Supporting Information

for

Excited-State Intramolecular Hydrogen Transfer of Compact Molecules Controls Amyloid Aggregation Profiles

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Materials and Methods. All chemical reagents were purchased from commercial suppliers. 9,10-Anthraquinone (**9,10-AQ**), 1-hydroxyanthracene-9,10-dione (**HQ**), 1,4-dihydroxyanthracene-9,10-dione (**Qui**), 1,2,4-trihydroxyanthracene-9,10-dione (**Pur**), and 1,8-dihydroxy-3-(hydroxylmethyl)-anthracene-9,10-dione (**Alo**) were obtained from TCI (Chuo-ku, Tokyo, Japan). 1,2-Dihydroxyanthracene-9,10-dione (**Ali**), 1,8-dihydroxyanthracene-9,10-dione (**Dan**), and 4,5-dihydroxy-9,10-dioxoanthracene-2-carboxylic acid (**Rhe**) were purchased from Acros (Thermofisher, Waltham, MA, USA) and Alfa Aesar (Ward Hill, MA, USA), respectively. $A\beta_{40}$ (DAEFRHDSGYEVHHQKLVFFAEDVGSNKGAIIGLMVGGVV) and $A\beta_{42}$ (DAEFRHDSGYE-VHHQKLVFFAEDVGSNKGAIIGLMVGGVVIA) were obtained from Peptide Institute, Inc. (Osaka, Japan). HEPES (2-[4-(2-hydroxyethyl)piperazin1-yl]ethanesulfonic acid) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The buffered solution was prepared in doubly distilled water [ddH_2O; a Milli-Q Direct 16 system (18.2 MΩ·cm; Merck KGaA, Darmstadt, Germany)]. Trace metal contamination was removed from the solutions by treating with Chelex (Sigma-Aldrich) overnight. Optical and luminescence spectra were recorded on an Agilent 8453 UV−Vis spectrophotometer (Santa Clara, CA, USA) and a QM-400 fluorometer [KAIST Analysis Center for Research Advancements (KARA), Daejeon, Republic of Korea], respectively. PR160L Kessil lamp (467 nm; Kessil Lighting, Richmond, CA, USA) was used for light exposure of samples. Mass spectrometric analysis of compounds' interactions with $A\beta_{40}$ in the absence and presence of metal ions and light exposure was conducted by an Agilent 6530 AccurateMass quadrupole time-of-flight (Q-TOF) liquid chromatography/mass spectrometry (LC/MS). Images gained by gel electrophoresis with Western blotting (gel/Western blot) were visualized by a ChemiDoc MP imaging system (Bio-Rad, Hercules, CA, USA). Transmission electron microscopic images were taken by a Tecnai F30 transmission electron microscope (FEI; KARA).

Calculation of the Energy Transfer Barrier. All calculations were performed based on the density functional theory (DFT)[1] with the Jaguar 9.1 suite[2] at the PBE0[3] level of theory. The optimization of the **AQ** series' structures were carried out with the 6-31G** basis set.[4-6] Following geometry optimization, electronic energies of the optimized structures of the **AQ** series were recalculated with a high-quality triple-ζ basis set cc-pVTZ(-f).[7] Vibrational frequencies for the optimized structures were calculated at the same level of theory as the geometry optimization procedure. Vibrational entropy correction with the zero point vibrational energies were considered for proper thermodynamic approximations. Based on the optimized gas-phase geometries, solvation correction energies were deduced. Self-consistent reaction field (SCRF)[8-10]

approximations were considered to calculate the linearized Poisson-Boltzmann equations with the dielectric constant (ε). The solvation energy used in the system was treated with water (ε = 78.4). The Gibbs free energies in solution phase were computed as the following equations:

$$G(sol) = G(gas) + G(solv) \quad (1)$$
$$G(gas) = H(gas) - TS(gas) \quad (2)$$
$$H(gas) = E(SCF) + ZPE \quad (3)$$

G(sol) represents the Gibbs free energy with solvation correction G(solv) from the gas phase free energy G(gas); H(gas) is the enthalpy of the molecule in gas phase; T is the temperature (298.15 K); S(gas) is the entropy of the molecule in the gas phase; E(SCF) is the self-consistent field converged electronic energy; ZPE represents the vibrational zero-point energy. To calculate the energy transfer barrier, the following equation was derived from the Marcus theory[11-13] as:

$$\Delta G = (\Delta G + \lambda)^2 / 4\lambda$$

ΔG indicates the thermodynamic driving force which is the energy difference of the triplet acceptor and the triplet donor; λ represents the reorganization energy which is the cost of the structural distortion required for the energy transfer. λ can be approximated as the following equations.

$$E_T = G(T_1) - G(S_0) \quad (1)$$
$$\lambda_D(T) = {}^TE_{1D} - {}^TE_{3D} \quad (2)$$
$$\lambda_A(T) = {}^TE_{1A} - {}^TE_{3A} \quad (3)$$
$$\lambda = \lambda_D(T) + \lambda_A(T) \quad (4)$$

E_T stands for the triplet energy which is the free energy difference between the ground state singlet and the triplet of the molecule; ${}^xE_y$ is the energy of the state x (T for triplet, S for singlet) in the geometry of y (1D = singlet donor, 3D = triplet donor, 1A = singlet acceptor, 3A = triplet acceptor). Note that we did not consider the reorganization energy of the acceptor (i.e., λ_A) since we were not able to obtain the exact configuration of O_2 under our DFT conditions.

TD-DFT Calculations. The energy for the stepwise process was calculated with time-dependent DFT (TD-DFT) with the Q-Chem 5.0 software.[14] Structures of the **AQ** series without the ESIHT

process were optimized with DFT calculations with the same conditions stated in the previous section with the Jaguar stop_rxn function and the TD-DFT method was used with the TD-PBE0/6-31G(d,p) level of theory.

UV–Vis Spectroscopy. Absorbance of the **AQ** series in solution was monitored at room temperature by UV–Vis spectroscopy. Compounds [50 μM; 1% v/v dimethyl sulfoxide (DMSO)] were added in DMSO or 20 mM HEPES, pH 7.4, 150 mM NaCl.

Fluorescence Spectroscopy. Luminescence spectra of the **AQ** series (50 μM; 1% v/v DMSO) in DMSO or 20 mM HEPES, pH 7.4, 150 mM NaCl were measured by a fluorometer at room temperature.

$^1O_2$ Generation. The amount of singlet oxygen ($^1O_2$) produced upon treatment of the **AQ** series were determined according to previously reported methods.[15,16] The solution containing the **AQ** series (25 μM; H_2O with 1% v/v DMSO) and 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA as a $^1O_2$ substrate; 100 μM) was irradiated with a PR160L Kessil lamp (Kessil Lighting). The change in the absorbance of ABDA was monitored for 5 min with a 1 min interval. The quantum yield (Φ) for each compound was calculated through the following equation.

$$\Phi_{s(x)} = \Phi_{s(std)} \times (S_x/S_{std}) \times (F_{std}/F_x)$$

x stands for the unknown sample while *std* stands for the standard sample; *S* is the slope from the absorbance difference of ABDA at 399 nm. The *F* value can be derived from the following equation from the optical density (O.D.) measured separately at 25 μM.

$$F = 1 - 10^{-\text{O.D.}}$$

ESI–MS. $A\beta_{40}$ (25 μM) was incubated with the **AQ** series (50 μM; 1% v/v DMSO) in the absence and presence of Cu(II) or Zn(II) (25 μM) in 20 mM ammonium acetate, pH 7.4 at 37 °C for 3 h with constant agitation. For the illuminated samples, PR160L Kessil lamp (Kessil Lighting) was applied for 1 h prior to incubation. The incubated samples were diluted by 5 fold with ddH_2O and then injected into the mass spectrometer. The capillary voltage, nozzle voltage, and gas temperature were set to 5.8 kV, 2 kV, and 300 °C, respectively.

ESI–MS^2. The singly, and the singly, doubly, and triply oxidized Aβ_{40} species generated with light-activated **Pur** and **Alo**, respectively, were further analyzed by tandem MS. ESI parameters and experimental conditions were the same as the ESI–MS methods. Collision induced dissociation (CID) was carried out by applying the collision energy in the trap at 60 V. More than 200 spectra were obtained for each sample and averaged for the analysis.

Aβ Aggregation Experiments. Aβ was dissolved in ammonium hydroxide [1% w/w NH_4OH (aq)]. The resulting solution was aliquoted, lyophilized overnight, and stored at –80 °C. A stock solution of Aβ was then prepared by dissolving the lyophilized peptide using 1% w/w NH_4OH (aq) (10 μL) and diluting with ddH_2O. All Aβ samples were prepared following previously reported procedures.[17-20] The concentration of the peptide solution was determined by measuring the absorbance of the solution at 280 nm (ε = 1,450 $M^{-1}cm^{-1}$ for Aβ_{40}; ε = 1,490 $M^{-1}cm^{-1}$ for Aβ_{42}). Aβ samples were prepared in 20 mM HEPES, pH 6.6 or pH 7.4, 150 mM NaCl. For the inhibition studies, compounds (final concentration, 50 μM; 1% v/v DMSO) were added to the samples of Aβ (25 μM) in the absence and presence of Cu(II) or Zn(II) (25 μM) followed by incubation for 24 h at 37 °C with constant agitation. For the disaggregation studies, Aβ (25 μM) was incubated with and without Cu(II) or Zn(II) (25 μM) for 24 h at 37 °C with constant agitation to generate preformed Aβ aggregates. The resulting Aβ aggregates were then treated with compounds (50 μM) and incubated for an additional 24 h with constant agitation. For the illuminated samples, PR160L Kessil lamp (Kessil Lighting) was applied for 1 h prior to 24 h incubation.

Gel/Western Blot. The resultant Aβ species from the inhibition and disaggregation experiments were analyzed by gel/Western blot using an anti-Aβ antibody (6E10; Covance, Princeton, NJ, USA).[17-20] The samples (10 μL) were separated on a 10–20% Tris-tricine gel (Invitrogen, Carlsbad, CA, USA). Following separation, the proteins were transferred onto nitrocellulose membranes and blocked with bovine serum albumin (BSA; 3% w/v; Sigma-Aldrich) in Tris-buffered saline (TBS) containing 0.1% v/v Tween-20 (Sigma-Aldrich) (TBS-T) for 4 h at room temperature or overnight at 4 °C. The membranes were incubated with 6E10 (1:2,000; Covance) in a solution of BSA (2% w/v in TBS-T) for 2 h at room temperature or overnight at 4 °C. After washing with TBS-T (three times, 10 min), a horseradish peroxidase-conjugated goat anti-mouse secondary antibody (1:5,000 in 2% w/v BSA in TBS-T; Cayman Chemical Company, Ann Arbor, MI, USA)

was added for 2 h at room temperature. Lastly, a homemade ECL kit[21-23] was used to visualize gel/Western blots on a ChemiDoc MP Imaging System (Bio-Rad).

TEM. Samples for TEM were prepared according to the previously reported methods with slight modifications.[17-22] Glow-discharged grids (Formvar/Carbon 300-mesh, Electron Microscopy Sciences, Hatfield, PA, USA) were treated with Aβ species (5.5 μL, 25 μM) for 2 min at room temperature. Excess samples were removed using filter paper and by washing once with ddH_2O. Each grid incubated with uranyl acetate (5.5 μL, 1% w/v in ddH_2O) for 1 min was blotted off and was dried overnight at room temperature. Images for each sample were taken on a transmission electron microscope (200 kV; 29,000x magnification). For the TEM measurements, we randomly selected locations of samples on the grids for imaging and collected at least 25 images from each grid.

Cell Viability Measurements. The human neuroblastoma SH-SY5Y (5Y) cell line was purchased from the American Type Culture Collection (ATCC, VA, USA). The cell line was maintained in media containing 50% v/v minimum essential medium (MEM; GIBCO, NY, USA) and 50% v/v F12 (GIBCO), and supplemented with 10% v/v fetal bovine serum (Sigma-Aldrich), 100 U/mL penicillin, and 100 mg/mL streptomycin (GIBCO). Cells were grown and maintained at 37 °C in a humidified atmosphere with 5% CO_2. The cells used for our studies did not indicate mycoplasma contamination. Cell viability upon treatment with compounds was determined by the MTT assay. Two types of the samples were prepared: the **AQ** series with and without light exposure. In the case of preparing the light-activated **AQ** series, compounds were illuminated for 1 h prior to addition using the PR160L Kessil lamp (Kessil Lighting). Cells were seeded in a 96 well plate (10,000 cells in 100 μL per well) and treated with the resultant samples (final concentration of 5, 10, and 25 μM). After 24 h incubation, MTT [25 μL of 5 mg/mL in PBS (pH 7.4; GIBCO)] was added to each well, and the plate was incubated for 4 h at 37 °C. Formazan produced by cells was solubilized using an acidic solution of dimethylformamide (DMF; pH 4.5, 50% v/v, aq) and sodium dodecyl sulfate (SDS; 20% w/v) overnight at room temperature in the dark. The absorbance was measured at 600 nm by a microplate reader. Cell viability was calculated relative to that of the cells containing an equivalent amount of DMSO. All measurements were conducted in triplicate.

PAMPA-BBB. PAMPA-BBB measurements for the **AQ** series were conducted employing the PAMPA explorer kit (*p*ION, Inc. Billerica, MA, USA) following previously reported protocols with

minor modifications.[24,25] Stock solutions of the **AQ** series was diluted with Prisma HT buffer (pH 7.4; *p*ION) to a final concentration of 50 μM (1% v/v DMSO] and was added to the wells in the donor plate (200 μL, number of replicates = 12). BBB-1 lipid formulation (5 μL; *p*ION) was used to coat the polyvinylidene fluoride (PVDF; 0.45 μM) filter membrane on the acceptor plate. The acceptor plate was placed on top of the donor plate, forming a sandwich, and the brain sink buffer (BSB; 200 μL; *p*ION) was added to each well of the acceptor plate. The sandwich was incubated for 4 h at ambient temperature without stirring. UV−Vis spectra of the solutions in the reference, acceptor, and donor plates were measured on a microplate reader. The PAMPA Explorer software, v. 3.5 (*p*ION), was used to calculate the $-\log P_e$ value of each compound. CNS+/– designations were assigned by referring to compounds that were identified in previous reports.[24,25]

In Vivo Studies. C57BL/6J wild-type mice were obtained from Jackson Laboratory. All mice were maintained on a 12 h light/dark cycle, and food and water were available ad libitum. For injection and immunohistochemistry, 6-month-old male mice were used. All procedures for animal use were approved by the KAIST Institutional Animal Care and Use Committee (IACUC-14-145). Fresh $A\beta_{42}$ peptides (500 μM) with and without **AIo** (500 μM) in vehicle (20 mM HEPES, pH 7.4, 150 mM NaCl with 1% v/v DMSO) were exposed to blue light using the PR160L Kessil lamp (Kessil Lighting) for 1 h and incubated for 2 h at 37 °C with constant agitation (250 rpm). All samples were diluted with vehicle yielding a final concentration of 150 μM. For stereotactic surgeries, mice were anesthetized with 1.5 to 2% isoflurane and placed in a stereotactic setup. A single dose of 1 μL $A\beta_{42}$ (150 μM) with or without **AIo** (150 μM) was administered into the hippocampus (bregma, –1.94 mm; lateral 1.9 mm; depth 1.3mm) at a rate of 8.3 nL/s. Control mice were injected only with vehicle in the same manner. Mice were anesthetized with avertin by intraperitoneal injection and transcardially perfused with 15 mL of 0.1 M phosphate-buffered saline (PBS) followed by 20 mL of 4% PFA after 15 d for brain sample preparation. Brains were dissected and post-fixed in the same fixative for 1.5 h at 4 °C, cryoprotected with 30% sucrose in PBS, embedded in an OCT (optimal cutting temperature) compound (Tissue-Tek® #4583; Sakura Finetek, Torrance, CA, USA), and frozen at –20 °C. The frozen brain samples were stored at –80 °C until they were sectioned at 20 μm using a cryo-microtome (Leica cryostat CM1520; Leica Biosystems, Buffalo Grove, IL, USA). To visualize the distribution of Aβ species in brain sections, hippocampal coronal sections on slides (20 μm thick) were double stained with antibodies (6E10 for Aβ species or A11 for Aβ oligomers) or a fluorescent dye [thioflavin S (ThS) for Aβ fibrils]. Sections on slides were washed three times with PBS for 10 min, permeabilized in 0.3% Triton

X-100 for 30 min, washed three times with PBS for 10 min, incubated with blocking solution (PBS containing 2% normal donkey serum, 017-000-121; Jackson Immunoresearch, West Grove, PA, USA) for 2 h at room temperature, and incubated with 6E10 (1:500; 803003; Biolegend, San Diego, CA, USA) or A11 (1:500; AB9234; Merck KGaA) diluted with the blocking solution overnight at 4 °C. Afterwards, the sections were washed three times with PBS for 10 min, incubated with fluorescent-conjugated secondary antibodies (1:500; Cy™3 AffiniPure Donkey Anti-Mouse IgG, 715-165-151; Jackson ImmunoResearch or 1:500; Alexa Fluor 647-AffiniPure Donkey Anti-Rabbit IgG, 711-605-152; Jackson ImmunoResearch), diluted with PBS for 3 h at room temperature, and washed three times with PBS for 10 min. For ThS staining, sections on slides were incubated for 8 min (dark) at a concentration of 0.125% w/v ThS (Sigma-Aldrich) dissolved in 50% ethanol (filtration before use), washed two times in 50% PBS/ethanol for 3 min, washed three times in PBS for 2 min, and coverslipped in VECTASHIELD Antifade Mounting Media with DAPI (H-1200-10; Vector Laboratories, Burlingame, CA, USA). Brain sections were imaged with a slide scanner (10x; ZEISS Axio Scan.Z1, Carl Zeiss, Oberkochen, Germany) and high sensitivity laser scanning confocal microscope (10x; ZEISS LSM 780, Carl Zeiss).

Table S1. Values (MW, *c*log*P*, HBA, HBD, PSA, logBB, and –logP_e) of the **AQ** series.

	MW[a]	*c*log*P*[b]	HBA[c]	HBD[d]	PSA[e]	logBB[f]	–logP_e[g]	CNS(+/–)
9,10-AQ	208.2	3.67	2	0	34.14	0.183	5.54 ± 0.11	n.d.[h]
HQ	224.2	3.40	3	1	54.37	–0.158	4.81 ± 0.12	CNS+
Ali	240.2	2.90	4	2	74.60	–0.533	4.01 ± 0.04	CNS+
Qui	240.2	3.13	4	2	74.60	–0.498	5.18 ± 0.11	CNS+
Pur	256.2	2.61	5	3	94.83	–0.877	4.26 ± 0.02	CNS+
Dan	240.2	3.13	4	2	74.60	–0.498	5.12 ± 0.06	CNS+
Rhe	284.2	3.00	6	3	111.90	–1.070	5.97 ± 0.03	CNS–
Alo	270.2	2.42	5	3	94.83	–0.905	3.25 ± 0.14	CNS+
Lipinski's rules & Others	≤ 450	≤ 5	≤ 10	≤ 5	≤ 90	< –1	< 5.4 (CNS+); > 5.7 (CNS–)	

[a]MW, molecular weight; [b]*c*log*P*, calculated logarithm of the octanol/water partition coefficient; [c]HBA, hydrogen bond acceptor; [d]HBD, hydrogen bond donor; [e]PSA, polar surface area; [f]logBB: –0.0148 × PSA + 0.152 × *c*log*P* + 0.139 (logBB < –1.0, poorly distributed in the brain); [g]–logP_e values were determined by the PAMPA and the average –logP_e values were calculated by the PAMPA 9 Explorer software v. 3.5. Compounds categorized as CNS+ possess the ability to penetrate the BBB and are available in the CNS. Compounds assigned as CNS– have poor BBB permeability and, thus, their bioavailability into the CNS is considered to be minimal. [h]n.d., not determined.

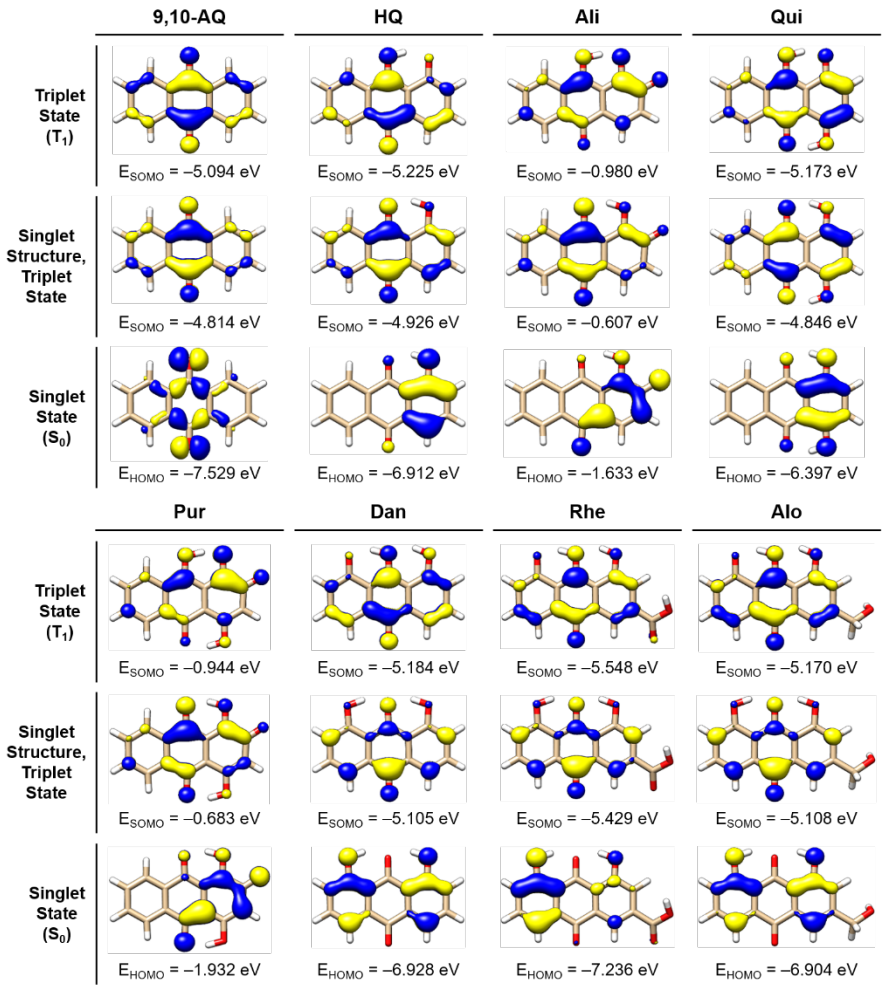


Figure S1. Electronic properties of the ground and excited states of the **AQ** series calculated by DFT. Isosurface plots (isodensity value = 0.05 a.u.) and the orbital energies of the SOMO of the triplet state at the triplet and singlet geometry and the HOMO of the singlet ground state at the singlet geometry.

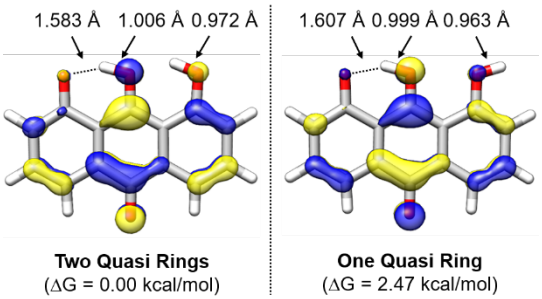
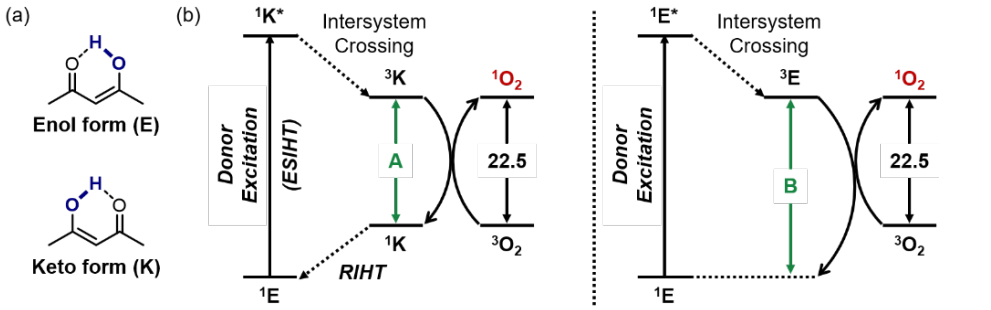


Figure S2. Dual effect of the additional hydroxyl group in ^{3}**Dan** against the intramolecular hydrogen bond.

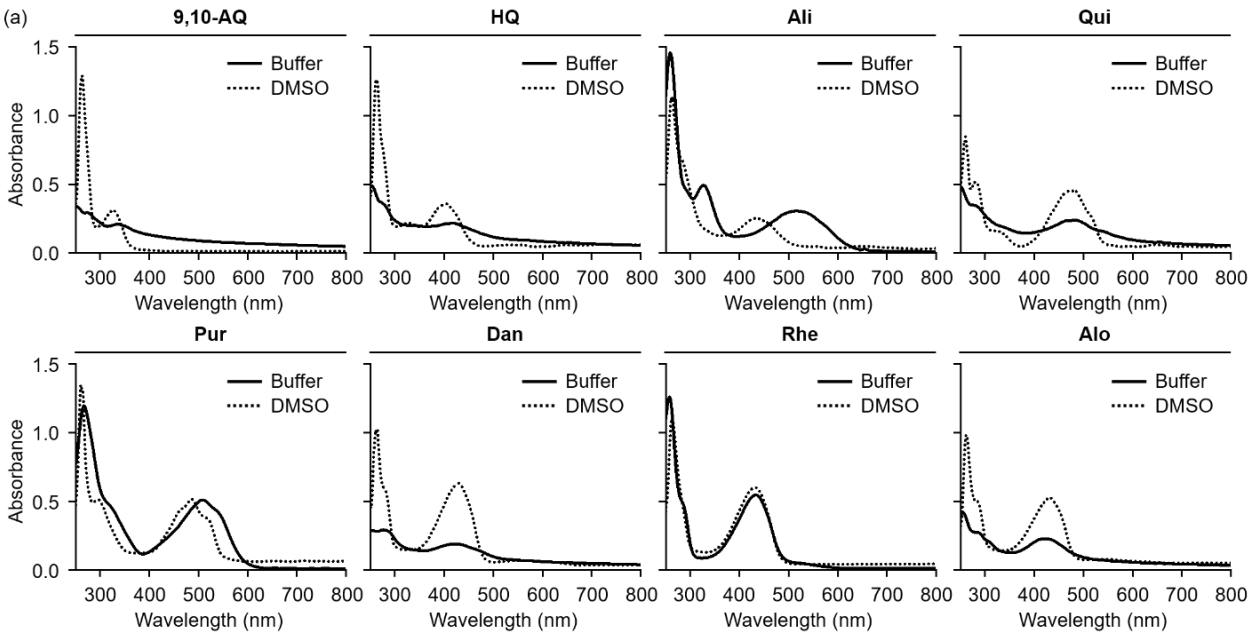


(c) Unit: kcal/mol

	HQ	Ali	Qui	Pur	Dan	Rhe	Alo	O_2
A	22.00	10.85	19.86	18.07	23.15	21.61	23.24	22.5
B	42.56	12.45	n.d.[a]	18.88	43.26	40.61	43.43	

Figure S3. Influence of intramolecular proton transfer following the stepwise mechanism. (a) Schematic description of the enol (E) and keto (K) forms. (b) Mechanism of the stepwise mechanism with (left) and without (right) ESIHT. (c) Singlet-triplet energy gap of the relaxation process calculated by TD-DFT. [a]n.d. = not determined due to the failure of structure optimization.

(a)



(b)

Compound		9,10-AQ	HQ	Ali	Qui	Pur	Dan	Rhe	Alo
λ_{max} (nm)	Buffer	335	418	516	485	507	425	433	422
	DMSO	326	404	434	481	486	429	432	431

Figure S4. UV–Vis studies of the **AQ** series. (a) Absorption spectra of the **AQ** series in the buffered solution (solid line) and DMSO (dotted line). (b) Summary of the wavelengths (λ_{max}) of the **AQ** series with the strongest photon absorption in the visible light region. Conditions: [compound] = 50 μM; 20 mM HEPES, pH 7.4, 150 mM NaCl or DMSO.

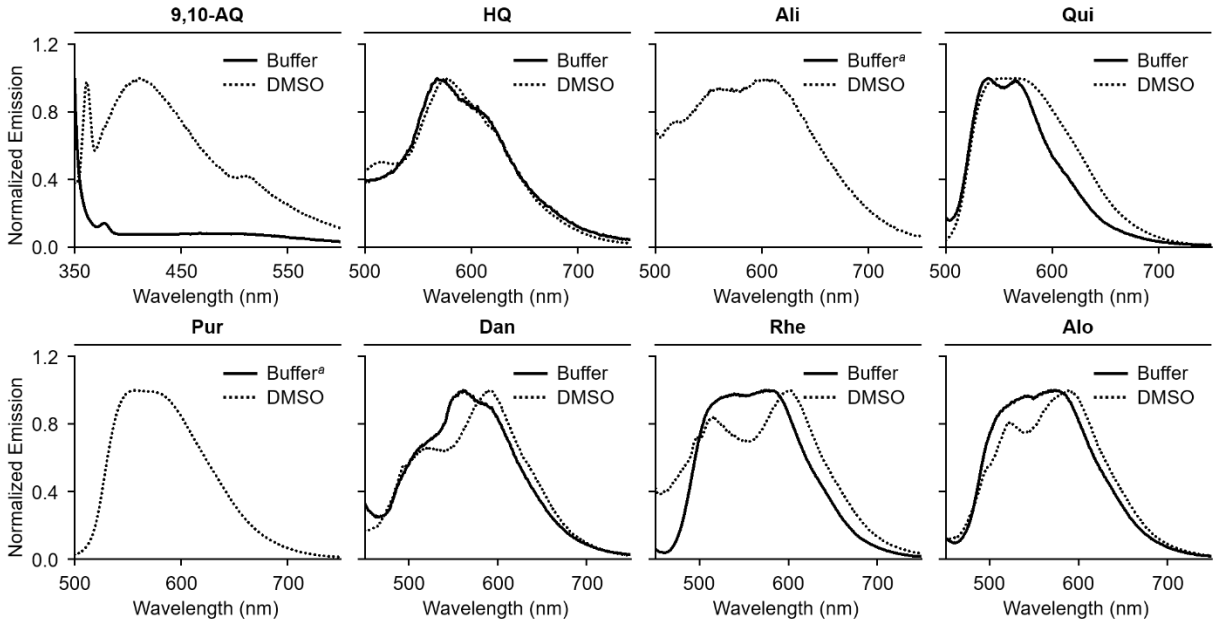
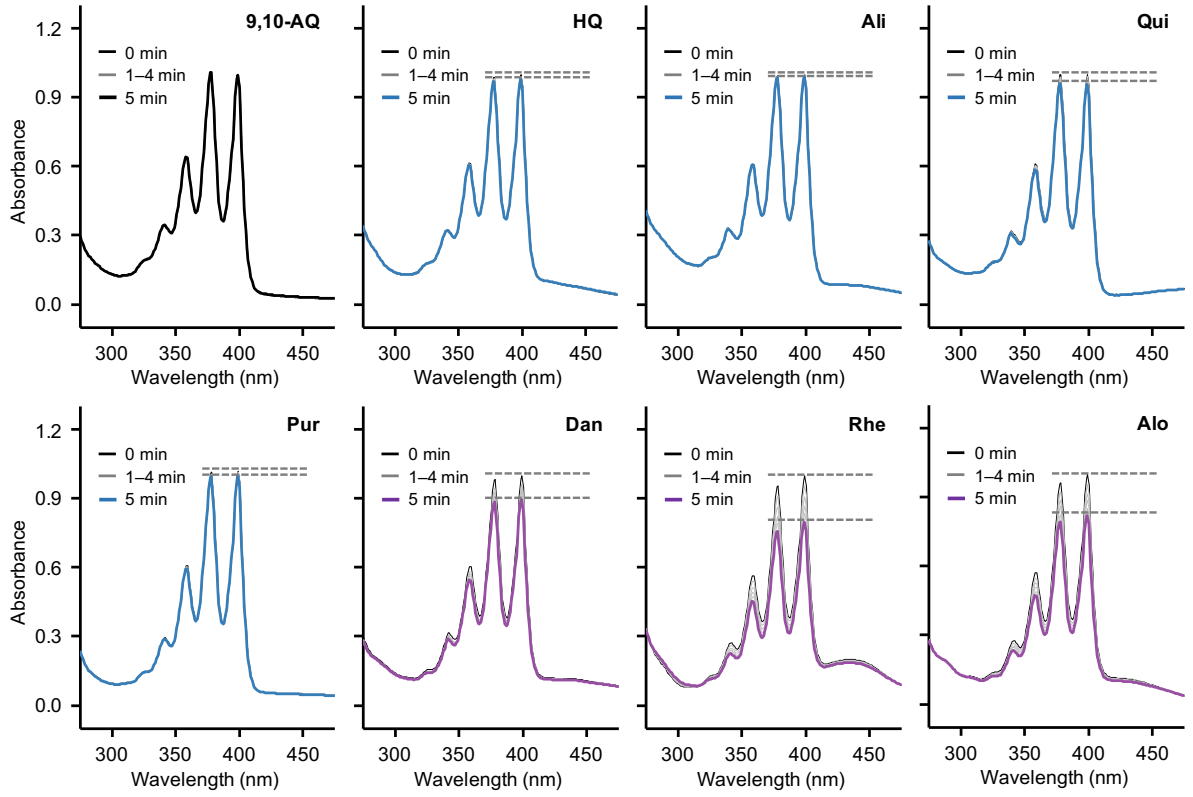


Figure S5. Luminescence spectra of the **AQ** series. Conditions: [compound] = 50 μM; 20 mM HEPES, pH 7.4, 150 mM NaCl or DMSO. [a]Luminescence of **Ali** and **Pur** was not observed in the buffered solution.



	9,10-AQ	HQ	Ali	Qui	Pur	Dan	Rhe	Alo
Slope (S)	n.d.[a]	0.0047 (± 0.0002)	0.0033 (± 0.0010)	0.0095 (± 0.0006)	0.0065 (± 0.0019)	0.0179 (± 0.0050)	0.0345 (± 0.0077)	0.0311 (± 0.0060)
Optical density	0.0315	0.0527	0.0939	0.0727	0.0758	0.1077	0.1288	0.0589
F value	0.0700	0.1143	0.1944	0.1541	0.1602	0.2196	0.2566	0.1268
Φ	n.d.[a]	0.031 (± 0.001)	0.013 (± 0.004)	0.047 (± 0.003)	0.031 (± 0.009)	0.062 (± 0.017)	0.103 (± 0.023)	0.188 (± 0.036)

Figure S6. Time-dependent change in the absorbance of ABDA through $^1O_2$ generated by the **AQ** series with photoirradiation. Conditions: [compound] = 25 μM, [ABDA] = 100 μM; room temperature; Kessil lamp (467 nm) for 0, 1, 2, 3, 4, and 5 min. [a]n.d., not determined due to the limited production of $^1O_2$.

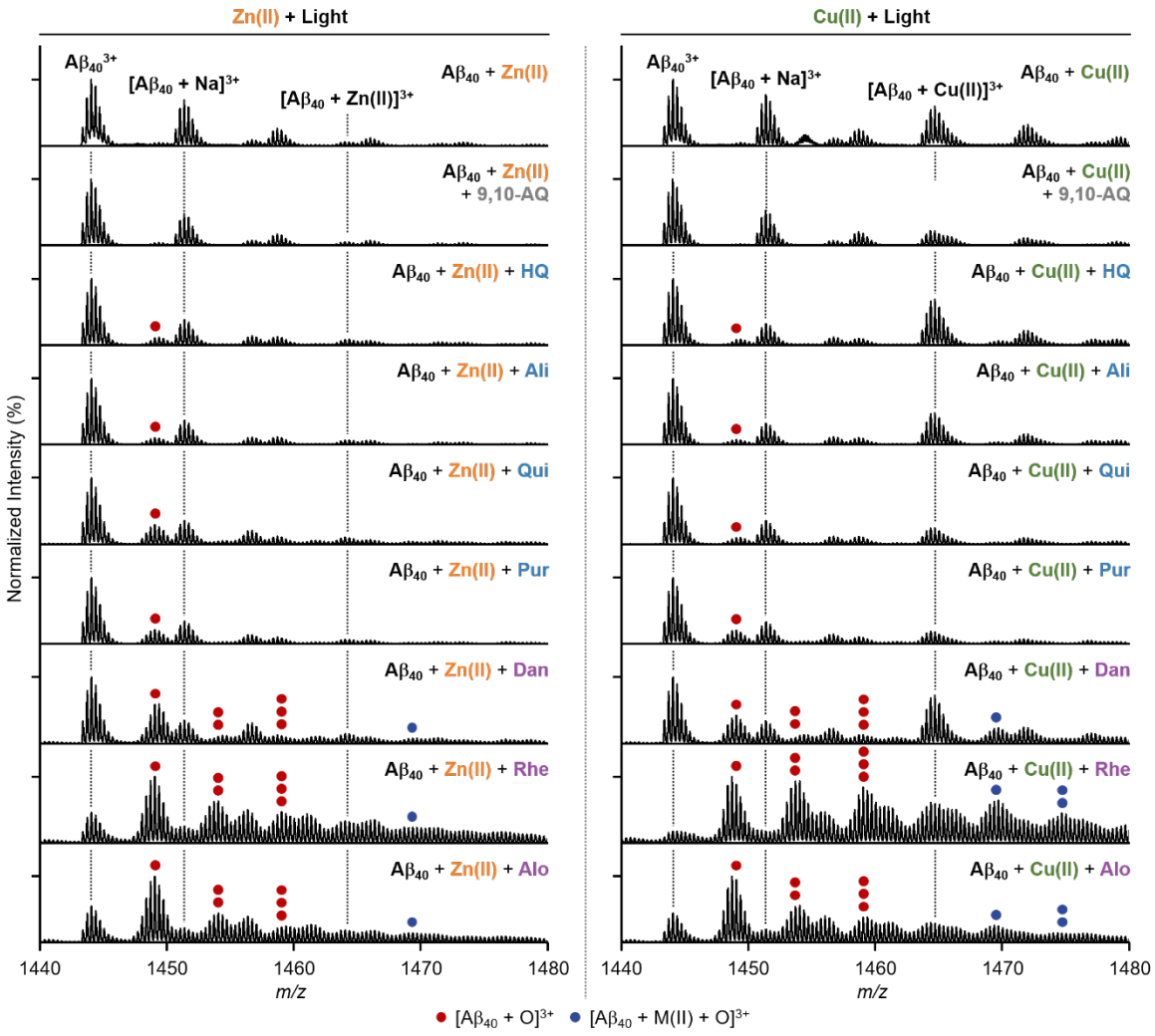


Figure S7. Analysis of metal–$A\beta_{40}$ species produced upon treatment with the **AQ** series in the presence of light by ESI–MS. The number of red and blue dots represents the number of oxygen atoms incorporated into $A\beta_{40}$ without and with metal ions, respectively. Conditions: [$A\beta_{40}$] = 25 μM; [M(II)] = 25 μM; [compound] = 50 μM; 20 mM ammonium acetate, pH 7.4; 37 °C; 3 h; constant agitation (250 rpm); Kessil lamp (467 nm) for 1 h. The samples were diluted by five fold with ddH_2O before injection to the mass spectrometer.

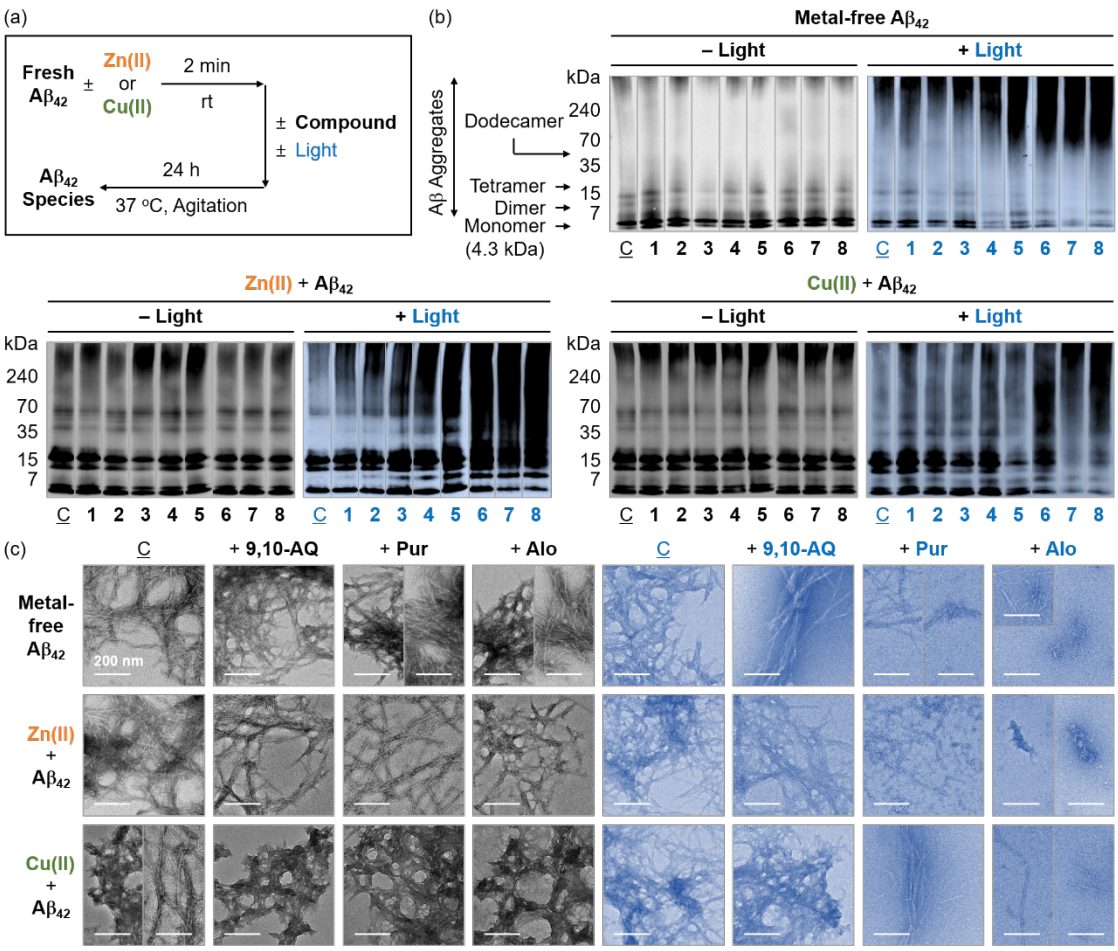


Figure S8. Effect of the **AQ** series on the formation of metal-free or metal-treated $A\beta_{42}$ aggregates with and without light activation. (a) Scheme of the inhibition experiments. (b) Gel/Western blots (6E10) of the resultant $A\beta_{42}$ species upon incubation of metal-free and metal-added $A\beta_{42}$ with and without treatment of compounds and light. Lanes: (C) $A\beta_{42}$; (1) $A\beta_{42}$ + **9,10-AQ**; (2) $A\beta_{42}$ + **HQ**; (3) $A\beta_{42}$ + **Ali**; (4) $A\beta_{42}$ + **Qui**; (5) $A\beta_{42}$ + **Pur**; (6) $A\beta_{42}$ + **Dan**; (7) $A\beta_{42}$ + **Rhe**; (8) $A\beta_{42}$ + **Alo**. (c) TEM images of the aggregates obtained by 24 h incubation of metal-free and metal-treated $A\beta_{42}$ with and without compounds in the absence and presence of light. Conditions: [$A\beta_{42}$] = 25 μM; [M(II)] = 25 μM; [compound] = 50 μM; 20 mM HEPES, pH 7.4 [for metal-free or Zn(II)-containing samples] or pH 6.6 [for Cu(II)-added samples], 150 mM NaCl; 37 °C; 24 h; constant agitation (250 rpm); Kessil lamp (467 nm) for 1 h. Scale bar = 200 nm.

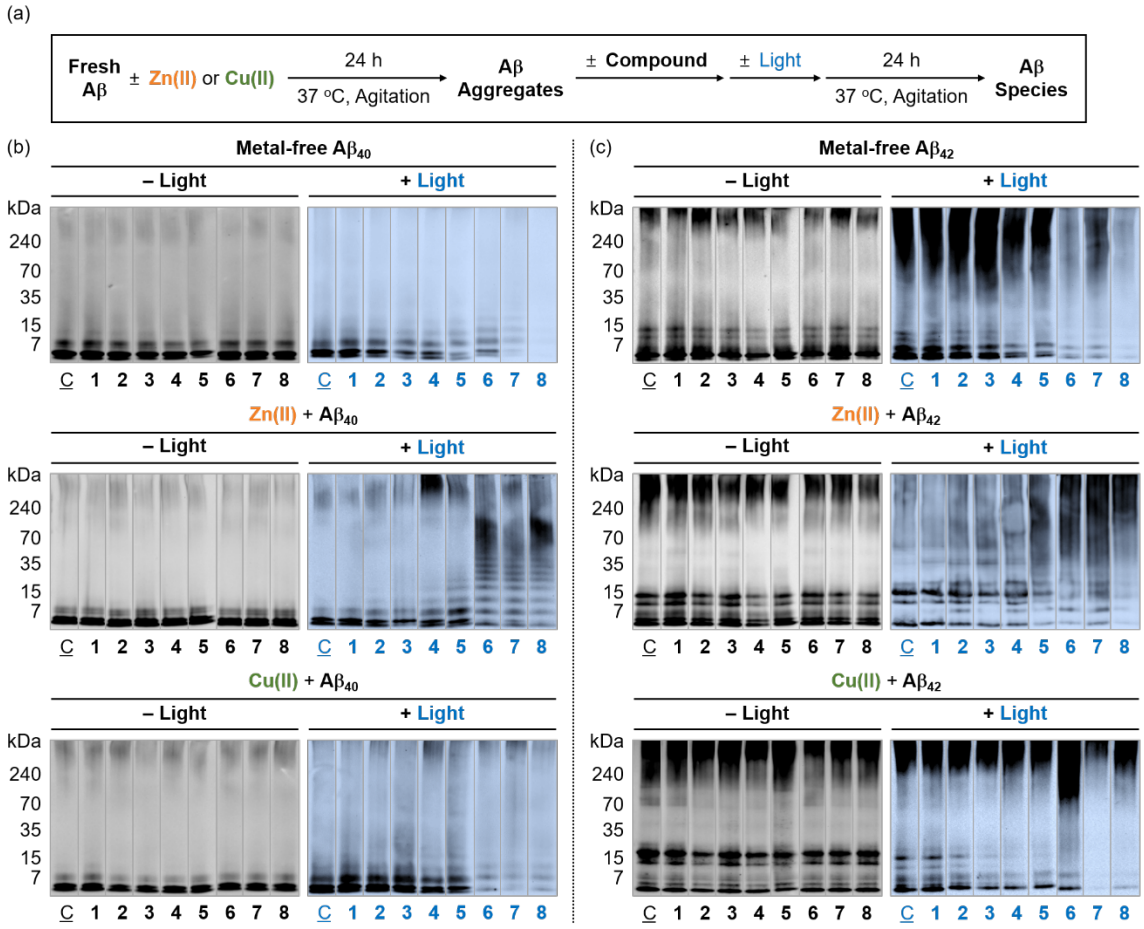


Figure S9. Impact of the illuminated **AQ** series against the disassembly of preformed metal-free and metal-added Aβ aggregates. (a) Scheme of the disaggregation experiments. (b and c) Gel/Western blot (6E10) of the resultant Aβ species upon incubation of preformed metal-free and metal-added (b) $A\beta_{40}$ and (c) $A\beta_{42}$ species with and without treatment of compounds and light. Lanes: (C) Aβ; (1) Aβ + **9,10-AQ**; (2) Aβ + **HQ**; (3) Aβ + **Ali**; (4) Aβ + **Qui**; (5) Aβ + **Pur**; (6) Aβ + **Dan**; (7) Aβ + **Rhe**; (8) Aβ + **Alo**. Conditions: [Aβ] = 25 μM; [M(II)] = 25 μM; [compound] = 50 μM; 20 mM HEPES (1% v/v DMSO), pH 7.4 [for metal-free or Zn(II)-containing samples] or pH 6.6 [for Cu(II)-added samples], 150 mM NaCl; 37 °C; 24 h; constant agitation (250 rpm); Kessil lamp (467 nm) for 1 h.

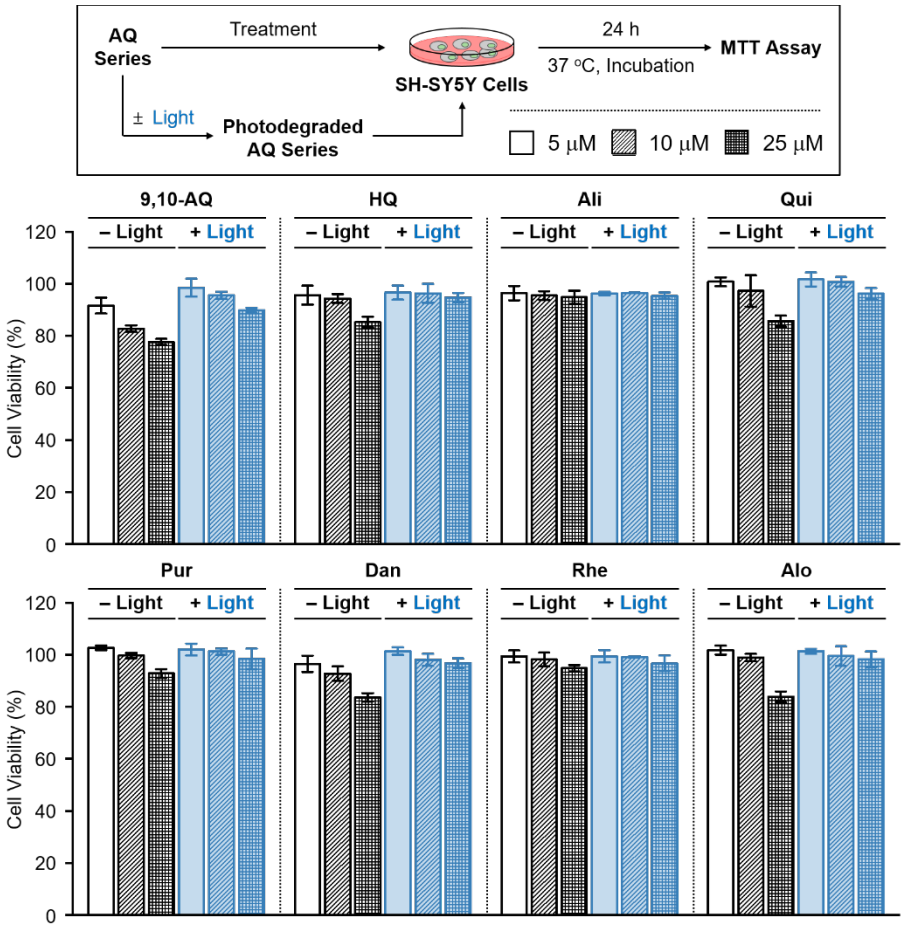


Figure S10. Cytotoxicity of the freshly prepared and photodegraded **AQ** series. Viability (%) of cells was measured by the MTT assay in comparison of that of the cells treated with an equivalent amount of DMSO. Conditions: [compound] = 5, 10, and 25 μM; 24 h, 37 °C; Kessil lamp (467 nm) for 1 h. Error bars represent the standard error of the mean from three independent experiments.

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Appendix A. Cartesian coordinates of the optimized **AQ** geometries.

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9,10-AQ (S_0)

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C	-0.912514031	0.454508573	-4.304567337
C	-0.912582099	0.460102797	-2.909705400
C	-0.912517846	-0.838482380	-2.187571287
C	-0.912564158	1.680916190	-2.216895580
C	-0.912465215	1.726775050	-0.731788635
C	-0.912485957	0.428201795	-0.009674966
C	-0.912520111	-0.792627215	-0.702467382
C	-0.912550688	1.653610468	-5.004907608
C	-0.912664354	2.881347179	-2.927373409
O	-0.912361145	2.789311409	-0.128794372
C	-0.912485957	0.433754683	1.385188937
C	-0.912622809	-1.993055224	0.007991301
C	-0.912648201	-1.979443431	1.396546960
C	-0.912558019	-0.765341997	2.085522890
H	-0.912441790	1.392732978	1.893834233
H	-0.912677526	-2.921463966	-0.554530919
H	-0.912747681	-2.915651560	1.947269440
H	-0.912596762	-0.757987201	3.171671867
C	-0.912674308	2.867710352	-4.315922260
H	-0.912403047	-0.504506052	-4.813137531
O	-0.912465453	-1.901027083	-2.790551424
H	-0.912485719	1.646257162	-6.091050148
H	-0.912711322	3.809745073	-2.364830256
H	-0.912770748	3.803925753	-4.866622925

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9,10-AQ (T_1)

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C	-0.917777002	0.448705524	-4.294497013
C	-0.915535986	0.446205258	-2.885601759
C	-0.910557270	-0.830832660	-2.184049845
C	-0.917847931	1.667763472	-2.192291498
C	-0.917399049	1.718119025	-0.737317145
C	-0.916560471	0.443912894	-0.035007618
C	-0.914845526	-0.778943181	-0.728808284
C	-0.918439865	1.638106704	-4.990272045
C	-0.917450488	2.876512527	-2.917403698
O	-0.914798498	2.809889078	-0.116778210
C	-0.915083110	0.440467894	1.374533415
C	-0.918621242	-1.986277342	-0.003449602
C	-0.919107854	-1.973412395	1.373651624
C	-0.918130934	-0.748227537	2.069070101
H	-0.912755370	1.400115967	1.883007050
H	-0.920160294	-2.914737701	-0.567258298
H	-0.919910848	-2.909880161	1.923012376
H	-0.919237196	-0.739875257	3.154641151
C	-0.919114053	2.862856388	-4.294836521
H	-0.918658197	-0.511928320	-4.801896095
O	-0.910312653	-1.920340300	-2.802710295
H	-0.918200195	1.629090190	-6.076476097
H	-0.914978445	3.805498123	-2.354497194
H	-0.919632852	3.800128698	-4.843795300

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HQ (S_0)

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C	-0.913066804	0.454902709	-4.306647301
C	-0.912887692	0.461226076	-2.912742853
C	-0.912880123	-0.834617853	-2.185584545
C	-0.912436187	1.682545781	-2.221638918
C	-0.912120700	1.719491601	-0.742618144
C	-0.912555337	0.453401953	-0.017748542
C	-0.912588954	-0.784285843	-0.699427068
C	-0.912711799	1.654109716	-5.007508755
C	-0.912066936	2.883709192	-2.931231976
O	-0.911230266	2.807469130	-0.146487564
C	-0.912805319	0.463571936	1.396043181
C	-0.912287176	-1.977471471	0.003363605
C	-0.912006378	-1.952958941	1.401507020
C	-0.912288249	-0.755590141	2.092895269
H	-0.912229419	-2.907744884	-0.554213941
H	-0.911615908	-2.887442350	1.955413938
H	-0.912196636	-0.722425222	3.177385807
C	-0.912182212	2.868468285	-4.319762230
H	-0.913412452	-0.504438519	-4.814540863
O	-0.913033664	-1.897100687	-2.787894249
H	-0.912804008	1.646262407	-6.093617916
H	-0.911655247	3.813689709	-2.371758699
H	-0.911841393	3.804336071	-4.870850086
O	-0.913644791	1.591028214	2.099290848
H	-0.915195286	2.331687450	1.442553878

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HQ (T_1)

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C	-0.911989748	0.454806685	-4.296439171
C	-0.912284911	0.454715312	-2.895237446
C	-0.912584901	-0.821443915	-2.180431366
C	-0.912324131	1.692768693	-2.199352741
C	-0.912625611	1.700913310	-0.775579393
C	-0.912090242	0.471487612	-0.051997583
C	-0.912418902	-0.750619709	-0.723002553
C	-0.911753237	1.645208001	-4.997000217
C	-0.912136614	2.900153637	-2.931744337
O	-0.913539708	2.865855217	-0.145344138
C	-0.911019266	0.479424685	1.415189266
C	-0.912586987	-1.980374575	0.020843217
C	-0.912215531	-1.985535979	1.402580857
C	-0.911383688	-0.779627025	2.102816343
H	-0.913043499	-2.896658897	-0.561184287
H	-0.912512600	-2.926784515	1.943465948
H	-0.910912097	-0.740547299	3.187381506
C	-0.911838055	2.872186661	-4.309089184
H	-0.911942601	-0.507254422	-4.799017906
O	-0.912893951	-1.917950153	-2.766539574
H	-0.911502004	1.636240959	-6.083062649
H	-0.912207961	3.839440823	-2.389222383
H	-0.911658764	3.803735495	-4.867492676
O	-0.909545004	1.563871384	2.055702448
H	-0.915155351	2.656555891	0.828733683

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Ali (S_0)

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C	-0.912659705	0.454798222	-4.279732704
C	-0.912611425	0.454877734	-2.882595539
C	-0.912626088	-0.857642114	-2.165099144
C	-0.912509441	1.682225108	-2.199461937
C	-0.912188649	1.722445607	-0.720184565
C	-0.912565768	0.459225237	-0.018251523
C	-0.912683189	-0.791229367	-0.731619775
C	-0.912696838	1.648429871	-4.986293793
C	-0.912616193	2.882183790	-2.916867495
O	-0.911568403	2.832638741	-0.135624081
C	-0.912495553	0.471221209	1.383359551
C	-0.912728131	-1.975351810	0.022327470
C	-0.912631631	-1.978897691	1.398917556
C	-0.912412643	-0.775456131	2.183016777
H	-0.912791371	-2.907110929	-0.539116561
H	-0.912560225	-2.912953138	1.955634475
C	-0.912713230	2.868990660	-4.303767204
H	-0.912630856	-0.513830125	-4.771467209
O	-0.912541926	-1.906967282	-2.833806276
H	-0.912719607	1.636243939	-6.074151993
H	-0.912609160	3.809608221	-2.351877213
H	-0.912772298	3.804325342	-4.858278751
O	-0.912400782	1.603233933	2.076972485
H	-0.913293183	2.327468634	1.394278526
O	-0.912170053	-0.734095693	3.424480677

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Ali (T_1)

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C	-0.912534833	0.490878046	-4.266431808
C	-0.912720382	0.482140064	-2.864580393
C	-0.912670970	-0.797075152	-2.154044628
C	-0.912712276	1.718848705	-2.157954931
C	-0.912679851	1.721660614	-0.733963430
C	-0.912651122	0.491327018	-0.006116427
C	-0.912601233	-0.740385652	-0.688173354
C	-0.912361324	1.679297209	-4.971599102
C	-0.912575364	2.925146580	-2.896622896
O	-0.912490368	2.865679026	-0.073896274

C	-0.912400305	0.549571574	1.438986063
C	-0.912488043	-1.957700253	0.050419040
C	-0.912328303	-1.938062668	1.413384914
C	-0.912257433	-0.710020900	2.195092678
H	-0.912428141	-2.881957293	-0.519273937
H	-0.912167966	-2.859504223	1.991795659
C	-0.912414789	2.904851675	-4.273980618
H	-0.912467480	-0.473802477	-4.766357899
O	-0.912623882	-1.886370063	-2.760179520
H	-0.912196398	1.672006965	-6.058835983
H	-0.912516952	3.860686302	-2.345885992
H	-0.912322104	3.840983868	-4.828108788
O	-0.912240803	1.683608651	2.036164761
H	-0.912213743	2.544643879	0.947746456
O	-0.912006557	-0.737822711	3.445813179

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Qui (S_0)

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C	-0.912746072	0.456302941	-4.309530258
C	-0.912710726	0.462293148	-2.914428711
C	-0.912679017	-0.823843241	-2.185156822
C	-0.912458181	1.683690071	-2.221284628
C	-0.912314773	1.717064142	-0.743221641
C	-0.912556171	0.450246662	-0.027189059
C	-0.912554443	-0.788966238	-0.730405748
C	-0.912592351	1.655785799	-5.008575439
C	-0.912365913	2.884658337	-2.931326389
O	-0.911897779	2.804651499	-0.142188385
C	-0.912687898	0.460075974	1.375289917
C	-0.912452281	-1.997995257	-0.019708410
C	-0.912334740	-1.963897586	1.394167185
C	-0.912453473	-0.771220148	2.071095228
H	-0.912175298	-2.911468267	1.923038006
C	-0.912435651	2.869915724	-4.319541454
H	-0.912837386	-0.501216888	-4.820430756
O	-0.912716508	-1.897640824	-2.810481310
H	-0.912596464	1.648775935	-6.094665527
H	-0.912198126	3.814157009	-2.371050596
H	-0.912360847	3.805963278	-4.870408535
O	-0.913010776	1.579847217	2.091254234
H	-0.913516521	2.324713469	1.436427236
H	-0.912391007	-0.739259779	3.155791998
O	-0.912459075	-3.187009573	-0.613849998
H	-0.912643969	-3.006852388	-1.589120507

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Qui (T_1)

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C	-0.909854949	0.446733773	-4.317304134
C	-0.911446810	0.444715589	-2.906935930
C	-0.911903620	-0.778974235	-2.176562786
C	-0.913148463	1.680868030	-2.208307743
C	-0.915345788	1.713865399	-0.756569207
C	-0.912351727	0.442668110	-0.054723799
C	-0.911541164	-0.765399158	-0.744691968
C	-0.909820318	1.640464783	-5.006599903
C	-0.913170159	2.881905556	-2.931942940
O	-0.920558035	2.800477982	-0.114809439
C	-0.910823166	0.431886554	1.397347093
C	-0.910245359	-2.037575006	-0.014436604
C	-0.912099838	-1.983666778	1.410263419
C	-0.912473202	-0.783351779	2.093675852
H	-0.912852287	-2.932687998	1.936119318
C	-0.911451101	2.863715410	-4.313184261
H	-0.908659518	-0.504201949	-4.839203835
O	-0.912965059	-1.921360016	-2.827362061
H	-0.908511460	1.636256814	-6.092543602
H	-0.914552510	3.812513828	-2.373782635
H	-0.911358654	3.797497988	-4.867459297
O	-0.907262921	1.570011854	2.050692081
H	-0.898728013	2.297703743	1.337495923
H	-0.913400531	-0.746355712	3.177861691
O	-0.907351792	-3.131612778	-0.652525663
H	-0.916572332	-2.642884016	-2.105737448

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Pur (S_0)

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C	-0.912380993	0.450239509	-4.277907848
C	-0.912373424	0.450621217	-2.878580332
C	-0.912457824	-0.840565681	-2.155471563
C	-0.912018955	1.682043791	-2.194142818
C	-0.911926746	1.720535994	-0.720915914
C	-0.912005424	0.459325969	-0.028909804
C	-0.912079155	-0.787856042	-0.749390066
C	-0.912100732	1.643444538	-4.983030319
C	-0.911749303	2.880627632	-2.915323496
O	-0.911701024	2.828980207	-0.119331904
C	-0.911896348	0.469357997	1.368314981
C	-0.911789000	-2.004846334	0.007748473
C	-0.911916077	-1.993837237	1.391597748
C	-0.912034512	-0.793630302	2.167141676
H	-0.911904275	-2.939164400	1.924541235
C	-0.911792219	2.865873337	-4.301023960
H	-0.912525952	-0.515519857	-4.774290562
O	-0.912839890	-1.924526691	-2.826642513
H	-0.912070513	1.630736709	-6.070713997
H	-0.911480546	3.808671236	-2.351251602
H	-0.911553323	3.800328016	-4.856855392
O	-0.911737323	1.595998883	2.051142931
H	-0.911799967	2.318434000	1.346638322
O	-0.911356509	-3.164428234	-0.652800441
H	-0.910491228	-2.902160645	-1.632996440
O	-0.912208498	-0.736307621	3.405802488

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Pur (T_1)

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C	-0.912453890	0.460385799	-4.294706345
C	-0.912510157	0.449543834	-2.892683983
C	-0.912581980	-0.817069888	-2.178484917
C	-0.912609518	1.682063103	-2.181692600
C	-0.913222492	1.678686857	-0.759820402
C	-0.912830651	0.445775568	-0.029336806
C	-0.912757099	-0.782733142	-0.721647739
C	-0.912268043	1.651273131	-4.994509697
C	-0.912240863	2.890821934	-2.915671110
O	-0.914132893	2.818492174	-0.100615501
C	-0.912108302	0.510748208	1.409059882
C	-0.912766993	-2.014839888	0.032402880
C	-0.912386417	-1.975369215	1.400032043
C	-0.911935210	-0.748076558	2.171788454
H	-0.912333250	-2.907637358	1.956792593
C	-0.912040412	2.874450684	-4.292076588
H	-0.912569642	-0.499977022	-4.802067280
O	-0.912538826	-1.911543608	-2.807781696
H	-0.912253201	1.648041964	-6.081440449
H	-0.912108898	3.824084997	-2.361350536
H	-0.911710560	3.812277079	-4.843110561
O	-0.911281288	1.650148869	2.004620552
H	-0.916299939	2.497600317	0.931725502
O	-0.911366343	-0.760462701	3.417704582
O	-0.913006604	-3.196419239	-0.612085760
H	-0.913247168	-2.964661121	-1.577381372

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Dan (S_0)

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C	-0.912599087	0.456822067	-4.289968014
C	-0.912599504	0.471287310	-2.905936956
C	-0.912617505	-0.826904178	-2.180989265
C	-0.912523270	1.693449616	-2.196104765
C	-0.912333488	1.711248994	-0.740570486
C	-0.912514150	0.452472448	-0.009534638
C	-0.912576377	-0.783663452	-0.694741905
C	-0.912534356	1.666668892	-4.991313457
C	-0.912576735	2.909859657	-2.918147326
O	-0.911912441	2.806602240	-0.118920512
C	-0.912540793	0.456370056	1.405041218
C	-0.912580490	-1.979277134	0.002585451
C	-0.912535489	-1.960976243	1.400883079
C	-0.912502766	-0.766160071	2.095846653
H	-0.912613630	-2.906669855	-0.559708595
H	-0.912534595	-2.897425175	1.951361537
H	-0.912483692	-0.735999227	3.180376768
C	-0.912517428	2.876003265	-4.321945190
H	-0.912620425	-0.501517177	-4.797709942
O	-0.912647665	-1.888914347	-2.783738852
H	-0.912489414	1.659036160	-6.077543736

H	-0.912473321	3.822499990	-4.852283001
O	-0.912722349	4.099606514	-2.324571609
H	-0.913089395	3.932686090	-1.352494001
O	-0.912639856	1.576087117	2.121992826
H	-0.912947416	2.324931145	1.480051637

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Dan (T_1)

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C	-0.913092732	0.468619168	-4.307547092
C	-0.912812471	0.464816183	-2.871294260
C	-0.912991643	-0.817409396	-2.174949408
C	-0.912417948	1.669694424	-2.171685457
C	-0.913056195	1.683590889	-0.747338355
C	-0.912659168	0.475931734	-0.008493264
C	-0.912634313	-0.770262122	-0.709367633
C	-0.912855208	1.651384354	-5.024679184
C	-0.911267877	2.931549072	-2.920046091
O	-0.914329469	2.855790615	-0.099537387
C	-0.912538111	0.455733061	1.422531009
C	-0.912442088	-1.972289562	-0.004097003
C	-0.912361622	-1.962759614	1.383829832
C	-0.912417591	-0.761876106	2.092057943
H	-0.912396371	-2.894241095	-0.575227022
H	-0.912266016	-2.900755882	1.931570172
H	-0.912366688	-0.742979765	3.176791668
C	-0.911959708	2.872984886	-4.353000164
H	-0.913550854	-0.502831101	-4.792100906
O	-0.913391709	-1.885302305	-2.809820414
H	-0.913293719	1.629725456	-6.109941483
H	-0.911640048	3.822428942	-4.878560066
O	-0.909416258	4.041241169	-2.318485260
H	-0.917315245	3.571166039	-0.806798875
O	-0.912537754	1.568994403	2.166407585
H	-0.912471294	2.343370199	1.578490615

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Rhe (S_0)

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C	-0.991081834	0.417602181	-4.269510746
C	-0.952747941	0.450486600	-2.887097120
C	-0.937616944	-0.838317573	-2.146435976
C	-0.929599345	1.683654547	-2.194188356
C	-0.891588569	1.722079158	-0.742862344
C	-0.884405434	0.469631195	0.007734658
C	-0.900519788	-0.775727212	-0.657689631
C	-1.007119536	1.618625522	-4.987493038
C	-0.944595575	2.890711784	-2.933277369
O	-0.864754200	2.821825743	-0.131762564
C	-0.850756049	0.496409833	1.420555711
C	-0.880546153	-1.961131811	0.054183096
C	-0.872332752	-1.927157879	1.454322934
C	-0.848671436	-0.714752316	2.129105091
H	-0.875104725	-2.909110785	-0.472338915
H	-0.784709752	-0.651350498	3.211965322
C	-0.984317720	2.836981297	-4.336209297
H	-1.007894039	-0.546887279	-4.765271664
O	-0.957697570	-1.908429742	-2.730900288
H	-1.037764430	1.595368147	-6.073005676
H	-0.995939314	3.776004553	-4.879477978
O	-0.923620701	4.088765621	-2.358641148
H	-0.896229446	3.941162348	-1.385072351
O	-0.819816113	1.623243451	2.122597694
H	-0.829266667	2.364671469	1.470982432
C	-0.847070336	-3.239941359	2.179932594
O	-0.403008282	-4.243800163	1.689365625
O	-1.350293636	-3.243523359	3.428940058
H	-1.805229068	-2.412032366	3.605631828

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Rhe (T_1)

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C	-0.976783454	0.420542389	-4.288590908
C	-0.943376005	0.440087765	-2.854078054
C	-0.939334929	-0.762854934	-0.683357358
C	-0.797980905	1.610193014	-5.023039818
C	-0.899254620	2.913696527	-2.935844898
O	-1.002795696	2.869040728	-0.114513710
C	-1.034082770	0.480422974	1.431110978
C	-0.947207272	-1.955299854	0.034423586
C	-0.924583673	-0.834227741	-2.137392759
C	-0.932488799	1.652304769	-2.173143625
C	-0.898678064	1.687131882	-0.748302817
C	-0.882556856	0.491916925	0.007443577
C	-0.893834472	-0.765743375	-0.671769261
C	-0.999666214	1.593152881	-5.022204876
C	-0.957254529	2.902483225	-2.937472582
O	-0.882464111	2.867340088	-0.118877046
C	-0.848122656	0.493486524	1.436966658
C	-0.876140654	-1.955848336	0.048180144
C	-0.873248398	-1.933625579	1.438502550
C	-0.847514629	-0.711816072	2.124444008
H	-0.873222947	-2.899610996	-0.485993445
H	-0.778166771	-0.655196726	3.207418442
C	-0.990553319	2.823248386	-4.368381977
H	-0.983270586	-0.557364643	-4.759882927
O	-0.937550247	-1.907050371	-2.755919456
H	-1.024863839	1.555414557	-6.106643677
H	-1.008230448	3.765017748	-4.907367706
O	-0.950609982	4.019005775	-2.350022078
H	-0.893849254	3.575498104	-0.834209859
O	-0.810978889	1.614832044	2.164765358
H	-0.817079008	2.382906675	1.568251491
C	-0.873353839	-3.246461153	2.156859159
O	-0.485569596	-4.270204544	1.656303883
O	-1.341761231	-3.234571218	3.421371460
H	-1.755232453	-2.384634018	3.611032486

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Alo (S_0)

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C	-0.827243865	0.415918618	-4.287564278
C	-0.870753348	0.449458867	-2.903556347
C	-0.880367875	-0.839865804	-2.160030842
C	-0.904173374	1.682593465	-2.211428165
C	-0.947906911	1.721181989	-0.755149186
C	-0.962841392	0.473693609	-0.007951147
C	-0.932503045	-0.774376392	-0.673332691
C	-0.816704810	1.616592765	-5.006081104
C	-0.894213974	2.890350580	-2.950664282
O	-0.972013652	2.827874660	-0.149884939
C	-1.006804943	0.491537452	1.406834841
C	-0.941139817	-1.957504153	0.041526459
C	-0.987068355	-1.934031963	1.445501447
C	-1.019363999	-0.721985698	2.114106417
H	-0.907430589	-2.892364025	-0.510692239
H	-1.062998533	-0.693763375	3.197741270
C	-0.849460602	2.835761070	-4.354304790
H	-0.802319765	-0.549173534	-4.781665802
O	-0.846639991	-1.911662340	-2.746673107
H	-0.782482803	1.593726158	-6.091625690
H	-0.842046559	3.774486542	-4.898366451
O	-0.925697863	4.088554382	-2.373238325
H	-0.958455324	3.933386564	-1.398684740
O	-1.039613724	1.621630073	2.106463432
H	-1.033846855	2.361211061	1.452521086
C	-1.023435235	-3.234057188	2.217333078
O	-0.709105849	-3.106899023	3.581039906
H	0.212572008	-2.836146832	3.648544788
H	-2.042430162	-3.638530731	2.178443670
H	-0.379578710	-3.970056772	1.710210204

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Alo (T_1)

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C	-0.810306430	0.435598880	-4.292285919
C	-0.867105901	0.447590768	-2.857597589
C	-0.876678288	-0.826335490	-2.147271395
C	-0.910699844	1.660839558	-2.172846317
C	-0.965612233	1.690188527	-0.749875307
C	-0.981069267	0.491800874	0.000990194

C	-1.004445314	-1.946256995	1.425235987
C	-1.045776367	-0.729618132	2.111384153
H	-0.903408527	-2.882461548	-0.529768467
H	-1.089989662	-0.715822935	3.195236683
C	-0.841427207	2.839166880	-4.366836071
H	-0.777921975	-0.540707827	-4.765804291
O	-0.833630741	-1.902012467	-2.767912388
H	-0.754579246	1.575579882	-6.107125759
H	-0.833594441	3.782511711	-4.903148651
O	-0.939679503	4.029916286	-2.347910166
H	-0.980036378	3.577470779	-0.827072859
O	-1.074721217	1.600249171	2.164387941
H	-1.066271305	2.369290590	1.569640994
C	-1.048038840	-3.242423534	2.199903965
O	-0.587911546	-3.133408546	3.524941683
H	0.333967566	-2.857288122	3.491765738
H	-2.089051485	-3.580380440	2.275063038
H	-0.507252216	-4.019083977	1.636790633

Appendix B. Vibrational frequencies of the optimized **AQ** structures.

9,10-AQ (S_0)

50.06	115.57	134.39	161.17	227.51	227.81
297.51	368.78	395.92	410.54	423.74	432.94
450.66	484.33	497.32	627.76	637.84	671.17
691.88	697.38	725.46	734.70	789.00	808.27
830.14	835.01	923.71	936.02	939.56	972.36
1005.05	1008.58	1024.92	1025.69	1068.41	1072.25
1119.29	1121.15	1181.62	1186.55	1198.86	1219.58
1244.81	1292.00	1345.96	1349.55	1408.51	1419.77
1499.81	1511.55	1528.37	1532.81	1653.37	1666.32
1675.51	1679.37	1791.01	1796.61	3215.62	3215.68
3229.75	3229.89	3242.31	3242.64	3245.34	3245.91

9,10-AQ (T_1)

57.79	124.40	159.87	166.23	226.43	230.25
295.27	369.52	369.63	387.64	416.43	431.99
449.91	488.99	498.51	565.84	599.95	630.66
654.83	655.27	678.63	698.74	765.61	780.71
794.58	823.37	870.54	889.07	937.31	945.29
969.92	978.76	1004.69	1006.02	1061.43	1066.77
1120.84	1133.06	1157.66	1182.46	1201.10	1221.58
1230.03	1248.89	1302.51	1339.13	1430.12	1436.59
1475.35	1480.03	1494.68	1509.29	1529.58	1619.32
1636.64	1658.64	1667.00	2104.24	3212.50	3216.45
3222.18	3224.83	3229.51	3232.18	3237.83	3241.94

HQ (S_0)

51.75	98.48	135.13	170.77	212.94	215.88
262.60	314.55	353.43	395.90	427.44	428.62
435.00	462.46	487.89	504.52	562.52	565.20
627.98	674.37	676.91	702.99	723.62	747.52
799.18	800.28	817.07	840.39	864.50	911.22
928.19	941.13	945.22	1006.31	1009.88	1025.69
1056.75	1075.38	1096.98	1121.08	1183.31	1189.32
1199.89	1231.63	1268.07	1312.40	1339.83	1390.71
1412.52	1424.38	1446.72	1508.04	1524.23	1533.83
1540.02	1655.45	1659.23	1674.99	1682.34	1741.81
1794.58	3216.93	3220.84	3231.08	3243.91	3245.43
3247.27	3252.20	3331.98			

HQ (T_1)

64.98	97.34	148.85	166.10	199.63	220.76
258.58	314.28	356.09	387.33	397.37	404.48
431.20	475.71	485.16	512.12	525.70	568.07
601.29	619.89	669.41	682.91	691.77	710.18
778.39	794.67	796.09	817.73	889.15	903.31
908.84	920.30	926.22	989.66	995.15	1017.12
1047.38	1066.98	1089.87	1125.17	1156.75	1161.96
1188.75	1212.70	1264.36	1291.64	1329.57	1405.22
1414.71	1439.38	1456.82	1482.12	1501.75	1509.84
1536.15	1561.78	1585.79	1618.35	1625.18	1640.39
1681.62	3211.55	3215.22	3227.11	3229.41	3244.38
3245.82	3249.45	3250.73			

Ali (S_0)

48.97	96.02	123.96	152.79	177.52	201.53
246.13	300.16	331.45	340.08	357.87	399.99
424.28	435.93	463.82	472.17	499.02	517.13
568.99	580.63	635.95	671.19	682.08	687.62
733.90	761.13	776.21	798.45	813.26	842.60
853.29	913.18	915.61	916.51	989.53	993.87
1007.68	1043.67	1065.28	1084.71	1115.19	1170.11
1184.06	1215.89	1236.10	1277.51	1309.79	1357.33
1393.43	1405.64	1431.76	1464.77	1507.19	1518.80
1540.19	1594.72	1619.22	1642.92	1671.35	1704.50
1707.92	1732.00	3188.93	3196.34	3200.21	3208.26
3214.65	3231.46	3234.40			

Ali (T_1)

56.99	98.72	118.88	152.57	179.87	206.82
257.21	291.32	315.12	333.04	368.62	405.22
426.62	432.02	444.15	479.49	506.48	525.34
550.29	571.79	625.50	646.72	670.48	679.17
703.41	733.85	767.99	770.17	792.41	841.65
845.46	875.51	914.51	976.65	981.06	990.43
1033.11	1057.37	1076.76	1121.70	1162.22	1177.69
1184.46	1197.71	1226.91	1268.37	1292.21	1309.25
1379.68	1412.60	1421.09	1456.66	1488.58	1502.12
1516.98	1574.19	1589.79	1608.50	1621.42	1644.88
1672.69	1681.87	2114.74	3187.50	3199.78	3206.08
3227.45	3232.58	3235.04			

Qui (S_0)

57.27	95.74	148.01	156.92	180.26	207.55
236.08	320.16	331.15	376.81	400.85	427.00
429.53	435.66	440.34	468.55	491.51	514.53
530.63	591.20	614.84	671.06	674.69	710.74
730.73	742.80	771.02	801.25	818.35	863.24
865.49	871.92	908.25	919.72	927.55	988.09
1005.95	1010.99	1025.71	1067.34	1106.13	1122.25
1178.96	1193.44	1197.85	1265.36	1289.94	1312.31
1369.93	1386.53	1404.79	1422.76	1432.46	1489.64
1513.94	1532.77	1539.49	1542.17	1653.12	1663.71
1671.15	1675.86	1729.27	1750.22	3217.16	3231.38
3236.00	3245.18	3248.02	3250.28	3292.39	3295.12

Qui (T_1)

66.31	94.51	140.70	153.62	175.05	216.14
245.25	337.07	343.05	355.63	385.61	401.10
423.15	432.37	453.77	473.46	487.75	530.29
540.00	583.57	596.67	641.22	665.91	704.51
705.87	717.46	766.34	766.63	793.90	837.87
878.26	903.42	917.67	948.96	991.79	995.84
1016.50	1047.21	1052.10	1063.38	1097.29	1127.50
1172.24	1191.34	1203.23	1263.48	1312.41	1317.75
1326.74	1408.43	1422.30	1446.14	1478.50	1492.08
1502.01	1523.87	1554.64	1576.02	1589.49	1609.68
1642.75	1643.92	1674.78	1693.99	2765.77	2824.57
3218.06	3231.86	3238.67	3246.85	3250.62	3252.30

Pur (S_0)

52.57	93.91	126.14	160.94	167.27	202.80
222.37	243.60	309.17	332.77	369.29	385.69
414.00	423.01	434.20	437.46	448.29	473.27
506.68	524.57	565.33	610.77	653.35	662.56
689.64	718.94	720.59	744.32	776.21	786.88
810.68	835.73	837.66	909.72	921.22	988.56
993.10	997.86	998.01	1005.33	1061.53	1103.80
1122.95	1170.78	1200.56	1228.80	1267.18	1282.31
1315.34	1347.93	1393.35	1401.98	1449.25	1461.55
1481.33	1513.98	1535.64	1565.11	1611.52	1641.24
1647.29	1680.03	1696.42	1721.60	1730.79	2856.95
2952.04	3190.84	3209.59	3233.24	3233.56	3236.96

Pur (T_1)

54.33	84.33	112.62	151.74	168.10	202.93
203.68	253.71	285.96	327.04	369.26	385.62
392.58	408.60	424.40	429.75	459.32	460.86
516.00	522.37	550.55	596.78	616.53	639.62
654.30	697.99	726.76	733.14	733.56	755.01
782.25	838.09	853.51	871.67	873.89	918.54
977.60	979.57	988.98	1053.36	1079.53	1124.01
1165.95	1186.45	1201.50	1206.30	1238.79	1266.43
1292.95	1321.14	1350.99	1394.99	1417.91	1443.97
1468.90	1494.19	1509.20	1555.08	1573.30	1586.66
1621.45	1629.61	1651.91	1668.10	1699.24	2038.22
3190.39	3209.37	3229.17	3231.54	3237.21	3255.38

Dan (S_0)

52.09	83.92	125.97	179.94	204.35	212.40
241.53	277.76	316.40	347.07	374.23	435.77
451.30	456.74	480.62	484.70	495.72	532.65

553.69 586.61 592.91 639.13 678.76 711.47
722.21 773.12 776.52 797.40 812.79 828.64
836.34 848.25 867.13 937.64 940.82 945.16
1010.37 1011.16 1018.50 1074.69 1091.88 1113.90
1186.24 1188.85 1198.21 1250.77 1271.82 1331.89
1356.56 1392.78 1395.82 1440.08 1450.34 1457.41
1508.56 1516.31 1541.54 1545.41 1645.22 1650.08
1673.33 1684.16 1722.25 1794.61 3221.90 3221.98
3246.18 3246.26 3252.81 3253.27 3385.22 3420.07

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Dan (T_1)

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62.90 81.78 122.58 166.81 195.87 212.99
236.25 283.98 324.98 348.99 368.63 397.28
429.78 464.37 475.14 485.50 500.04 502.90
545.34 575.64 597.77 606.66 618.06 629.56
690.34 693.23 732.74 761.65 789.14 807.83
829.10 845.35 910.61 918.07 928.41 939.64
989.43 999.63 1024.46 1058.09 1085.98 1098.64
1150.07 1169.69 1184.10 1226.25 1274.65 1298.89
1350.05 1364.47 1416.01 1419.89 1425.90 1466.83
1493.19 1499.93 1506.56 1536.01 1563.04 1593.13
1620.31 1629.45 1644.09 1685.24 3018.14 3220.73
3228.38 3244.54 3246.21 3251.21 3252.64 3683.78

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Rhe (S_0)

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36.55 55.94 73.98 119.72 123.38 129.65
190.69 217.06 224.77 245.80 270.18 291.14
324.81 355.30 396.47 427.73 445.67 465.02
472.13 480.16 507.10 518.37 526.90 555.91
569.51 594.00 622.31 660.37 675.95 707.78
724.42 752.06 771.81 778.46 790.49 812.04
836.00 836.51 840.91 904.14 930.27 942.46
957.63 971.52 1013.61 1042.88 1085.86 1109.27
1126.82 1188.03 1192.86 1211.61 1240.85 1267.02
1309.30 1328.64 1366.04 1390.75 1407.62 1446.29
1453.40 1456.78 1490.29 1516.27 1537.38 1547.61
1638.43 1648.14 1673.66 1690.02 1723.51 1799.50
1900.72 3221.61 3223.77 3247.30 3253.52 3260.62
3382.96 3433.99 3868.01

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Rhe (T_1)

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40.82 56.33 72.70 116.10 124.65 133.39
170.84 207.04 225.03 241.97 272.42 304.03
327.38 349.39 397.88 401.21 442.37 453.69
472.60 486.18 488.00 506.75 523.35 544.93
558.55 581.50 604.46 625.96 628.71 645.82
690.94 698.38 732.75 741.94 769.20 782.10
816.88 824.23 885.89 898.39 916.29 942.11
959.83 973.71 993.35 1045.23 1074.42 1096.92
1117.55 1151.74 1169.57 1197.83 1231.65 1272.46
1277.80 1326.28 1344.27 1384.25 1413.66 1420.45
1434.12 1464.92 1491.33 1496.41 1518.54 1537.15
1566.25 1582.56 1621.89 1628.54 1647.75 1692.69
1891.50 3007.34 3217.84 3230.46 3247.05 3252.17
3259.68 3679.91 3868.13

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Alo (S_0)

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42.09 77.31 81.26 127.76 137.62 155.25
198.28 224.60 237.78 247.40 268.65 297.06
327.06 357.88 372.27 416.52 449.08 455.05
474.81 488.69 504.79 525.48 554.84 563.70
584.14 601.23 661.88 677.21 681.17 725.72
753.47 774.25 782.84 822.42 836.53 838.92
845.83 895.98 933.34 938.75 946.26 982.82
992.88 1009.96 1051.50 1083.36 1107.54 1134.42
1166.75 1186.85 1195.53 1216.49 1238.10 1269.49
1309.18 1351.96 1369.02 1391.02 1402.09 1420.17
1441.72 1456.05 1462.80 1489.83 1496.93 1513.94
1535.66 1548.26 1635.66 1645.04 1668.80 1685.94
1717.02 1788.11 3024.74 3098.01 3221.39 3229.18
3245.68 3247.85 3253.20 3368.89 3404.66 3877.09

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Alo (T_1)

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43.29 72.80 73.59 119.96 136.30 158.66
178.70 209.34 236.85 240.15 271.80 313.31
329.23 360.11 365.75 406.58 415.77 454.30
464.34 482.09 490.05 525.28 545.42 549.61
581.64 591.98 611.32 631.41 654.78 662.05
690.78 732.14 742.80 768.26 811.60 825.76
892.63 903.02 910.56 933.07 935.65 987.23
989.30 993.83 1051.14 1071.36 1094.99 1125.74
1148.34 1170.18 1173.12 1210.97 1219.25 1273.35
1284.55 1340.55 1365.39 1385.81 1411.40 1418.98
1427.92 1431.53 1467.38 1488.37 1494.36 1499.14
1517.86 1535.61 1562.13 1581.96 1621.86 1628.80
1637.85 1691.62 3026.34 3033.96 3095.37 3228.18
3229.55 3246.40 3246.74 3251.33 3685.20 3877.10