–540 s. The spectra (d,e) show the changes from the absorption spectrum at the starting time in the shown time range.

The color changes were almost completed within 10 min under the more intense UV light (20 mW cm^{-2}, Fig.S6). There were no other noticeable influences from the light intensity change.

UV light irradiation to an aqueous solution of IC

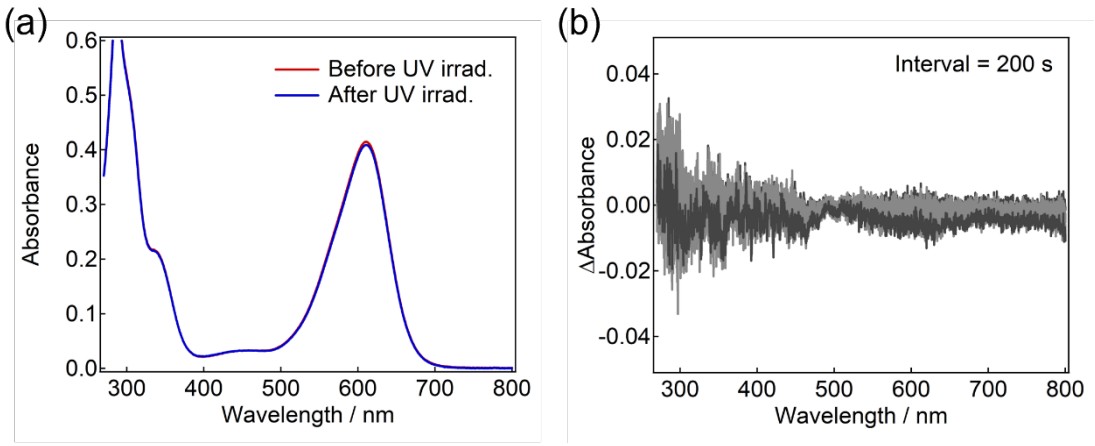

Fig. S7 (a) Absorption spectra of an aqueous solution of IC and TEOA (200 μM IC, 10 mM TEOA; 1.0 mm cuvette) before and after 365-nm light irradiation (3.9 mW cm^{-2}, 2400 s). (b) The absorption spectral changes under the 365-nm light irradiation.

Cyclability of the photochromism of the AQDS-IC hydrogel

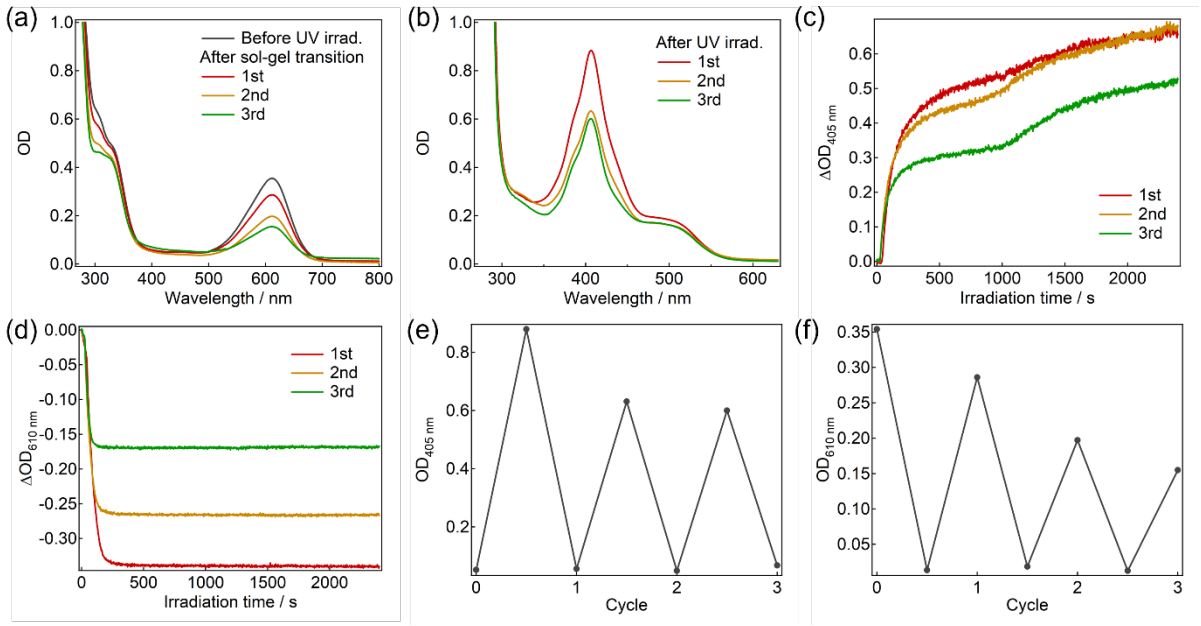

Fig. S8 Cyclability test of the photochromism of the AQDS-IC hydrogel (200 μM IC, 400 μM AQDS, 10 mM TEOA; 1.0 mm cuvette). Each cycle contained 365-nm light irradiation (3.9 mW cm^{-2}) and thermally induced sol–gel transition. (a,b) The absorption spectra (a) before and (b) after the UV light irradiation in each cycle. (c,d) The absorption changes at (c) 405 and (d) 610 nm under the UV light in each cycle. (e,f) The optical densities at (e) 405 and (f) 610 nm in each cycle.

Two-step photoreduction of AQS and AQDS

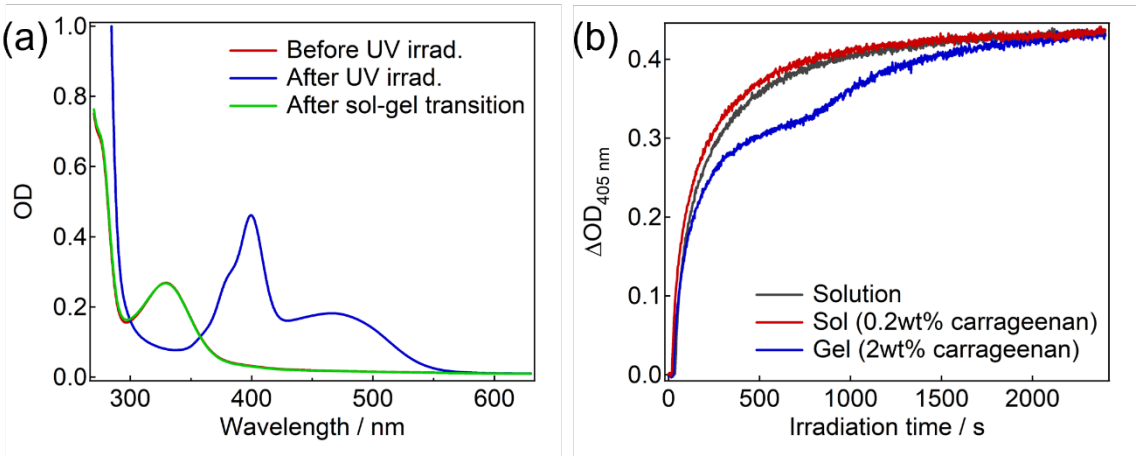

Fig. S9 (a) Absorption spectra of AQDS in the 2wt% ι-carrageenan hydrogel (400 μM AQDS, 10 mM TEOA; 1.0 mm cuvette) before and after 365-nm light irradiation (3.9 mW cm^{-2}) and after the sol–gel transition. (b) Absorption changes at 405 nm of AQDS (400 μM AQDS, 10 mM TEOA; 1.0 mm cuvette) in aqueous samples containing different ι-carrageenan concentrations under 365-nm light irradiation (3.9 mW cm^{-2}). The 0.2wt% ι-carrageenan sample was in the sol state even at room temperature, whereas the 2wt% sample was in the gel state.

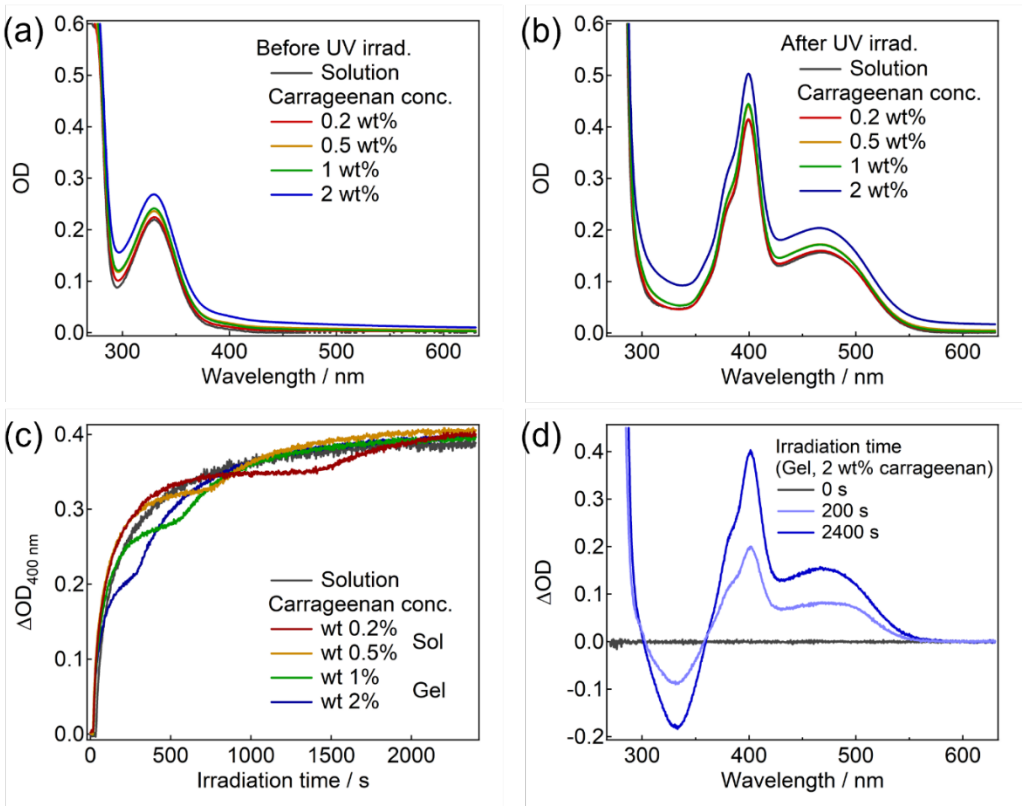

Fig. S10 (a,b) Absorption spectra of AQS in aqueous samples containing different ι-carrageenan concentrations (400 μM AQS, 10 mM TEOA; 1.0 mm cuvette) (a) before and (b) after 365-nm light irradiation (3.9 mW cm^{-2}). (c) The absorption changes at 400 nm under the 365-nm light irradiation. (d) The absorption spectral changes before and after the inflection point in 2 wt% ι-carrageenan sample. The 0.2wt% ι-carrageenan sample was in the sol state even at room temperature. The 0.2 and 0.5wt% ι-carrageenan samples were in the sol state even at room temperature, whereas the 1 and 2wt% samples were in the gel state.

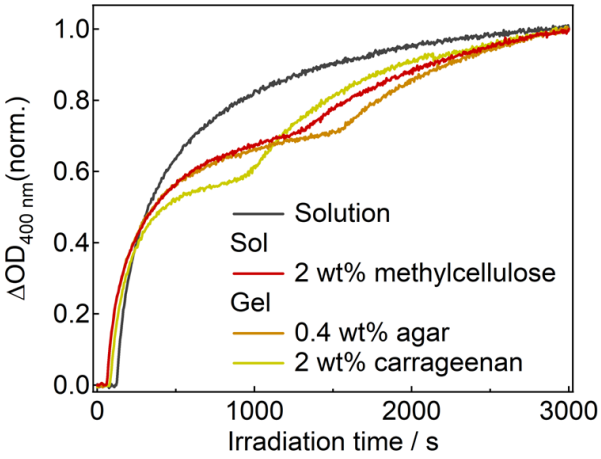

Fig. S11 Absorption changes at 400 nm of AQS in different aqueous polysaccharides (400 μM AQS, 10 mM TEOA; 1.0 mm cuvette) under 365-nm light irradiation (1.2 mW cm^{-2}, without the rod lens); (red) the 0.4wt% agar gel, (orange) the 2wt% ι-carrageenan gel, (yellow) the 2wt% methylcellulose sol, (black) the solution without polysaccharide as the reference.

Photoreduction-based coloration of AQDS showed an inflection point at around 950 s in the 2wt% ι-carrageenan hydrogel, leading to a two-step-like coloration behavior. In contrast, no obvious inflection point was observed in the 0.2wt% sol sample (Fig. S9b, red). The inflection in photoreduction was more significant in the case of AQS, and an inflection point was found even in the 0.2wt% ι-carrageenan sol sample (Fig. S10). Notably, the shapes of the absorption spectral changes were almost identical before and after the inflection point (Fig. S10d).

The mechanism of the two-step coloration was unclear, but some trends were observed. First, AQS, which is more hydrophobic than AQDS, showed more significant two-step coloration. Second, at higher concentrations of ι-carrageenan, the inflection point was observed earlier and at a smaller ΔOD. These trends provide a hypothesis that the two-step coloration resulted from the adsorption of anthraquinone (AQ) sulfonates on or the inclusion of those into the ι-carrageenan; the first coloration step would be brought by the photoreduction of AQ sulfonates in bulk water, and the second coloration would be caused by those adsorbed on or included into ι-carrageenan. It is well known that polysaccharides such as amylose have hydrophobic spaces in their helical structure and form inclusion complexes with hydrophobic molecules.[2] Unfortunately, we found no reports on inclusion complexes of carrageenan, but the formation of inclusion complexes of carrageenan or similar structures might be possible.

AQS also showed the two-step photoreduction in the aqueous samples of agar and methylcellulose (Fig. S11). This result showed some generality of the two-step photoreduction in aqueous polysaccharides.

Density functional theory calculation of AQDS reduced forms

All density functional theory (DFT) calculations were carried out using the Gaussian 16 program (Revision D.01)[3]. The molecular structure was fully optimized at the CAM-B3LYP/6-31G+(d,p)-PCM (water) level of theory, and an analytical second derivative was computed using vibrational analysis to confirm each stationary point to be a minimum. Time dependent DFT (TDDFT) calculations were performed at the CAM-B3LYP/6-31G+(d,p)-PCM (water) level of the theory for the optimized structures.

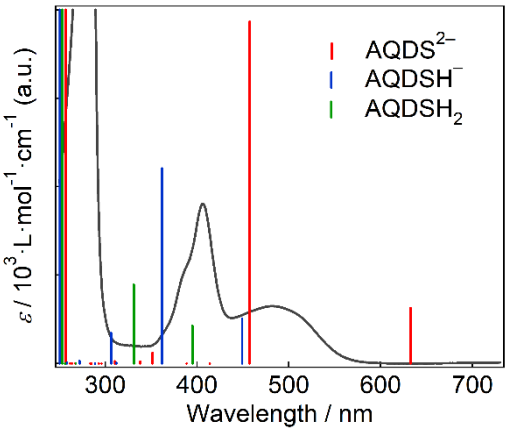

Fig. S12 Calculated absorption spectra of (red) $AQDS^{2-}$, (blue) $AQDSH^{-}$, and (green) $AQDSH_2$ and (black) the experimental absorption spectrum of the photogenerated reduced form of AQDS in water (400 μM AQDS, 10 mM TEOA). The calculation details are shown below.

Table S1. Standard orientation of the optimized geometry for $AQDS^{2-}$.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.3522200	0.3796490	-0.0054630
2	C	0.9768280	-1.0133090	-0.0021620
3	C	2.0197990	-1.9868460	-0.0052140
4	C	3.3433590	-1.6463370	-0.0093950
5	C	3.7032530	-0.2656840	-0.0117080
6	C	2.7387390	0.7030860	-0.0098420
7	C	0.3877610	1.4378960	-0.0026430
8	C	-0.9768310	1.0133190	0.0032190
9	C	-1.3522220	-0.3796400	0.0065190
10	C	-0.3877610	-1.4378860	0.0041540
11	C	-2.0198050	1.9868540	0.0057530
12	C	-3.3433660	1.6463420	0.0094390
13	C	-3.7032580	0.2656880	0.0117290
14	C	-2.7387410	-0.7030790	0.0103530

15	O	0.7294690	2.6960510	-0.0057410
16	O	-0.7294740	-2.6960420	0.0063840
17	S	5.4333100	0.1649620	0.0016520
18	S	-5.4333070	-0.1649700	-0.0023930
19	O	6.0383970	-0.4857510	-1.1984690
20	O	5.5133010	1.6504820	-0.0546910
21	O	5.9933380	-0.3875490	1.2712770
22	O	-5.9927180	0.3873530	-1.2723720
23	O	-5.5133110	-1.6504830	0.0541230
24	O	-6.0389860	0.4859110	1.1973390
25	H	1.7217240	-3.0300530	-0.0038440
26	H	4.1143820	-2.4100070	-0.0126500
27	H	3.0135660	1.7504860	-0.0113390
28	H	-1.7217320	3.0300620	0.0043840
29	H	-4.1143920	2.4100110	0.0122890

SCF Done: E(RCAM-B3LYP) = -1935.34432293 A.U.

Zero-point correction = 0.184260 (Hartree/Particle)
Thermal correction to Energy = 0.203067
Thermal correction to Enthalpy = 0.204011
Thermal correction to Gibbs Free Energy = 0.136298
Sum of electronic and zero-point Energies = -1935.160063
Sum of electronic and thermal Energies = -1935.141256
Sum of electronic and thermal Enthalpies = -1935.140312
Sum of electronic and thermal Free Energies = -1935.208025

Low frequencies --- -16.5704 -8.3963 -3.4906 -0.0015 0.0016 0.0021
Low frequencies --- 1.9665 12.8462 19.4395

The Results of the TDDFT calculation

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 1.9600 eV 632.56 nm f=0.0798 <S**2>=0.000
95 -> 96 0.70316

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -1935.27229278

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State	2:	Singlet-A	2.7122 eV	457.13 nm	f=0.4912	<S**2>=0.000
95 -> 97	0.69581					
Excited State	3:	Singlet-A	2.9965 eV	413.77 nm	f=0.0000	<S**2>=0.000
95 -> 98	0.60143					
95 ->101	-0.23394					
95 ->102	0.18977					
95 ->107	0.12763					
95 ->111	0.11556					
Excited State	4:	Singlet-A	3.1903 eV	388.63 nm	f=0.0000	<S**2>=0.000
95 ->101	0.45269					
95 ->102	0.52854					
Excited State	5:	Singlet-A	3.5264 eV	351.59 nm	f=0.0156	<S**2>=0.000
95 -> 99	0.22571					
95 ->100	0.62923					
95 ->105	-0.12668					
95 ->108	-0.10943					
Excited State	6:	Singlet-A	3.6664 eV	338.16 nm	f=0.0029	<S**2>=0.000
95 -> 99	0.62387					
95 ->100	-0.23594					
95 ->105	-0.17041					
95 ->108	0.10255					
Excited State	7:	Singlet-A	3.9906 eV	310.69 nm	f=0.0001	<S**2>=0.000
95 -> 98	-0.28313					
95 ->101	-0.16615					
95 ->102	0.13241					
95 ->103	0.32027					
95 ->107	0.45724					
95 ->111	0.16667					
95 ->115	0.11034					

Excited State	8:	Singlet-A	3.9914 eV	310.63 nm	f=0.0033	<S**2>=0.000
95 ->104		0.59236				
95 ->112		0.35186				
Excited State	9:	Singlet-A	4.1897 eV	295.93 nm	f=0.0000	<S**2>=0.000
95 -> 98		0.20935				
95 ->101		0.37124				
95 ->102		-0.33258				
95 ->103		0.36428				
95 ->107		0.16831				
95 ->111		-0.18536				
Excited State	10:	Singlet-A	4.2321 eV	292.96 nm	f=0.0000	<S**2>=0.000
95 ->101		-0.16170				
95 ->102		0.12916				
95 ->103		0.46357				
95 ->107		-0.41647				
95 ->113		-0.21498				
Excited State	11:	Singlet-A	4.3504 eV	285.00 nm	f=0.0000	<S**2>=0.000
94 -> 96		0.68457				
Excited State	12:	Singlet-A	4.3710 eV	283.65 nm	f=0.0000	<S**2>=0.000
95 ->106		-0.32702				
95 ->109		0.59158				
95 ->114		-0.14153				
Excited State	13:	Singlet-A	4.5511 eV	272.43 nm	f=0.0000	<S**2>=0.000
93 -> 96		0.68099				
94 ->114		-0.10479				
Excited State	14:	Singlet-A	4.6367 eV	267.40 nm	f=0.0000	<S**2>=0.000
95 ->106		0.57255				
95 ->109		0.34990				
95 ->114		0.10565				
95 ->120		-0.15147				

Excited State 15:	Singlet-A	4.6991 eV	263.85 nm	f=0.0000	<S**2>=0.000
95 -> 99	-0.18714				
95 ->105	-0.38098				
95 ->108	0.30158				
95 ->110	0.41803				
95 ->118	0.15950				
Excited State 16:	Singlet-A	4.7352 eV	261.83 nm	f=0.0002	<S**2>=0.000
95 -> 99	0.13466				
95 ->100	0.14453				
95 ->105	0.50681				
95 ->108	0.20533				
95 ->110	0.36132				
95 ->117	0.12082				
Excited State 17:	Singlet-A	4.8234 eV	257.05 nm	f=0.9587	<S**2>=0.000
90 -> 97	0.15634				
91 ->102	-0.10687				
92 -> 96	0.64872				
Excited State 18:	Singlet-A	4.8898 eV	253.56 nm	f=0.0004	<S**2>=0.000
95 ->108	0.55083				
95 ->110	-0.37497				
95 ->119	0.18171				
Excited State 19:	Singlet-A	5.0433 eV	245.84 nm	f=0.0000	<S**2>=0.000
95 ->106	-0.14088				
95 ->114	0.65962				
95 ->120	0.13364				
Excited State 20:	Singlet-A	5.0451 eV	245.75 nm	f=0.0102	<S**2>=0.000
95 ->104	-0.36165				
95 ->112	0.58785				
95 ->123	0.11218				
Excited State 21:	Singlet-A	5.1394 eV	241.24 nm	f=0.0001	<S**2>=0.000
94 -> 97	0.69448				

Excited State 22: Singlet-A 5.1800 eV 239.35 nm f=0.0000 <S**2>=0.000

89 -> 96	-0.10196
89 -> 97	-0.18048
91 -> 96	0.61069
92 ->101	-0.14569
92 ->102	-0.16690

Excited State 23: Singlet-A 5.2035 eV 238.27 nm f=0.0000 <S**2>=0.000

95 ->101	0.18611
95 ->102	-0.16166
95 ->107	-0.15402
95 ->111	0.62223

Excited State 24: Singlet-A 5.3657 eV 231.07 nm f=0.0000 <S**2>=0.000

93 -> 97	0.69371

Excited State 25: Singlet-A 5.3758 eV 230.63 nm f=0.0001 <S**2>=0.000

95 ->117	0.52377
95 ->118	0.40494
95 ->119	0.12035

Excited State 26: Singlet-A 5.3881 eV 230.11 nm f=0.0382 <S**2>=0.000

89 ->102	0.10738
90 -> 96	0.54593
92 -> 97	-0.39715

Excited State 27: Singlet-A 5.4003 eV 229.59 nm f=0.0000 <S**2>=0.000

95 ->103	0.16875
95 ->107	-0.11186
95 ->113	0.63090
95 ->115	-0.17855

Excited State 28: Singlet-A 5.4013 eV 229.54 nm f=0.0000 <S**2>=0.000

93 ->100	0.36314
93 ->108	-0.10259
94 -> 98	0.45993
94 ->101	-0.21867
94 ->102	0.18925

Excited State 29:	Singlet-A	5.4618 eV	227.00 nm	f=0.1441	<S**2>=0.000
93 -> 98	0.41555				
93 ->101	-0.20539				
93 ->102	0.17782				
94 ->100	0.41761				
94 ->108	-0.11509				
Excited State 30:	Singlet-A	5.5746 eV	222.41 nm	f=0.0742	<S**2>=0.000
95 ->116	0.68103				
Excited State 31:	Singlet-A	5.6257 eV	220.39 nm	f=0.0203	<S**2>=0.000
90 -> 96	-0.21561				
92 -> 97	-0.32977				
95 ->121	0.48899				
95 ->123	0.15457				
95 ->129	-0.18833				
Excited State 32:	Singlet-A	5.7006 eV	217.49 nm	f=0.0000	<S**2>=0.000
95 ->107	-0.14180				
95 ->113	0.16055				
95 ->115	0.63575				
95 ->126	0.12503				
95 ->127	0.10675				
Excited State 33:	Singlet-A	5.7234 eV	216.63 nm	f=0.0000	<S**2>=0.000
89 -> 96	0.53152				
90 ->101	0.12145				
90 ->102	0.13916				
91 -> 96	0.14790				
91 -> 97	0.36994				
Excited State 34:	Singlet-A	5.9518 eV	208.31 nm	f=0.0002	<S**2>=0.000
95 ->105	0.20236				
95 ->110	-0.10326				
95 ->117	-0.28840				
95 ->118	0.49310				
95 ->119	-0.31421				

Excited State 35:	Singlet-A	5.9677 eV	207.76 nm	f=0.0000	<S**2>=0.000
91 -> 97	-0.13228				
95 ->106	0.18194				
95 ->120	0.63991				
Excited State 36:	Singlet-A	5.9837 eV	207.20 nm	f=0.4864	<S**2>=0.000
90 -> 96	0.32856				
92 -> 97	0.43981				
95 ->121	0.37918				
Excited State 37:	Singlet-A	6.0054 eV	206.46 nm	f=0.0000	<S**2>=0.000
94 ->101	0.44828				
94 ->102	0.51661				
Excited State 38:	Singlet-A	6.0608 eV	204.57 nm	f=0.0000	<S**2>=0.000
89 -> 96	-0.36744				
91 -> 97	0.55532				
95 ->120	0.14517				
Excited State 39:	Singlet-A	6.0781 eV	203.99 nm	f=1.0907	<S**2>=0.000
90 -> 97	0.64612				
92 -> 96	-0.17213				
Excited State 40:	Singlet-A	6.0799 eV	203.93 nm	f=0.0035	<S**2>=0.000
91 -> 99	-0.16777				
92 -> 98	0.59954				
92 ->101	-0.14311				
92 ->102	0.11427				
92 ->107	0.18189				
Excited State 41:	Singlet-A	6.0855 eV	203.74 nm	f=0.0138	<S**2>=0.000
95 ->108	-0.16574				
95 ->110	0.10061				
95 ->117	-0.27936				
95 ->118	0.20009				
95 ->119	0.55424				

Excited State 42:	Singlet-A	6.1512 eV	201.56 nm	f=0.0000	<S**2>=0.000
85 -> 96	0.11084				
89 -> 97	0.51393				
91 -> 96	0.25621				
92 ->101	0.21055				
92 ->102	0.24731				
Excited State 43:	Singlet-A	6.2310 eV	198.98 nm	f=0.0012	<S**2>=0.000
93 ->101	0.45089				
93 ->102	0.51927				
Excited State 44:	Singlet-A	6.3157 eV	196.31 nm	f=0.0007	<S**2>=0.000
91 -> 98	0.46409				
92 -> 99	-0.43731				
92 ->105	0.11336				
Excited State 45:	Singlet-A	6.4129 eV	193.33 nm	f=0.0905	<S**2>=0.000
87 -> 96	-0.20831				
91 ->109	-0.10694				
94 -> 99	0.14336				
95 ->121	0.18498				
95 ->123	-0.13401				
95 ->129	0.56177				
Excited State 46:	Singlet-A	6.4216 eV	193.07 nm	f=0.0000	<S**2>=0.000
87 -> 96	0.11451				
87 ->101	-0.15243				
87 ->102	-0.18055				
88 -> 96	0.62444				
88 -> 97	0.12163				
Excited State 47:	Singlet-A	6.4235 eV	193.02 nm	f=0.0419	<S**2>=0.000
87 -> 96	0.58882				
87 -> 97	0.11424				
88 -> 96	-0.10767				
88 ->101	-0.14367				
88 ->102	-0.17036				
95 ->129	0.18728				

Excited State	48:	Singlet-A	6.4384 eV	192.57 nm	f=0.0000	<S**2>=0.000
89 -> 99	0.23683					
90 -> 98	0.54331					
90 ->101	-0.13984					
90 ->102	0.12203					
91 ->100	-0.16337					
95 ->126	-0.10592					
Excited State	49:	Singlet-A	6.4592 eV	191.95 nm	f=0.0000	<S**2>=0.000
93 ->100	-0.34361					
93 ->108	0.12141					
94 -> 98	0.27122					
94 ->103	0.16093					
94 ->107	0.44868					
94 ->115	0.13130					
Excited State	50:	Singlet-A	6.4619 eV	191.87 nm	f=0.0109	<S**2>=0.000
93 ->103	0.25055					
94 -> 99	0.50955					
94 ->100	-0.13539					
94 ->105	-0.17306					
94 ->108	0.13029					
95 ->121	-0.21411					
95 ->129	-0.13400					

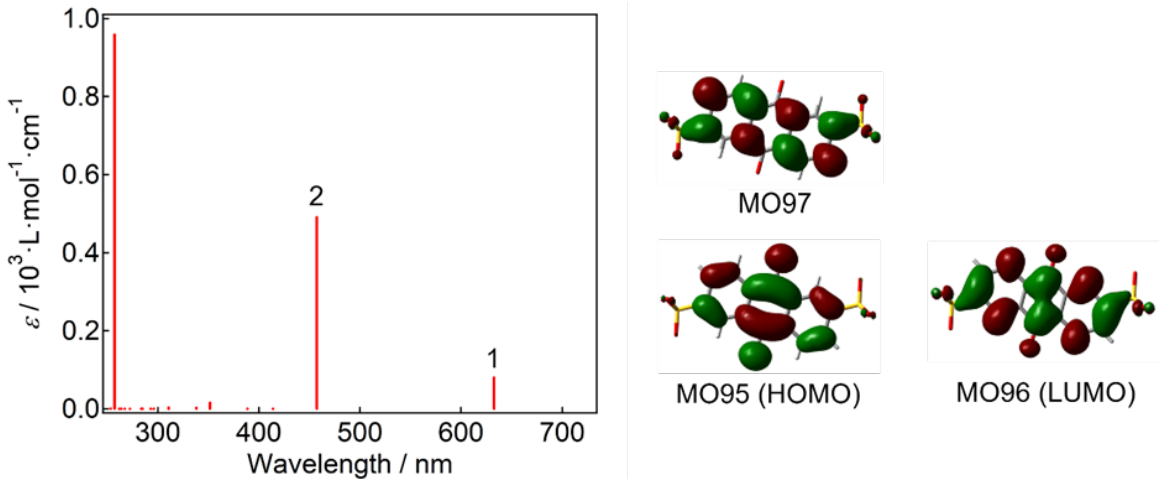

Fig. S13 The absorption spectra and the relevant molecular orbitals of $AQDS^{2-}$ calculated at the CAM-B3LYP/6-31G+(d,p)-PCM (water) level of the theory.

Table S2. Selected calculated electronic transition of $AQDS^{2-}$ at the CAM-B3LYP/6-31G+(d,p)-PCM (water) level.

No.	Wavelength (nm)	coefficients	Electronic Transition	*f*
1	632.56	0.70316	MO95 → MO96	0.0798
2	457.13	0.69581	MO95 → MO97	0.4912
3	413.77	0.60143	MO95 → MO98	0.0000
		-0.23394	MO95 → MO101	
		0.18977	MO95 → MO102	
		0.12763	MO95 → MO107	
		0.11556	MO95 → MO111	
4	388.63	0.45269	MO95 → MO101	0.0000
		0.52854	MO95 → MO102	

Table S3. Standard orientation of the optimized geometry for $AQDSH^{-}$.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	1.3564300	0.3549840	-0.0198010
2	C	0.9959480	-1.0302300	-0.0280870
3	C	2.0224920	-2.0061610	-0.0297350
4	C	3.3495800	-1.6658090	-0.0204430
5	C	3.6998200	-0.2900170	-0.0074680
6	C	2.7470390	0.6886220	-0.0078260
7	C	0.3630930	1.3446730	-0.0258160
8	C	-0.9887280	0.9930310	-0.0176760
9	C	-1.3740340	-0.3885350	-0.0215990
10	C	-0.3903100	-1.4498830	-0.0316680
11	C	-2.0298500	1.9783310	-0.0057580
12	C	-3.3473710	1.6220530	0.0021480
13	C	-3.7163110	0.2486830	-0.0028210
14	C	-2.7491980	-0.7207100	-0.0143590
15	O	0.7248810	2.6930170	0.0357830
16	O	-0.7208900	-2.6772620	-0.0407060
17	S	5.4375370	0.1485120	0.0268970
18	S	-5.4473580	-0.1769520	0.0220740
19	O	5.5030510	1.6325450	-0.0254070
20	O	5.9700360	-0.4077220	1.3025990
21	O	6.0429970	-0.5001670	-1.1697520

22	O	-5.5199990	-1.6616100	-0.0354530
23	O	-5.9936130	0.3760280	1.2956360
24	O	-6.0542570	0.4769300	-1.1735160
25	H	1.7199140	-3.0477050	-0.0384150
26	H	4.1224810	-2.4261950	-0.0233330
27	H	3.0433270	1.7296490	0.0067090
28	H	-1.7478970	3.0249680	0.0006890
29	H	-4.1177650	2.3865280	0.0118610

SCF Done: E(RCAM-B3LYP) = -1935.83645792 A.U. after 1 cycles

Zero-point correction	=	0.196719 (Hartree/Particle)
Thermal correction to Energy	=	0.216403
Thermal correction to Enthalpy	=	0.217347
Thermal correction to Gibbs Free Energy	=	0.147501
Sum of electronic and zero-point Energies	=	-1935.639739
Sum of electronic and thermal Energies	=	-1935.620055
Sum of electronic and thermal Enthalpies	=	-1935.619111
Sum of electronic and thermal Free Energies	=	-1935.688957

Low frequencies --- 0.0012 0.0019 0.0023 6.8320 8.1237 16.9519
Low frequencies --- 31.9492 55.0063 55.6570

The Results of the TDDFT calculation

Excited State 1: Singlet-A 2.7603 eV 449.16 nm f=0.1121 <S**2>=0.000
95 -> 96 0.70155
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1935.73501752
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.4275 eV 361.74 nm f=0.4871 <S**2>=0.000
94 -> 96 -0.15872
95 -> 97 0.68180

Excited State 3: Singlet-A 3.9703 eV 312.28 nm f=0.0021 <S**2>=0.000
95 -> 98 0.63402

95 ->100 0.11722
95 ->102 -0.21171
95 ->107 -0.11791

Excited State 4: Singlet-A 4.0465 eV 306.40 nm f=0.0764 <S**2>=0.000
95 ->100 -0.32847
95 ->101 0.60128

Excited State 5: Singlet-A 4.2906 eV 288.96 nm f=0.0000 <S**2>=0.000
93 -> 96 0.67517

Excited State 6: Singlet-A 4.5600 eV 271.89 nm f=0.0067 <S**2>=0.000
95 -> 99 0.29301
95 ->100 0.48451
95 ->101 0.28545
95 ->102 0.19811
95 ->105 -0.12660

Excited State 7: Singlet-A 4.7974 eV 258.44 nm f=0.0027 <S**2>=0.000
95 -> 99 0.58717
95 ->100 -0.25934
95 ->101 -0.13527
95 ->105 -0.13495
95 ->108 -0.10458

Excited State 8: Singlet-A 4.9494 eV 250.51 nm f=1.2484 <S**2>=0.000
92 -> 97 0.11231
94 -> 96 0.64304
95 -> 97 0.15935

Excited State 9: Singlet-A 5.0506 eV 245.48 nm f=0.0250 <S**2>=0.000
95 ->102 -0.17009
95 ->104 0.58604
95 ->110 -0.24607
95 ->111 0.11287
95 ->113 0.11263

Excited State 10: Singlet-A 5.1084 eV 242.71 nm f=0.0013 <S**2>=0.000

95 -> 98 0.24057
95 ->100 -0.14626
95 ->102 0.25700
95 ->103 0.25752
95 ->105 -0.14693
95 ->107 0.43782
95 ->112 0.15367

Excited State 11: Singlet-A 5.2887 eV 234.43 nm f=0.0016 <S**2>=0.000
95 ->100 -0.10336
95 ->102 0.44866
95 ->104 0.13393
95 ->105 0.16882
95 ->107 -0.38638
95 ->109 -0.17680
95 ->114 -0.10288

Excited State 12: Singlet-A 5.3713 eV 230.83 nm f=0.0002 <S**2>=0.000
95 ->102 -0.18914
95 ->103 0.60195
95 ->112 -0.15421
95 ->114 -0.13727

Excited State 13: Singlet-A 5.3867 eV 230.17 nm f=0.0136 <S**2>=0.000
92 -> 96 0.61558
94 -> 97 -0.21352

Excited State 14: Singlet-A 5.4651 eV 226.87 nm f=0.0050 <S**2>=0.000
94 ->101 0.11536
95 ->103 0.10197
95 ->105 -0.18299
95 ->106 -0.25322
95 ->107 -0.16868
95 ->108 0.16870
95 ->109 0.44855
95 ->110 0.17490
95 ->113 0.12050
95 ->114 -0.11048

Excited State	15:	Singlet-A	5.5714 eV	222.54 nm	f=0.0002	<S**2>=0.000
93 -> 97	0.69408					

Excited State	16:	Singlet-A	5.6594 eV	219.07 nm	f=0.1248	<S**2>=0.000
88 -> 96	0.14139					
90 -> 96	-0.35465					
91 -> 96	0.47333					
92 -> 97	0.17087					
92 ->101	0.11263					
95 ->109	-0.11362					
95 ->113	0.10107					

Excited State	17:	Singlet-A	5.7477 eV	215.71 nm	f=0.0172	<S**2>=0.000
88 -> 96	0.15160					
90 -> 96	0.16044					
90 -> 97	-0.13826					
91 -> 96	-0.18672					
91 -> 97	0.18726					
94 -> 97	-0.25347					
94 ->100	-0.10300					
94 ->101	0.17390					
95 ->108	-0.18555					
95 ->109	-0.14880					
95 ->110	0.16259					
95 ->112	-0.10855					
95 ->113	0.32001					

Excited State	18:	Singlet-A	5.7719 eV	214.80 nm	f=0.0041	<S**2>=0.000
91 -> 97	0.10834					
94 -> 97	-0.16270					
94 ->101	0.11348					
95 ->105	0.18361					
95 ->106	0.34256					
95 ->108	0.28626					
95 ->109	0.13931					
95 ->111	-0.30532					
95 ->119	-0.11329					

Excited State 19:	Singlet-A	5.7967 eV	213.89 nm	f=0.0009	<S**2>=0.000
95 ->106	0.38258				
95 ->108	-0.14810				
95 ->109	0.23743				
95 ->110	0.13089				
95 ->111	0.39913				
95 ->113	-0.10325				
95 ->121	0.13642				
Excited State 20:	Singlet-A	5.8485 eV	211.99 nm	f=0.0063	<S**2>=0.000
94 -> 97	0.16178				
95 -> 99	0.19573				
95 ->105	0.50707				
95 ->106	-0.23590				
95 ->107	0.17444				
95 ->117	-0.16048				
Excited State 21:	Singlet-A	5.9189 eV	209.47 nm	f=0.1643	<S**2>=0.000
91 -> 97	-0.11572				
92 -> 96	0.16257				
94 -> 97	0.33558				
95 ->106	0.18922				
95 ->110	0.26259				
95 ->111	-0.18307				
95 ->113	0.35091				
Excited State 22:	Singlet-A	5.9521 eV	208.30 nm	f=0.0125	<S**2>=0.000
88 -> 96	0.16228				
90 -> 97	-0.15303				
91 -> 97	0.21691				
92 -> 96	0.16539				
94 -> 97	0.36195				
94 ->100	-0.10001				
94 ->101	0.17900				
95 ->109	-0.16472				
95 ->110	-0.13800				
95 ->115	-0.18619				

95 ->118 -0.20103

Excited State 23: Singlet-A 6.0519 eV 204.87 nm f=0.0014 <S**2>=0.000
95 ->108 0.50183
95 ->109 -0.25366
95 ->110 0.14717
95 ->111 0.30658
95 ->120 -0.17712

Excited State 24: Singlet-A 6.0809 eV 203.89 nm f=0.2085 <S**2>=0.000
92 -> 97 0.15422
93 -> 98 0.37137
93 -> 99 -0.16629
93 ->100 -0.29220
93 ->101 -0.16781
93 ->102 -0.35937

Excited State 25: Singlet-A 6.1136 eV 202.80 nm f=0.0157 <S**2>=0.000
89 -> 96 0.63899
89 -> 97 0.12362
89 ->100 -0.11510
89 ->101 0.20656

Excited State 26: Singlet-A 6.1634 eV 201.16 nm f=0.0465 <S**2>=0.000
90 -> 96 0.51296
90 -> 97 0.11558
90 ->101 -0.15242
91 -> 96 0.31075
91 ->101 -0.10935
92 -> 97 0.21767

Excited State 27: Singlet-A 6.1862 eV 200.42 nm f=0.4429 <S**2>=0.000
91 -> 96 -0.26723
92 -> 97 0.54199
94 -> 96 -0.10711
95 ->110 -0.13142
95 ->113 0.11749

Excited State 28:	Singlet-A	6.2060 eV	199.78 nm	f=0.0399	<S**2>=0.000
91 -> 96	0.11356				
92 -> 97	-0.14801				
95 ->104	-0.26946				
95 ->110	-0.36849				
95 ->111	0.14034				
95 ->113	0.40165				
Excited State 29:	Singlet-A	6.2903 eV	197.11 nm	f=0.1934	<S**2>=0.000
88 -> 96	0.14832				
92 -> 96	0.11029				
94 -> 97	0.21661				
95 ->110	-0.19155				
95 ->115	0.35506				
95 ->116	-0.22537				
95 ->117	0.12028				
95 ->118	0.28678				
95 ->121	-0.12746				
Excited State 30:	Singlet-A	6.3595 eV	194.96 nm	f=0.0057	<S**2>=0.000
95 ->102	-0.20413				
95 ->107	-0.11778				
95 ->110	0.11317				
95 ->112	0.57474				
95 ->115	0.10542				
Excited State 31:	Singlet-A	6.3794 eV	194.35 nm	f=0.0007	<S**2>=0.000
86 -> 96	-0.13377				
93 ->100	-0.32765				
93 ->101	0.57485				
Excited State 32:	Singlet-A	6.4077 eV	193.49 nm	f=0.0020	<S**2>=0.000
94 -> 98	0.62495				
94 ->102	-0.13255				
94 ->107	-0.15170				
Excited State 33:	Singlet-A	6.4441 eV	192.40 nm	f=0.0031	<S**2>=0.000
73 -> 96	0.10017				

82 -> 96 0.15417
86 ->101 0.14090
87 -> 96 0.59024
93 ->101 0.11625

Excited State 34: Singlet-A 6.5063 eV 190.56 nm f=0.0029 <S**2>=0.000
95 ->103 0.11119
95 ->114 0.45705
95 ->115 -0.19201
95 ->116 -0.17810
95 ->117 0.29990
95 ->118 -0.12303
95 ->119 -0.21354

Excited State 35: Singlet-A 6.5365 eV 189.68 nm f=0.0002 <S**2>=0.000
92 -> 98 -0.15466
95 ->103 -0.10763
95 ->114 -0.38059
95 ->117 0.41082
95 ->118 -0.13353
95 ->119 -0.20981

Excited State 36: Singlet-A 6.6190 eV 187.32 nm f=0.0001 <S**2>=0.000
90 -> 98 -0.22988
90 -> 99 0.40954
90 ->100 0.10431
90 ->102 -0.16895
90 ->103 0.11154
90 ->105 0.10546
91 -> 98 -0.17941
91 -> 99 0.32209
91 ->102 -0.13006

Excited State 37: Singlet-A 6.6638 eV 186.06 nm f=0.0002 <S**2>=0.000
89 -> 98 0.39890
89 -> 99 0.37884
89 ->100 -0.20493
89 ->102 0.29027

89 ->103 -0.10264
89 ->105 0.10322

Excited State 38: Singlet-A 6.6739 eV 185.78 nm f=0.0335 <S**2>=0.000
82 -> 96 0.11048
86 -> 96 -0.24177
88 -> 96 0.41148
90 -> 97 0.24299
91 -> 97 -0.28519

Excited State 39: Singlet-A 6.6929 eV 185.25 nm f=0.0088 <S**2>=0.000
84 -> 96 0.11645
85 -> 96 -0.14649
86 -> 96 0.47940
87 -> 96 -0.12238
87 ->101 0.17420
88 -> 96 0.19769
90 -> 97 0.12277
91 -> 97 -0.14476

Excited State 40: Singlet-A 6.7303 eV 184.22 nm f=0.0064 <S**2>=0.000
95 ->115 -0.38263
95 ->116 0.15429
95 ->117 0.11183
95 ->118 0.51539

Excited State 41: Singlet-A 6.7520 eV 183.63 nm f=0.0001 <S**2>=0.000
90 -> 99 -0.10196
92 -> 98 0.44016
94 -> 99 -0.35872
94 ->100 0.11090
95 ->117 0.17700

Excited State 42: Singlet-A 6.8143 eV 181.95 nm f=0.0012 <S**2>=0.000
95 ->112 -0.10297
95 ->114 0.20130
95 ->115 0.21640
95 ->116 0.51167

95 ->117 0.16657
95 ->126 0.14800

Excited State 43: Singlet-A 6.8163 eV 181.89 nm f=0.0033 <S**2>=0.000
78 -> 96 0.12350
80 -> 96 0.10297
81 -> 96 -0.15360
82 -> 96 0.54094
84 -> 96 -0.12809
85 -> 96 -0.20008

Excited State 44: Singlet-A 6.8812 eV 180.18 nm f=0.0022 <S**2>=0.000
90 -> 96 -0.10265
90 -> 97 0.50865
90 ->113 0.11006
91 -> 97 0.41101

Excited State 45: Singlet-A 6.9087 eV 179.46 nm f=0.0070 <S**2>=0.000
90 -> 98 -0.30767
91 -> 98 0.40898
92 -> 99 0.26992
94 ->100 0.14412

Excited State 46: Singlet-A 6.9671 eV 177.96 nm f=0.0013 <S**2>=0.000
88 -> 96 0.17537
88 -> 97 -0.16238
88 -> 98 0.12588
91 -> 99 0.12355
92 -> 98 0.17998
92 ->100 -0.10010
92 ->102 -0.12067
94 -> 99 0.31158
94 ->100 0.17832
94 ->101 -0.21109
95 ->116 0.11536
95 ->119 -0.10402

Excited State 47: Singlet-A 6.9694 eV 177.90 nm f=0.0051 <S**2>=0.000

88 -> 96 -0.20531
88 -> 97 0.17017
88 -> 98 0.11620
91 -> 97 -0.11485
92 -> 98 0.15674
92 ->101 -0.15255
92 ->102 -0.10393
93 -> 98 -0.11084
94 -> 99 0.22756
94 ->100 -0.18629
94 ->101 0.29149
95 ->119 -0.10504

Excited State 48: Singlet-A 6.9755 eV 177.74 nm f=0.0134 <S**2>=0.000
93 -> 98 0.41750
93 ->100 0.25817
93 ->101 0.16665
93 ->107 -0.32560
93 ->108 0.11121
94 -> 99 0.11812

Excited State 49: Singlet-A 7.0108 eV 176.85 nm f=0.0106 <S**2>=0.000
81 -> 97 0.10081
83 -> 96 -0.13552
88 -> 96 0.12018
88 -> 97 0.32945
89 -> 97 0.14642
90 -> 97 -0.12841
91 -> 97 0.12296
92 ->100 0.14576
92 ->101 -0.26513
93 -> 99 -0.11509
94 ->100 0.10333
94 ->101 -0.26825

Excited State 50: Singlet-A 7.0338 eV 176.27 nm f=0.0031 <S**2>=0.000
94 -> 99 0.18618
95 ->105 0.15578

95 ->117	0.18565
95 ->119	0.42384
95 ->120	-0.24330
95 ->121	-0.21169

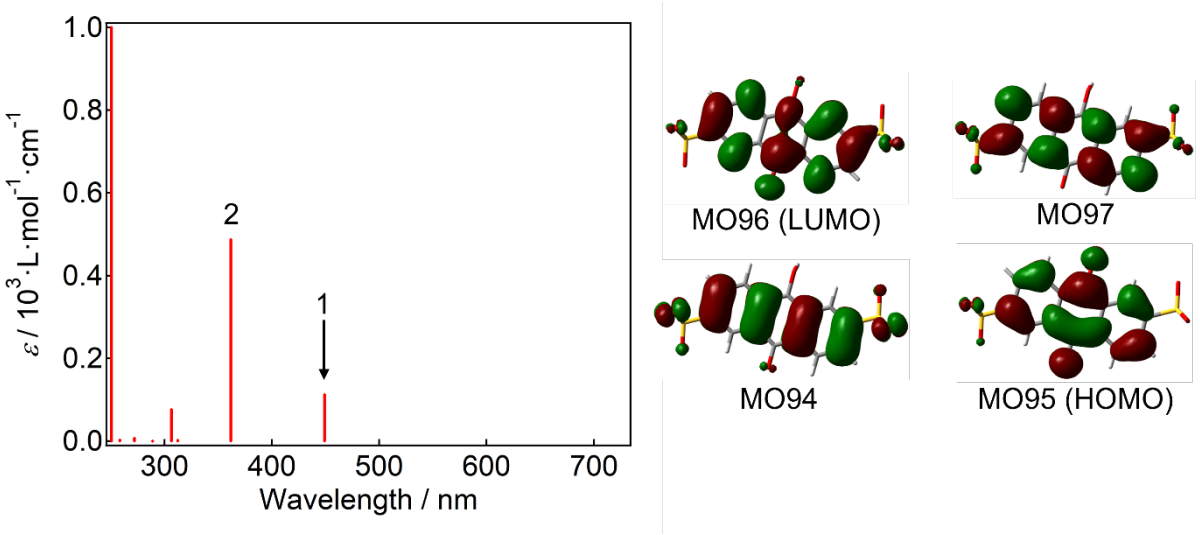

Fig. S14 The absorption spectra and the relevant molecular orbitals of $AQDSH^-$ calculated at the CAM-B3LYP/6-31G+(d,p)-PCM (water) level of the theory.

Table S4. Selected calculated electronic transition of $AQDSH^-$ at the CAM-B3LYP/6-31G+(d,p)-PCM (water) level.

No.	Wavelength (nm)	coefficients	Electronic Transition	*f*
1	449.16	0.70155	MO95 → MO96	0.1121
2	361.74	-0.15872	MO94 → MO96	0.4871
		0.68180	MO95 → MO97	

Table S5. Standard orientation of the optimized geometry for $AQDSH_2$.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-1.3654640	0.3698720	-0.0168030
2	C	-0.9929470	-1.0088860	-0.0163920
3	C	-2.0236580	-1.9997060	-0.0126330
4	C	-3.3385630	-1.6444820	-0.0070870
5	C	-3.7007760	-0.2663840	-0.0068270
6	C	-2.7523350	0.7103210	-0.0125660
7	C	-0.3727330	1.3603590	-0.0184550
8	C	0.9839970	1.0156830	-0.0166630

9	C	1.3597100	-0.3744810	-0.0170660
10	C	0.3636670	-1.3598050	-0.0183610
11	C	2.0269410	1.9979890	-0.0124270
12	C	3.3411320	1.6483860	-0.0066690
13	C	3.7031620	0.2710810	-0.0065600
14	C	2.7527370	-0.7007420	-0.0126680
15	O	-0.8141940	2.6521630	-0.0188630
16	O	0.6379350	-2.6970720	-0.0188590
17	S	-5.4415390	0.1596560	0.0150750
18	S	5.4418720	-0.1633370	0.0151210
19	O	-5.5067880	1.6418130	-0.0386080
20	O	-6.0263770	-0.4965460	-1.1853610
21	O	-5.9701770	-0.4026240	1.2874530
22	O	5.4910660	-1.6462080	-0.0339940
23	O	6.0267740	0.4852950	-1.1880710
24	O	5.9723980	0.3996390	1.2851150
25	H	-1.7385030	-3.0445260	-0.0135520
26	H	-4.1125580	-2.4038640	-0.0043800
27	H	-3.0452450	1.7518770	-0.0128970
28	H	1.7862450	3.0561870	-0.0124970
29	H	4.1121650	2.4101920	-0.0032920

SCF Done: E(RCAM-B3LYP) = -1936.30401266 A.U. after 1 cycles

Zero-point correction	=	0.209704 (Hartree/Particle)
Thermal correction to Energy	=	0.230055
Thermal correction to Enthalpy	=	0.230999
Thermal correction to Gibbs Free Energy	=	0.159286
Sum of electronic and zero-point Energies	=	-1936.094309
Sum of electronic and thermal Energies	=	-1936.073957
Sum of electronic and thermal Enthalpies	=	-1936.073013
Sum of electronic and thermal Free Energies	=	-1936.144726

Low frequencies --- -0.0014 -0.0011 0.0014 6.4485 8.0671 14.6264
Low frequencies --- 25.6942 46.9863 50.1894

The Results of the TDDFT calculation

Excited State 1: Singlet-A 3.1397 eV 394.90 nm f=0.1174 <S**2>=0.000
95 -> 96 0.70153
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1936.18863219
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.7432 eV 331.22 nm f=0.2446 <S**2>=0.000
94 -> 96 0.28338
95 -> 97 0.63634

Excited State 3: Singlet-A 4.6262 eV 268.01 nm f=0.0009 <S**2>=0.000
95 -> 99 0.69619

Excited State 4: Singlet-A 4.8392 eV 256.21 nm f=0.0000 <S**2>=0.000
95 -> 98 0.64804
95 ->102 -0.19109
95 ->105 -0.12431

Excited State 5: Singlet-A 4.9014 eV 252.96 nm f=2.1797 <S**2>=0.000
94 -> 96 0.62352
95 -> 97 -0.29289

Excited State 6: Singlet-A 5.2449 eV 236.39 nm f=0.0061 <S**2>=0.000
95 ->100 0.60194
95 ->101 -0.31111

Excited State 7: Singlet-A 5.4948 eV 225.64 nm f=0.0011 <S**2>=0.000
90 -> 96 -0.13154
91 -> 96 0.65474

Excited State 8: Singlet-A 5.6067 eV 221.14 nm f=0.0026 <S**2>=0.000
89 -> 96 -0.15321
90 -> 96 -0.18124
91 -> 97 0.19832
92 -> 96 0.52190
92 -> 99 0.16123
93 -> 96 0.12577

94 -> 99 -0.20938

Excited State 9: Singlet-A 5.6352 eV 220.02 nm f=0.0098 <S**2>=0.000
83 -> 96 0.10374
89 -> 96 0.21334
90 -> 96 0.11542
91 -> 97 -0.23639
92 -> 96 0.38589
92 -> 99 0.12772
93 -> 96 -0.31018
94 -> 99 0.23187
95 ->109 0.10646

Excited State 10: Singlet-A 5.6406 eV 219.81 nm f=0.0022 <S**2>=0.000
95 ->100 0.26613
95 ->101 0.52978
95 ->105 0.31252

Excited State 11: Singlet-A 5.6633 eV 218.93 nm f=0.0032 <S**2>=0.000
89 -> 96 0.10381
90 -> 96 0.14478
91 -> 97 -0.17682
92 -> 96 0.10284
93 -> 96 0.55893
93 -> 99 -0.19570
94 -> 99 0.15753

Excited State 12: Singlet-A 5.6781 eV 218.36 nm f=0.0272 <S**2>=0.000
89 -> 96 -0.30412
90 -> 96 0.39500
91 -> 96 0.10660
94 -> 97 0.42806

Excited State 13: Singlet-A 5.8791 eV 210.89 nm f=0.0291 <S**2>=0.000
89 -> 96 0.10789
90 -> 96 -0.19653
94 -> 97 0.18958
95 ->104 0.55704

95 ->110 0.28273

Excited State 14: Singlet-A 5.8830 eV 210.75 nm f=0.0011 <S**2>=0.000
95 -> 98 0.12293
95 ->100 -0.11893
95 ->101 -0.24055
95 ->103 0.18106
95 ->105 0.51056
95 ->106 0.23036
95 ->108 -0.15302

Excited State 15: Singlet-A 5.9744 eV 207.53 nm f=0.1700 <S**2>=0.000
89 -> 96 0.17595
90 -> 96 -0.35155
94 -> 97 0.48249
95 ->104 -0.25991
95 ->110 -0.13635

Excited State 16: Singlet-A 6.1219 eV 202.53 nm f=0.0001 <S**2>=0.000
95 -> 98 0.16277
95 ->102 0.54143
95 ->103 0.31168
95 ->105 -0.11376
95 ->113 -0.10011
95 ->114 -0.11617

Excited State 17: Singlet-A 6.1368 eV 202.03 nm f=0.0056 <S**2>=0.000
77 -> 96 0.10733
85 -> 96 0.13304
87 -> 96 -0.31558
87 -> 99 -0.17830
88 -> 96 0.53418
88 -> 99 -0.10571

Excited State 18: Singlet-A 6.2176 eV 199.41 nm f=0.0009 <S**2>=0.000
87 -> 96 -0.18921
88 -> 96 -0.12206
95 ->102 -0.26158

95 ->103 0.51628
95 ->111 -0.10595
95 ->113 0.13860
95 ->114 -0.10183

Excited State 19: Singlet-A 6.2441 eV 198.56 nm f=0.0001 <S**2>=0.000
85 -> 96 -0.17450
86 -> 96 0.18432
87 -> 96 0.44883
88 -> 96 0.27219
88 -> 99 -0.20293
95 ->102 -0.16371
95 ->103 0.18733

Excited State 20: Singlet-A 6.2745 eV 197.60 nm f=0.0003 <S**2>=0.000
89 -> 96 -0.29715
90 -> 96 -0.14449
95 ->107 -0.32917
95 ->109 0.48793

Excited State 21: Singlet-A 6.4312 eV 192.78 nm f=0.1094 <S**2>=0.000
89 -> 96 0.28417
90 -> 96 0.14973
90 -> 97 -0.27586
91 -> 97 0.42389
95 ->107 -0.18204
95 ->109 0.19996

Excited State 22: Singlet-A 6.5489 eV 189.32 nm f=0.1391 <S**2>=0.000
89 -> 96 0.12635
89 -> 97 -0.13368
90 -> 97 0.29240
95 ->104 0.15355
95 ->110 -0.25638
95 ->115 0.46192

Excited State 23: Singlet-A 6.5576 eV 189.07 nm f=0.1664 <S**2>=0.000
89 -> 96 0.17408

89 -> 97 -0.17697
90 -> 97 0.40654
91 -> 97 0.10344
93 -> 97 -0.10343
95 ->107 -0.10268
95 ->110 0.18895
95 ->115 -0.33410

Excited State 24: Singlet-A 6.6138 eV 187.46 nm f=0.0001 <S**2>=0.000
85 -> 96 0.51794
85 -> 99 0.17910
86 -> 96 0.14524
87 -> 96 0.17051
93 -> 97 0.29296

Excited State 25: Singlet-A 6.6148 eV 187.43 nm f=0.0011 <S**2>=0.000
85 -> 96 -0.25909
93 -> 96 -0.10297
93 -> 97 0.58741
93 ->109 -0.12807

Excited State 26: Singlet-A 6.6262 eV 187.11 nm f=0.0017 <S**2>=0.000
85 -> 96 0.14294
95 ->106 -0.18610
95 ->108 -0.32007
95 ->111 0.46607
95 ->113 0.18860
95 ->114 -0.10706

Excited State 27: Singlet-A 6.6385 eV 186.77 nm f=0.0000 <S**2>=0.000
85 -> 96 -0.11267
86 -> 96 0.58374
86 -> 99 -0.22044
87 -> 96 -0.18234
88 -> 96 -0.16597

Excited State 28: Singlet-A 6.6523 eV 186.38 nm f=0.0027 <S**2>=0.000
92 -> 96 -0.10852

92 -> 97 0.66345
92 ->109 0.14285

Excited State 29: Singlet-A 6.7165 eV 184.60 nm f=0.0011 <S**2>=0.000
89 -> 97 -0.15113
95 ->107 0.43572
95 ->109 0.36593
95 ->112 0.28047
95 ->121 -0.15601

Excited State 30: Singlet-A 6.7286 eV 184.26 nm f=0.0000 <S**2>=0.000
93 -> 98 -0.26731
93 ->100 0.31933
93 ->101 0.40311
93 ->102 -0.27443
93 ->103 0.13854
93 ->106 0.11188

Excited State 31: Singlet-A 6.7363 eV 184.05 nm f=0.0000 <S**2>=0.000
92 -> 98 0.40088
92 ->100 0.30937
92 ->101 0.20055
92 ->102 0.32057
92 ->106 0.13241
94 -> 98 -0.16639

Excited State 32: Singlet-A 6.7552 eV 183.54 nm f=0.0015 <S**2>=0.000
94 -> 98 -0.16622
95 ->100 0.14432
95 ->101 0.13055
95 ->105 -0.19733
95 ->106 0.50472
95 ->117 0.12283
95 ->120 -0.16513

Excited State 33: Singlet-A 6.7730 eV 183.06 nm f=0.0002 <S**2>=0.000
94 -> 98 0.57652
94 ->105 -0.16480

95 ->106 0.17888

Excited State 34: Singlet-A 6.7867 eV 182.69 nm f=0.0007 <S**2>=0.000
91 -> 97 -0.12065
95 ->107 -0.26531
95 ->109 -0.11606
95 ->112 0.59603
95 ->121 0.12171

Excited State 35: Singlet-A 6.8744 eV 180.36 nm f=0.0005 <S**2>=0.000
84 -> 96 -0.20211
89 -> 97 0.31965
90 -> 97 0.19930
91 -> 97 0.25920
94 -> 99 0.37133
94 ->109 0.12115
95 ->107 0.10439
95 ->112 0.13698

Excited State 36: Singlet-A 6.8922 eV 179.89 nm f=0.0105 <S**2>=0.000
83 -> 99 -0.11721
84 -> 96 0.60153
89 -> 99 0.12926
90 -> 97 0.12450
94 -> 99 0.12134

Excited State 37: Singlet-A 6.9136 eV 179.33 nm f=0.0019 <S**2>=0.000
95 ->108 0.53284
95 ->111 0.32972
95 ->117 -0.10742
95 ->120 -0.15179

Excited State 38: Singlet-A 7.0323 eV 176.31 nm f=0.0005 <S**2>=0.000
89 -> 97 0.44722
90 -> 97 0.11919
91 -> 97 -0.19241
94 -> 99 -0.39783

Excited State 39:	Singlet-A	7.0565 eV	175.70 nm	f=0.0032	<S**2>=0.000
76 -> 99	0.12393				
78 -> 96	0.52040				
80 -> 96	-0.10404				
82 -> 96	-0.16243				
87 -> 97	-0.10117				
88 -> 97	0.31759				
Excited State 40:	Singlet-A	7.0792 eV	175.14 nm	f=0.0015	<S**2>=0.000
83 -> 96	0.61324				
84 -> 99	-0.15775				
94 -> 99	-0.14267				
Excited State 41:	Singlet-A	7.0970 eV	174.70 nm	f=0.0002	<S**2>=0.000
78 -> 96	-0.34479				
86 -> 97	0.11015				
88 -> 97	0.51509				
88 ->109	-0.10022				
Excited State 42:	Singlet-A	7.1716 eV	172.88 nm	f=0.0089	<S**2>=0.000
95 ->104	-0.25538				
95 ->110	0.50728				
95 ->115	0.35180				
95 ->122	0.11381				
Excited State 43:	Singlet-A	7.1765 eV	172.76 nm	f=0.0026	<S**2>=0.000
88 -> 97	-0.10933				
89 -> 98	0.16046				
89 ->102	0.10111				
90 -> 98	0.12629				
91 -> 98	0.19841				
94 ->100	0.34760				
94 ->101	0.41346				
Excited State 44:	Singlet-A	7.2155 eV	171.83 nm	f=0.0004	<S**2>=0.000
85 -> 97	-0.13889				
86 -> 97	0.10798				
87 -> 97	0.42402				

95 ->102 0.11644
95 ->111 -0.14432
95 ->113 0.35336
95 ->119 -0.11318

Excited State 45: Singlet-A 7.2455 eV 171.12 nm f=0.0000 <S**2>=0.000
85 -> 97 -0.12386
86 -> 97 0.10519
87 -> 97 0.39884
95 ->102 -0.14208
95 ->111 0.14245
95 ->113 -0.36567
95 ->119 0.15127

Excited State 46: Singlet-A 7.3184 eV 169.42 nm f=0.0000 <S**2>=0.000
90 -> 98 0.14709
91 -> 98 -0.16502
94 ->100 0.34990
94 ->101 -0.24950
95 ->113 0.10325
95 ->114 0.29412
95 ->116 -0.19978
95 ->119 0.14572

Excited State 47: Singlet-A 7.3375 eV 168.97 nm f=0.0005 <S**2>=0.000
90 -> 98 -0.15822
94 ->100 0.41444
94 ->101 -0.27501
95 ->114 -0.27237
95 ->116 0.17762
95 ->119 -0.14904

Excited State 48: Singlet-A 7.4242 eV 167.00 nm f=0.0061 <S**2>=0.000
89 -> 98 -0.24031
90 -> 98 0.10478
90 ->100 0.11041
90 ->101 0.15730
91 -> 98 0.47706

94 ->101	-0.16907				
94 ->102	0.10239				
95 ->114	0.12859				
95 ->119	-0.13761				
Excited State 49:	Singlet-A	7.4425 eV	166.59 nm	f=0.2746	<S**2>=0.000
90 -> 99	-0.23429				
91 -> 99	0.58333				
95 ->115	-0.10270				
Excited State 50:	Singlet-A	7.4558 eV	166.29 nm	f=0.0003	<S**2>=0.000
84 -> 98	0.11073				
84 ->102	0.10253				
89 ->101	0.15658				
90 -> 98	0.21124				
91 -> 98	-0.12073				
91 ->100	0.18959				
91 ->101	0.19666				
94 ->102	0.36327				
94 ->105	0.15973				
95 ->114	-0.16064				
95 ->119	-0.14216				

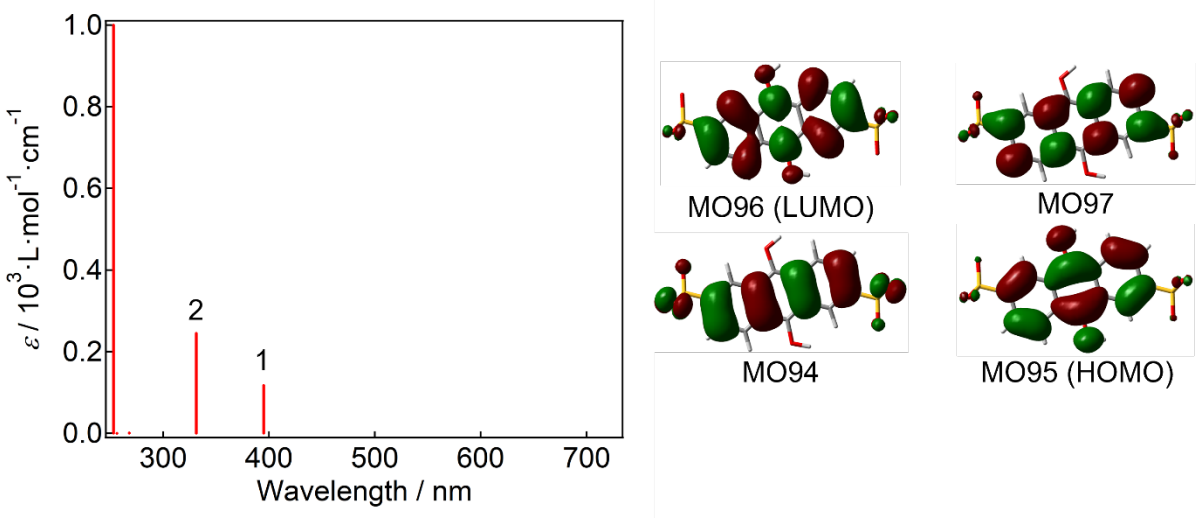

Fig. S15 The absorption spectra and the relevant molecular orbitals of $AQDSH_2$ calculated at the CAM-B3LYP/6-31G+(d,p)-PCM (water) level of the theory.

Table S6. Selected calculated electronic transition of $AQDSH_2$ at the CAM-B3LYP/6-31G+(d,p)-PCM (water) level.

No.	Wavelength (nm)	coefficients	Electronic Transition	*f*
1	394.90	0.70153	MO95 → MO96	0.1174
2	331.22	0.28338	MO94 → MO96	0.2446
		0.63634	MO95 → MO97	

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