SUPPORTING INFORMATION

Aquatic indirect photochemical transformations of natural peptidic thiols: Impact of thiol properties, solution pH, solution salinity and metal ions

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Section S1 Chemical sources and preparations

Disodium hydrogen phosphate, sodium acetate trihydrate, hydrogen chloride, monobromobimane, perinaphthenone, terephthalic acid, hydroxyterephthalic acid, horseradish peroxidase, strontium chloride hexahydrate, sodium sulfate, silver acetate, zinc acetate, iron chloride, and sodium bromide were obtained from Sigma Aldrich. Deuterium oxide (D_2O, 99.8 atom % D), sodium deuteroxide (1.0 M in deuterium oxide, 99.8 atom % D), and deuterium chloride (1.0 M in deuterium oxide, 99.8 atom % D) were obtained from Armar Chemicals. Acetic acid, boric acid, amplifu red, potassium chloride, cadmium chloride dihydrate, and sodium chloride were obtained from Fluka. Potassium dihydrogen phosphate, potassium carbontate, sodium carbonate, sodium hydrogen carbonate, magnesium chloride hexahydrate, calcium chloride, mercury chloride, copper sulfate, and borax were from Merck. Sodium acetate was from VWR. These chemicals were used as received. Furfuryl alcohol was obtained from Sigma Aldrich and distilled prior to use. Potassium terephthalic acid was prepared from terephthalic acid.[1, 2] All solutions were prepared using either purified water (milli-Q water, 18.2 MΩ•cm; from a Barnstead Nanopure Diamond Water Purification System) or D_2O.

Section S2 Sample analysis

Quantification of FFA

Quantification of FFA was conducted following the previously published method.[3, 4] Along with the photolyses, 80 μL solution aliquots containing FFA were added to an LC vial with glass insert. Subsequently, 5 μL of each sample was injected into Waters ACQUITY ultra performance liquid chromatography (UPLC) equipped with a Waters BEH130 C18 column (2.1 × 150 mm, 1.7 μM) at 35 °C. The mobile phase was an isocratic mixture of pH 5.9 sodium acetate buffer (A) and acetonitrile (B) with 70% A and 30% B. The absorbance of FFA at 219 nm was analyzed using a photodiode array detector (PDA).

Quantification of resorufin

Quantification of resorufin was conducted following the previously published method.[5] 80 μL photolysis solution aliquots containing resorufin were added to an LC vial with glass insert. Subsequently, 5 μL of each sample was injected into a Waters ACQUITY UPLC equipped with a Waters BEH130 C18 column (2.1 × 150 mm, 1.7 μM) at 35 °C. The mobile phase was an isocratic mixture of pH 7.4 sodium citrate buffer with 10% methanol (A) and methanol (B) with 55% A and 45% B. The flow rate was 0.15 mL/min. The fluorescence of resorufin was analyzed by a fluorescence detector (FLR, excitation at 565 nm and emission at 587 nm).

Quantification of hTPA

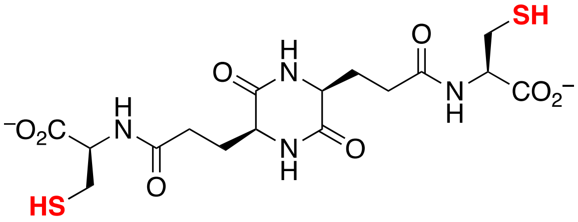
Quantification of hTPA was conducted following the previously published method.[6] 80 μL solution aliquots containing hTPA were added to an LC vial with glass insert. Subsequently, 5 μL of each sample was injected into a Waters ACQUITY UPLC equipped with a Waters BEH130 C18 column (2.1 × 150 mm, 1.7 μM) at 35 °C. The mobile phase was an isocratic mixture of pH 3.0 formic acid buffer with 10% methanol (A) and methanol (B) with 70% A and 30% B. The fluorescence of hTPA was analyzed by a FLR detector (excitation at 250 nm and emission at 410 nm).

Quantification of Thiols

Quantification of thiols was conducted following the previously published method.[7] Briefly, a mBBr stock solution (10 mM) was prepared in acetonitrile, stored in eppendorf tube at -20 °C, and used for relatively long time (over 6 months). mBBr stock solution was diluted to 100 µM with borate buffer (0.1 M, pH 8.8) before using. The derivatization of thiols was performed by mixing 80 µL thiol sample and 80 µL diluted mBBr in an LC vial insert. The mixture was vortexed for 10 seconds and 5 µL of mixture solution was injected into a Waters ACQUITY UPLC equipped with a Waters BEH130 C18 column (2.1 × 150 mm, 1.7 µM, 35 °C). The mobile phase was a mixture of sodium acetate buffer (40 mM) at pH 5.9 (A) and acetonitrile (B). The flow rate was 0.35 mL/min with the following solvent gradient: 0-0.5 min: 90% A - 10% B; 0.5-1 min: 80% A - 20% B; 1-1.5 min: 75% A - 25% B; 1.5-3.5 min: 65% A - 35% B; 3.5-4.5 min: 50%A - 50% B; 4.5-6.0 min: 35% A - 65% B; 6.0-6.5 min: 90% A - 10% B. The fluorescence of mBBr-derivatized thiol was analyzed by a FLR detector (excitation at 395 nm and emission at 475 nm).

Section S3 Proposed cyclic dimer of γEC

Slight formation of cyclic dimer for γEC over a storage period of weeks was observed on an Orbitrap high resolution mass spectrometry (HRMS) detector equipped with electrospray ionization (ESI-HRMS, Thermo Exactive) coupled to a Waters ACQUITY nanoUPLC. Nevertheless, this is not expected to impact the disappearance kinetics of γEC, as its photochemical transformations were cleanly first-order.



Section S4 Sorption of RC to self-assembled monolayers

Sorption activity of RC was investigated on a quartz crystal microbalance with dissipation monitoring (QCM-D) equipped with gold-coated sensors in flow-through cells. SAMs preparation was conducted according to literature procedures.[8] Briefly, self-assembled monolayers (SAMs) surfaces were formed from carboxyl terminus on the thoroughly cleaned sensors. The following solutions were flowed through SAMs at a constant flow rate of 20 µL /min: (*i*) 100 mM phosphate buffer (pH 7.3), (*ii*) 500 µg /mL RC prepared in phosphate buffer (pH 7.3), and (*iii*) 100 mM phosphate buffer (pH 7.3). RC adsorption and desorption to SAMs was measured by monitoring the changes in the resonance frequencies of an oscillating piezo-quartz crystal in the sensor.[8] Reversible sorption of RC was observed on negatively charged carboxyl surface. This result supports the capability of RC to ionic bond with carboxylate groups, and further supports the sorption of RC to CDOM macromolecules.

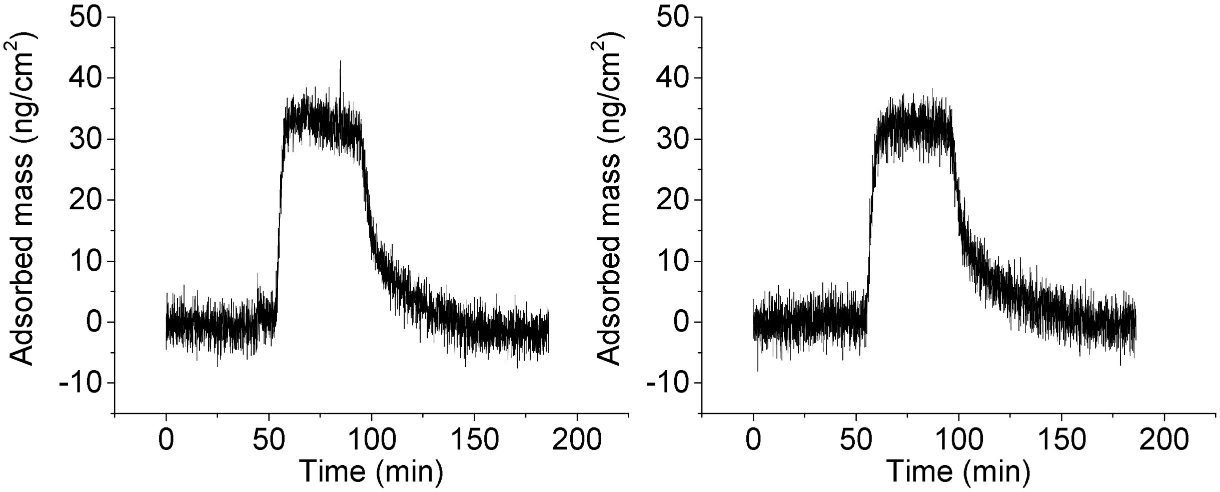


Figure S1. Sorption of RC on QCM-D equipped with SAMs constructed using carboxylate-terminated alkylthiols on gold. Duplicate experiments were conducted.

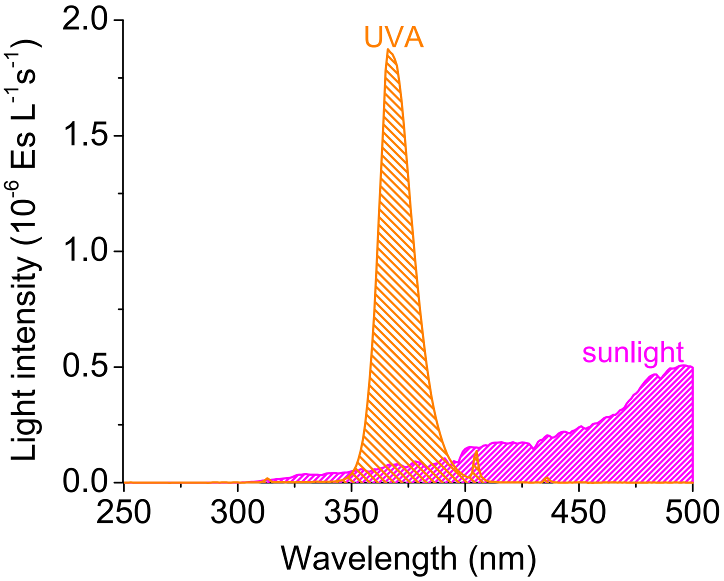


Figure S2. Spectrum of UVA light used in this study and comparison with of natural sunlight.

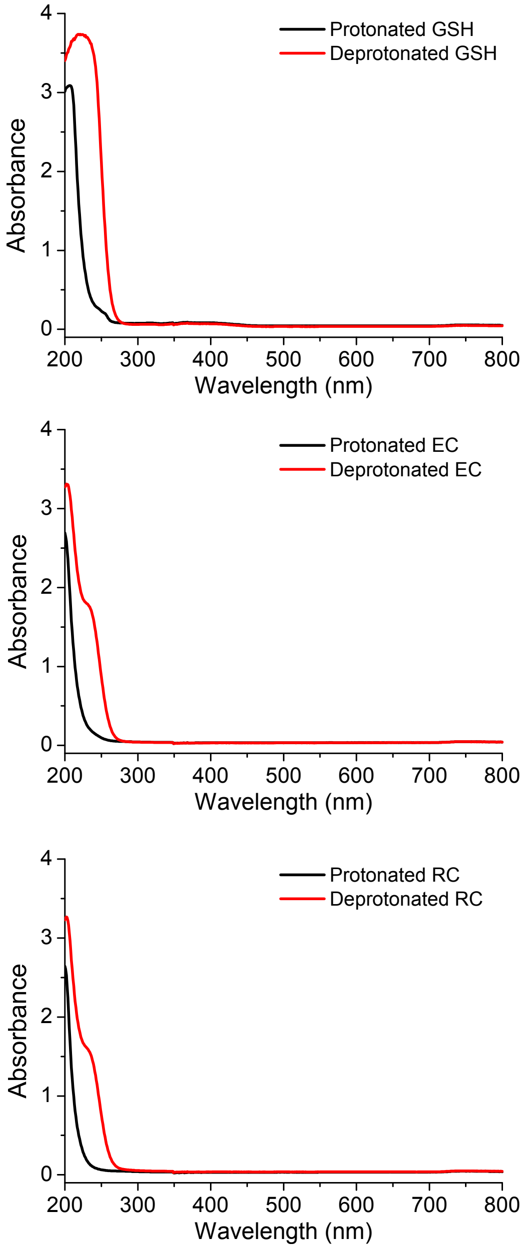


Figure S3. Absorbance spectra of protonated (1 mM at pH 5.7) and deprotonated thiols (1 mM at pH 9.9).

Table S1. PPRI generations in CDOM solutions.

	pH 5.7	pH 7.3	pH 7.9	pH 8.9	pH 9.9
$^1O_2$ (pM)	0.82±0.02	1.00±0.02	1.00±0.02	0.96±0.02	0.94±0.02
•OH (fM)	0.68±0.06	0.80±0.04	0.72±0.04	0.85±0.06	1.00±0.04
H_2O_2 (nM/s)	1.60±0.15	2.00±0.13	2.60±0.22	3.30±0.15	3.40±0.21

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