

## Supporting Information

### **Reactions of Dissolved Organic Matter with Hydroxyl Radicals: Effects on DOM Molecular Properties and Modulation by Cu(II)**

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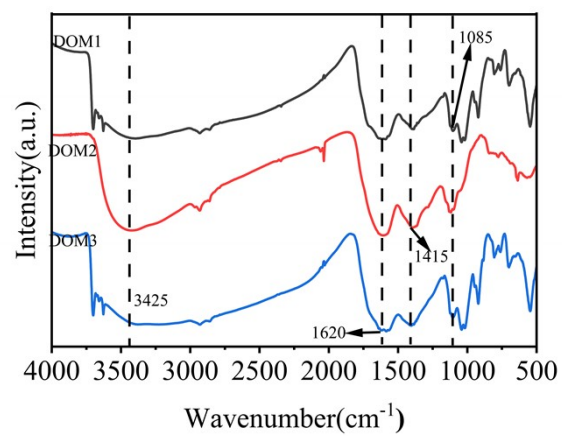


Figure S1 FT IR spectra of three kinds of DOM samples

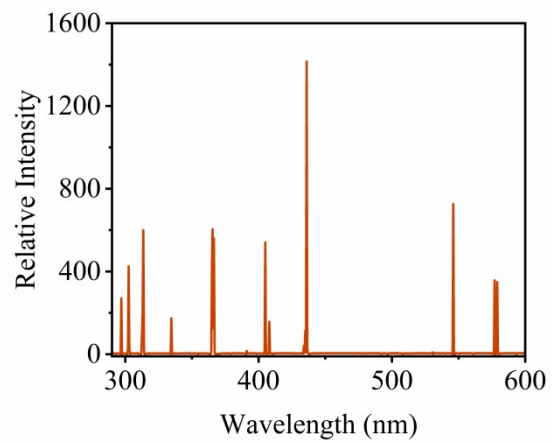


Figure S2 Emission spectra of 500 W mercury lamp

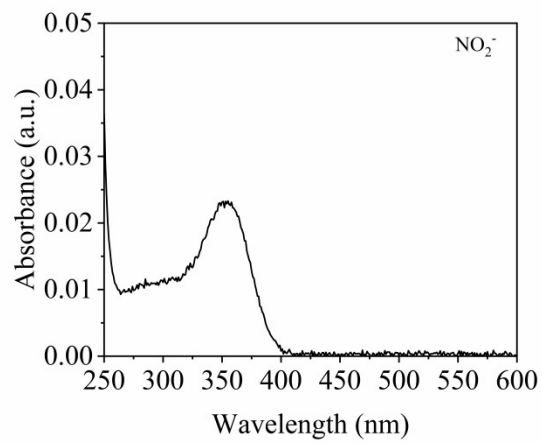


Figure S3 Absorbance spectrum of 100  $\mu\text{M}$  sodium nitrite in water

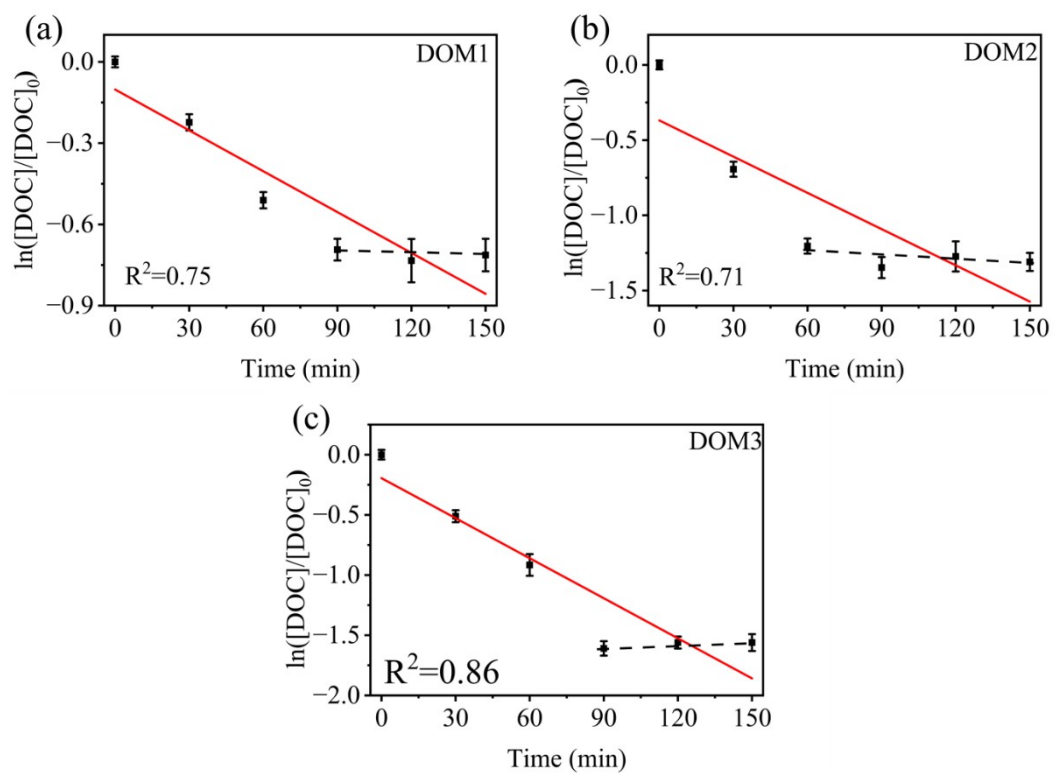


Figure S4 First-order kinetic fitting curve for TOC decay for three kinds of DOM samples in the H<sub>2</sub>O<sub>2</sub> system

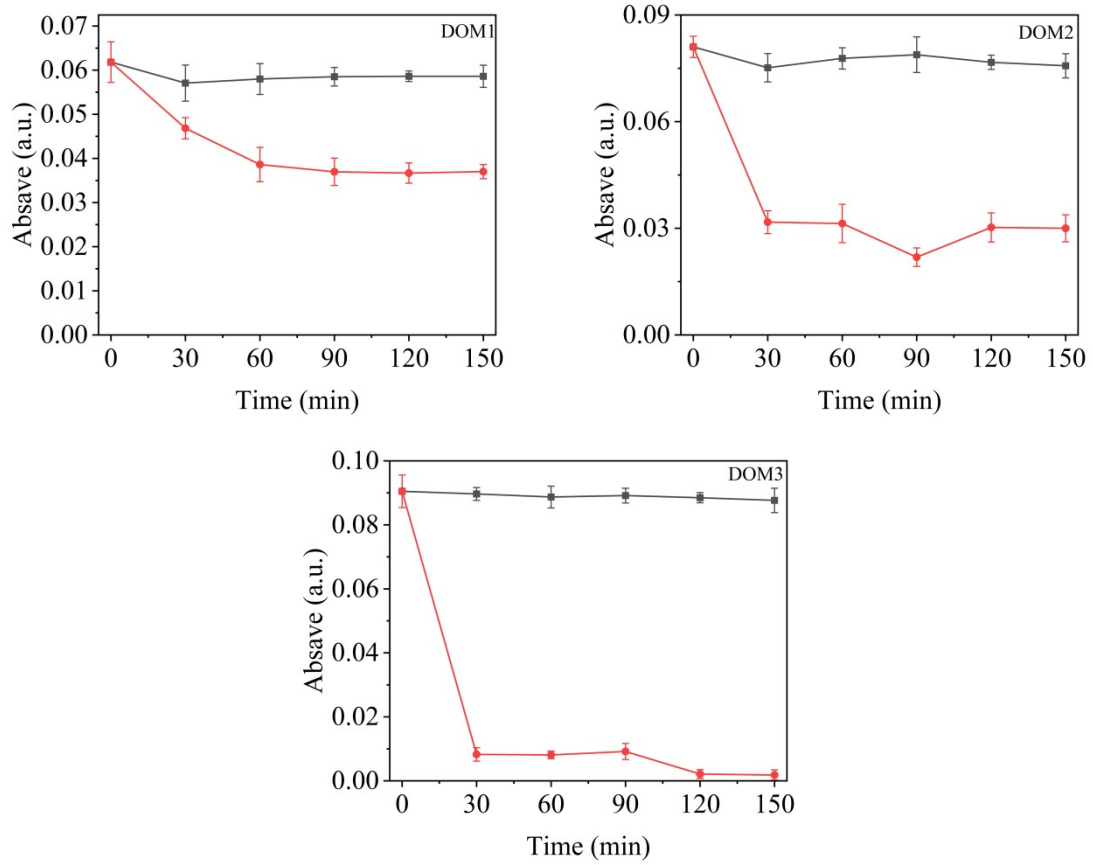


Figure S5 the changes of average absorbance (350-600 nm) of three kinds of DOM in the presence and absence of H<sub>2</sub>O<sub>2</sub>

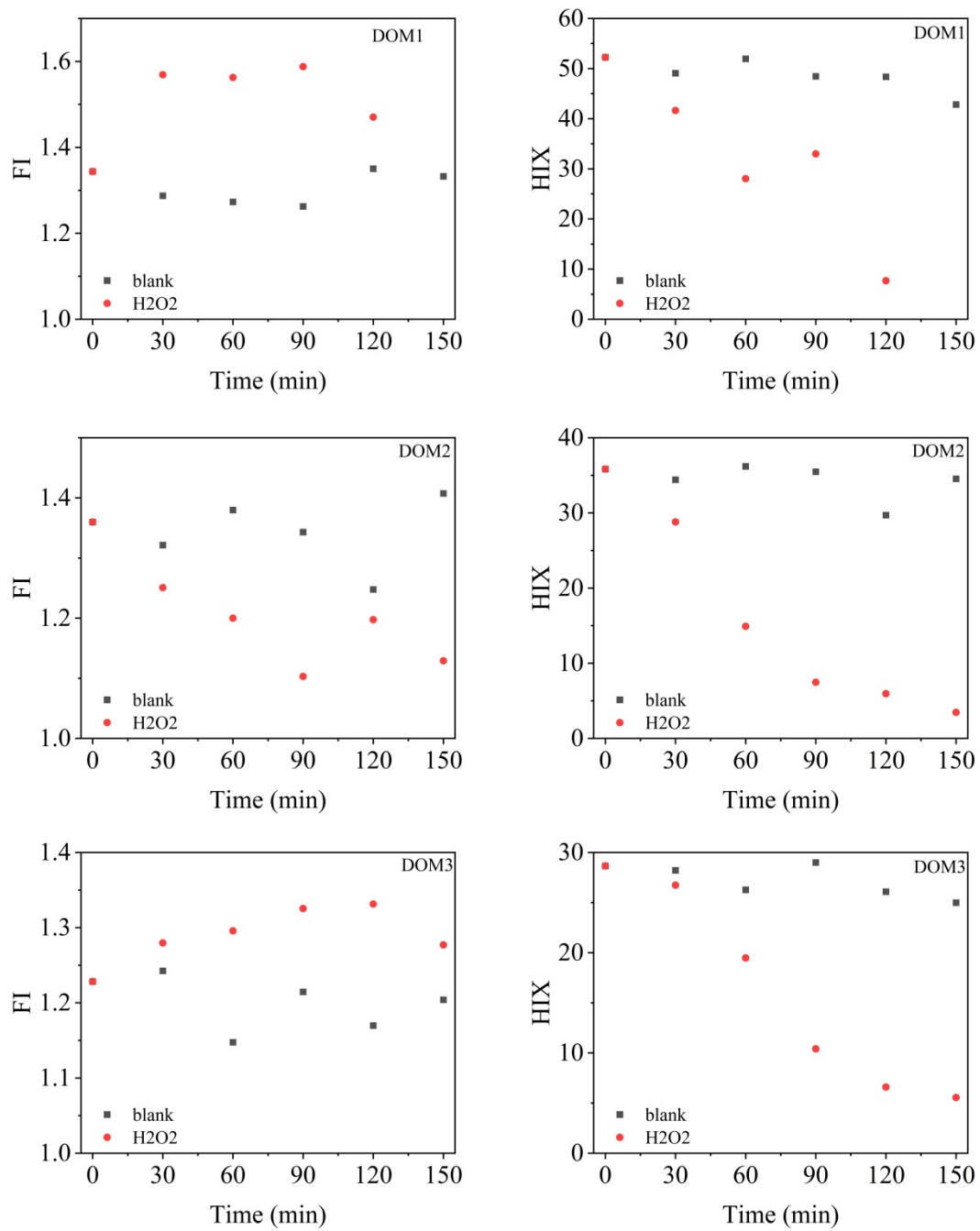


Figure S6 Changes of FI and HIX of three kinds of DOM in the absence and presence of H<sub>2</sub>O<sub>2</sub>

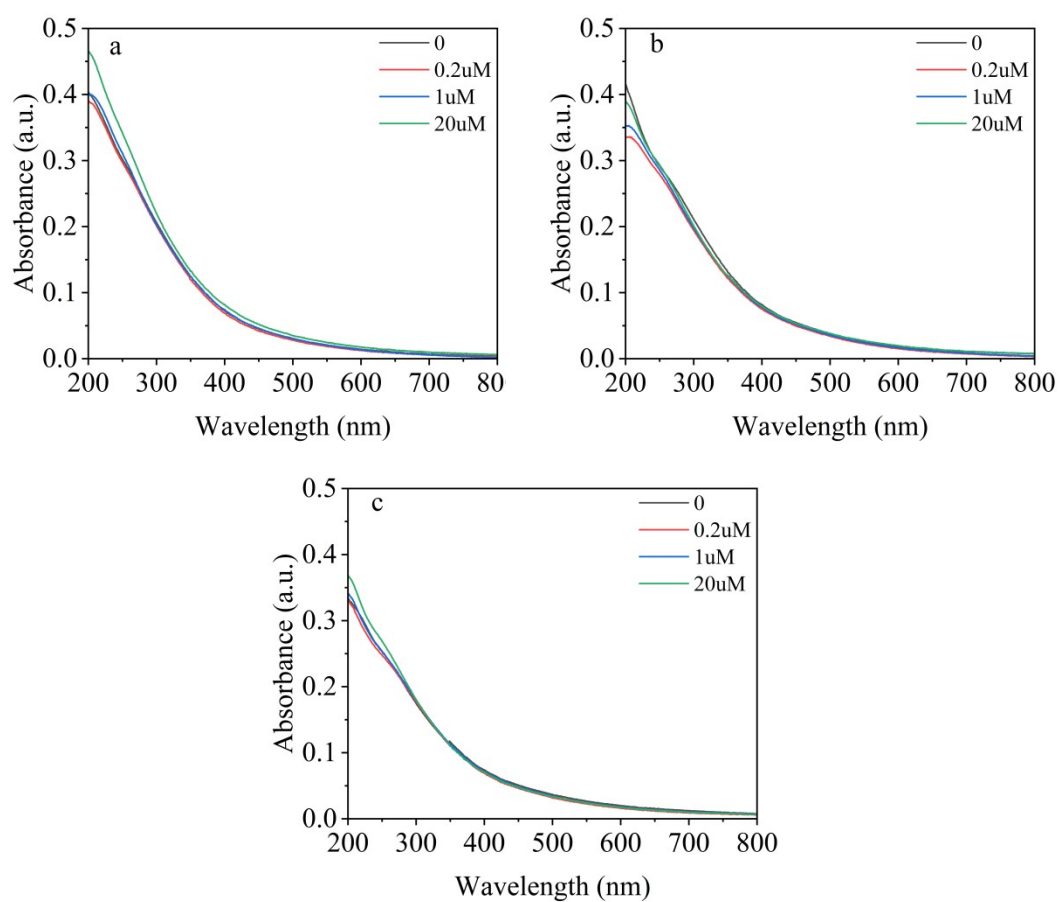


Figure S7 The changes of absorbance spectra of three kinds of DOM in the presence of different concentration of  $\text{Cu}^{2+}$  (a for DOM1, b for DOM2, c for DOM3)

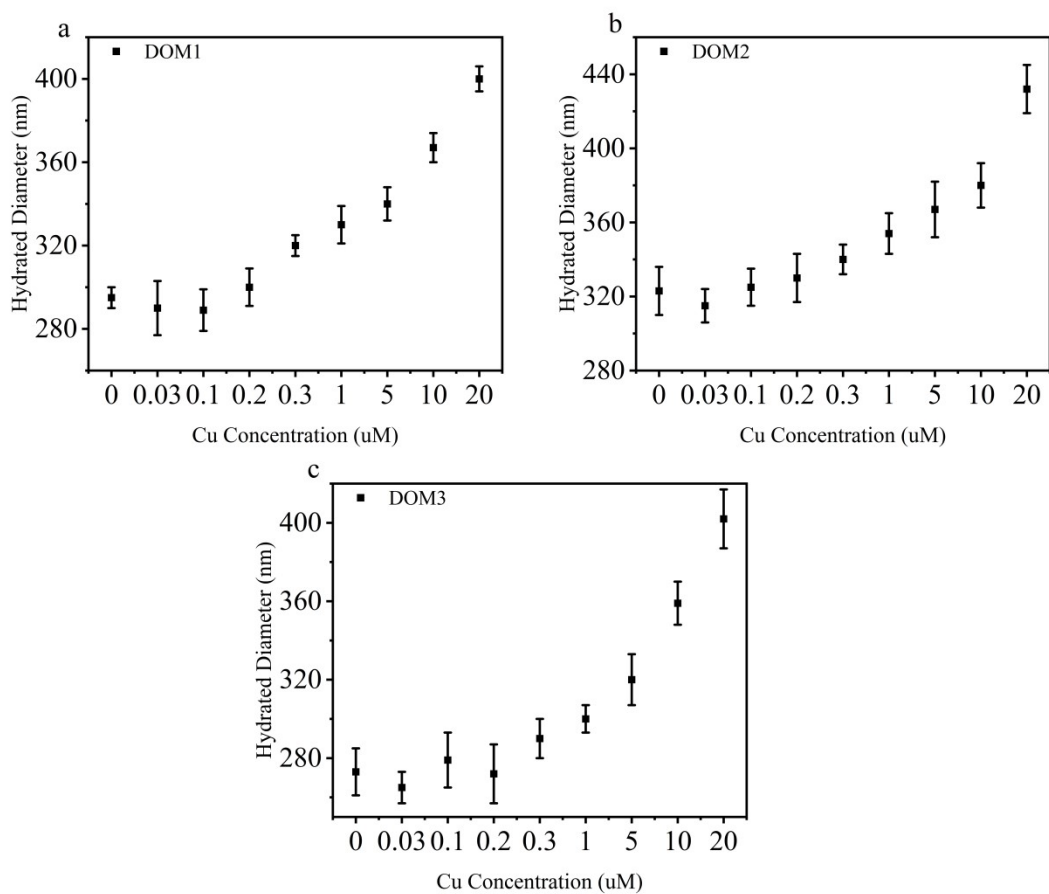


Figure S8 The increase of hydrated diameter of three kinds of DOM with increasing concentrations of  $\text{Cu}^{2+}$

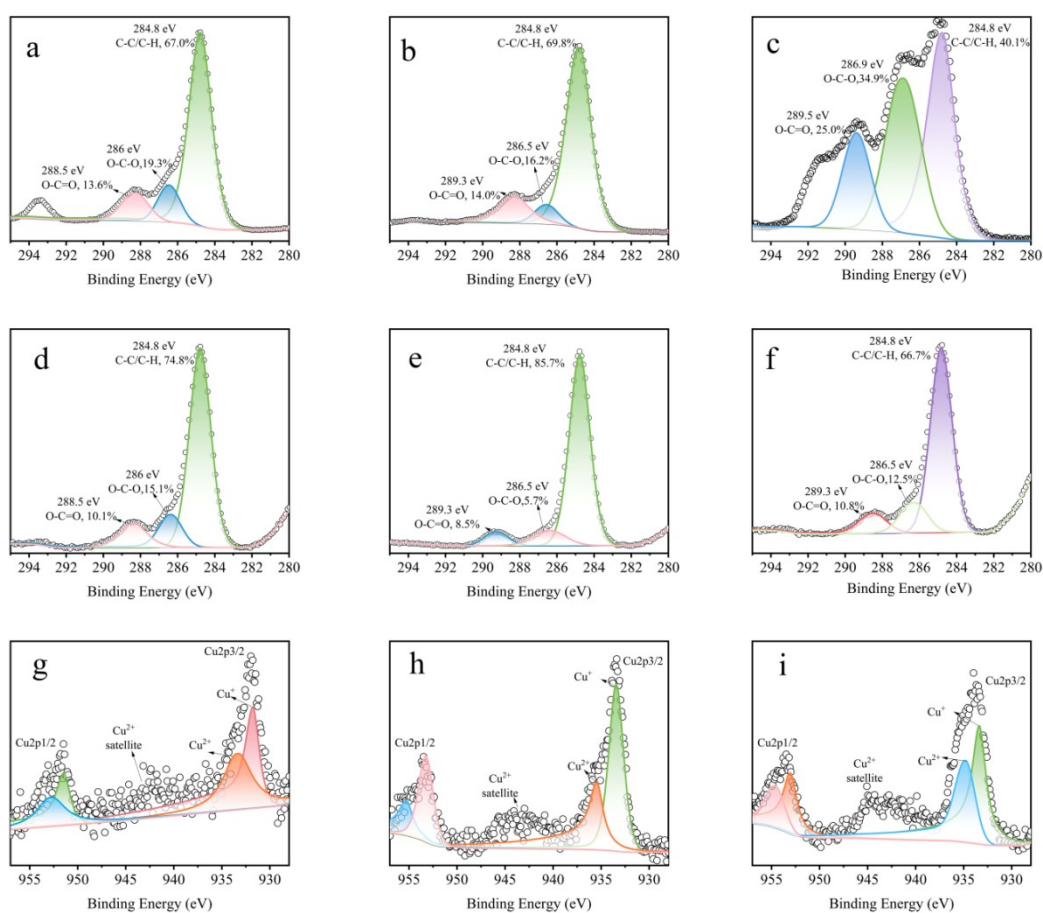


Figure S9 C 1s XPS and Cu 2P spectra before and after addition of Cu for all DOM solutions(a,C1s of DOM1 before Cu addition, d, C1s of DOM1 after Cu addition, and g, Cu 2p of DOM1 after Cu addition; b,C1s of DOM1 before Cu addition, e, C1s after Cu addition, and g, Cu 2p of DOM1 after Cu addition; c,C1s of DOM1 before Cu addition, f, C1s after Cu addition, and i, Cu 2p of DOM1 after Cu addition;)

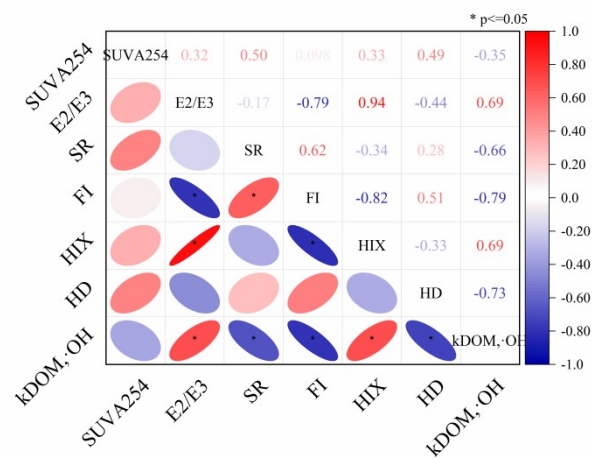


Figure S10 Correlation matrix between optical properties and  $k_{\text{DOM,OH}}$ .  $P < 0.05$ , \*. the size and color of the circles indicate the correlation coefficients; red is positive correlation and blue indicates negative correlation

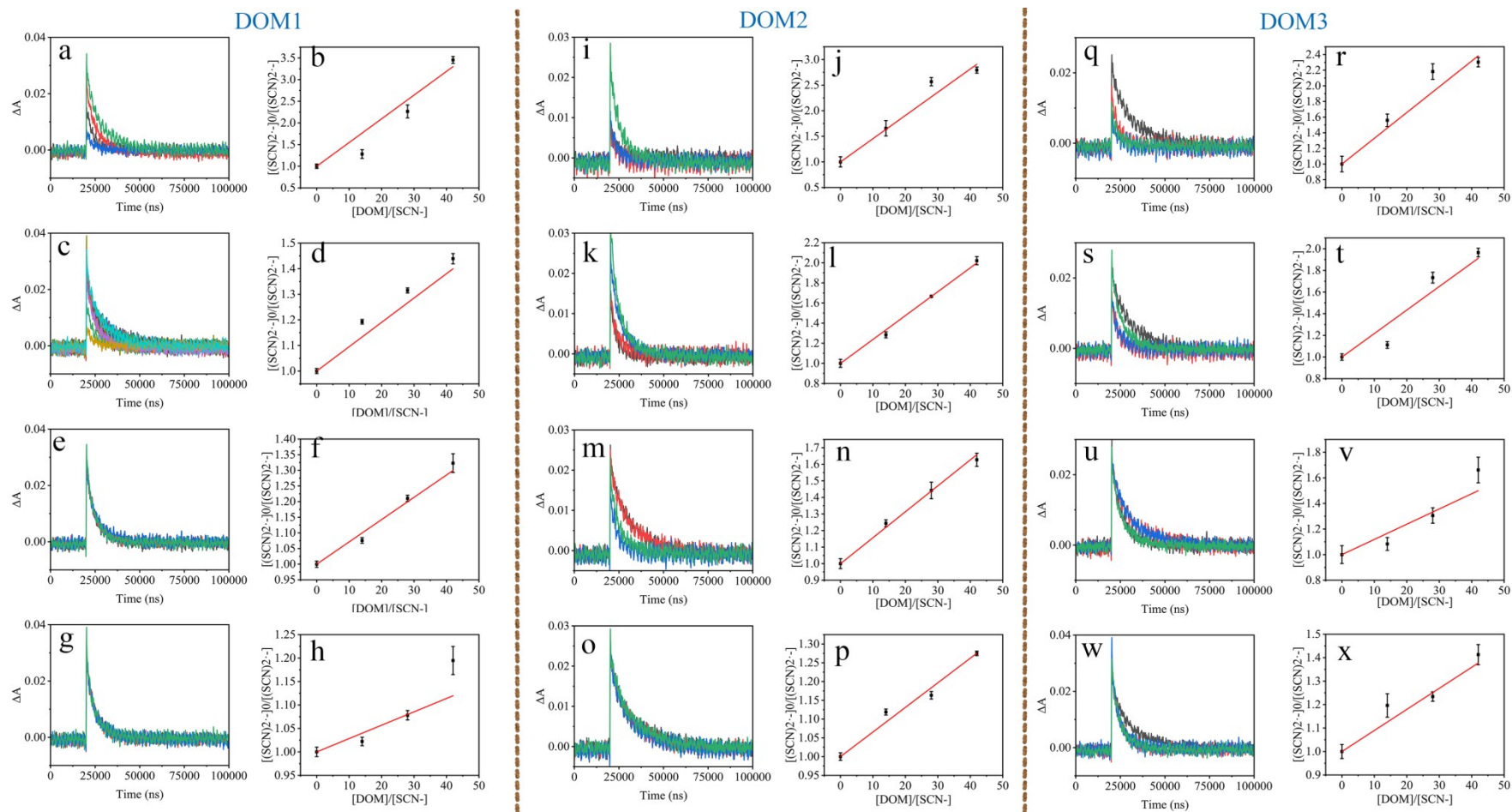


Figure S11 Transient decay kinetics of  $(\text{SCN})_2^{\bullet-}$ . Decay trace of  $(\text{SCN})_2^{\bullet-}$  at 475 nm at various concentration of three kinds of DOM samples.(a,c,

e, g for DOM1 at 0, 0.2, 1 and 20  $\mu\text{M}$   $\text{Cu}^{2+}$  respectively; i, k, m, o for DOM2 at 0, 0.2, 1 and 20  $\mu\text{M}$   $\text{Cu}^{2+}$  respectively; q, s, u, w for DOM3 at 0, 0.2, 1 and 20  $\mu\text{M}$   $\text{Cu}^{2+}$  respectively). Plot of the first-order decay rate constant  $k_{\text{obs}}$  vs [DOM], (a,c, e, g for DOM1 at 0, 0.2, 1 and 20  $\mu\text{M}$   $\text{Cu}^{2+}$  respectively; i, k, m, o for DOM2 at 0, 0.2, 1 and 20  $\mu\text{M}$   $\text{Cu}^{2+}$  respectively; q, s, u, w for DOM3 at 0, 0.2, 1 and 20  $\mu\text{M}$   $\text{Cu}^{2+}$  respectively).

Table S1. DOM Properties and the Second-Order Rate Constants for the Reactions of DOM and  $\cdot\text{OH}$  ( $k_{\text{DOM},\cdot\text{OH}}$ )

Sample	Cu	SUVA <sub>254</sub>	E2/E3	SR	FI	HIX	HD	Slope	$k_{\text{DOM},\cdot\text{OH}}$
DOM1	0	2.95	2.98	0.00853	1.22	0.985	295	0.702	7.38±0.42
	0.2	2.90	2.83	0.00856	1.15	0.984	301	0.172	1.81±0.09
	1	3.02	2.82	0.00915	1.23	0.975	330	0.0932	0.979±0.06
	20	3.32	2.69	0.00961	1.5	0.966	400	0.0682	0.716±0.08
DOM2	0	2.85	2.82	0.00738	1.15	0.977	323	0.453	4.77±0.22
	0.2	2.72	2.78	0.00756	1.14	0.975	326	0.237	2.49±0.10
	1	2.80	2.66	0.00800	1.25	0.973	354	0.156	1.65±0.085
	20	2.87	2.47	0.00843	1.47	0.941	432	0.0656	0.688±0.081
DOM3	0	2.48	2.75	0.00762	1.22	0.972	273	0.330	3.46±0.15
	0.2	2.43	2.65	0.00827	1.24	0.969	274	0.217	2.28±0.11
	1	2.47	2.57	0.00867	1.34	0.962	300	0.119	1.25±0.076
	20	2.62	2.47	0.0087	1.53	0.931	402	0.0900	0.943±0.073

[Cu<sup>2+</sup>], concentration of Cu<sup>2+</sup>; SUVA<sub>254</sub>= specific UV absorbance at 254 nm; E2/E3= absorbance at 254 nm divided by absorbance at 355 nm; SR= the ratio between spectra slope S<sub>275-290</sub> and S<sub>350-280</sub>; HD= hydrated diameter of DOM; Slope= liner fit from the results of Figure S11;

Table S2 Elemental Composition of Three Humic Acid Samples

	C	H	O	N	S	P
DOM1	53.21	3.89	40.15	2.43	0.32	n.d.
DOM2	57.66	3.94	34.68	3.19	0.53	0.34
DOM3	50.35	4.36	42.86	2.03	0.25	0.15