

Insight into the hetero-interactions of 4-nonylphenol with dissolved organic matter: Multi-spectroscopic methods, ^1H NMR study and principal component analysis

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Supplementary Information

S1. Experimental

S2. Supplementary Tables

S3. Supplementary Figures

S1. Experimental

1. 1 Analysis of the pristine and MW-fractionated HAs

The contents of C, H and N in HAs were determined using an elemental analyzer (Elementar Analysensysteme GmbH, Germany). The average molecular weights of the pristine- and MW-fractionated HAs were measured using a high-performance size-exclusion chromatography (HPSEC) unit with a UV detector (Shimadzu, Japan) and a Superdex 75 10/300 GL SEC column (GE, NJ). UV-visible absorption spectra were obtained using a spectrophotometer (Shimadzu, Japan). Specific UV absorbance at 254 nm ($SUVA_{254}$), which represented the aromaticity, was obtained via the division of the absorbance at 254 nm (m^{-1}) with TOC concentration. Fluorescence excitation (Ex)-emission (Em) matrix (EEM) spectra of the pristine- and MW-fractionated HAs were measured using a fluorescence spectrometer (Edinburgh, UK). The humification index (HIX), was determined as the relative ratio of fluorescence intensity areas of two different wavelength ranges (Em: 300-345 nm, 435-480 nm) at the Ex wavelength of 254 nm.

Table S1 Selective physiochemical parameters of 4-NP and used this study.

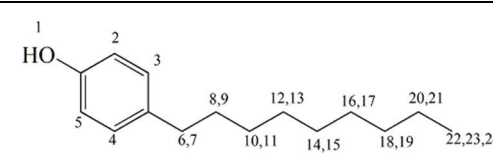
CAS	Formula	Molar mass (g/mol)	Log K _{ow}	Solubility (mg/L)	pKa	Molecular structure
104-40-5	C ₁₅ H ₂₄ O	220.35	5.76	5.4	10.7	

Table S2 Elemental compositions, atomic ratios, and spectroscopic parameters of the pristine- and MW-fractionated HAs.

HAs	Elemental Compositions (%)				Ash content (%)	atomic ratio			Mn (kDa)	Mw (kDa)	ρ	Carboxyl group (mmol/g)	Phenolic group (mmol/g)	Total acidity (mmol/g)	SUVA ₂₅₄	HIX
	C	H	N	O		H/C	O/C	Polarity index (O+N)/C								
pristine HA	53.8	6.61	3.99	34.5	1.11	1.47	0.48	0.55	5.05	15.7	3.10	4.08	2.04	6.12	9.19	16.8
> 100kDa HA	54.2	6.69	4.05	32.5	2.65	1.48	0.45	0.51	7.84	20.9	2.66	2.45	1.63	4.08	9.24	13.3
30-100 kDa HA	52.8	6.42	3.77	35.9	1.09	1.46	0.51	0.57	4.83	7.60	1.57	2.72	1.55	4.27	9.30	27.1
10-30 kDa HA	51.7	6.03	3.53	37.8	0.98	1.40	0.55	0.61	3.56	4.19	1.17	4.40	3.17	7.57	8.98	13.9
3-10 kDa HA	51.1	5.73	3.35	38.7	1.06	1.34	0.57	0.62	2.73	3.14	1.15	6.12	3.72	9.84	8.00	11.1
<3kDa HA	50.4	5.31	3.09	40.5	0.70	1.26	0.60	0.65	2.08	2.30	1.10	7.38	3.83	11.2	6.99	7.85

H/C: atomic ratio of hydrogen to carbon. O/C: atomic ratio of oxygen to carbon. (N+O)/C: atomic ratio of sum of oxygen and nitrogen to carbon. Weight-average molecular weight (Mw) and number-average molecular weight (Mn) measured using HPSEC. Polydispersity (ρ) calculated as Mw/Mn. Carboxyl and phenolic group contents and total acidity were measured using the method of potentiometric titration. SUVA₂₅₄ was calculated by dividing the absorption coefficient at 254 nm (a_{254}) with DOC concentration ($L \cdot (mg\ C \cdot m)^{-1}$). Humification index (HIX) was calculated as the ratio of the peak area under Em spectra 435-480 nm relative to that 300-345 nm at the Ex wavelength of 254 nm.

Table S3. Binding parameters of 4-NP-HAs induced by different pH values and ionic strengths based on the fluorescence titration experiments; T=298K.

pH	IS (mmol·L ⁻¹)	HAs	Stern-Volmer equation		Site-binding equation		
			K _{HA} (L·(mg·C) ⁻¹)	R ²	K (L·(mg·C) ⁻¹)	n	R ²
3		pristine HA	0.145	0.999	0.133	1.05	0.999
		> 100 kDa HA	0.151	0.999	0.144	1.03	0.998
		30-100 kDa HA	0.142	0.999	0.132	1.03	0.999
		10-30 kDa HA	0.131	0.999	0.121	1.05	0.998
		3-10 kDa HA	0.097	0.999	0.100	0.985	0.999
		< 3k Da HA	0.077	0.999	0.079	0.985	0.999
6	1	pristine HA	0.139	0.999	0.132	1.02	0.995
		> 100 kDa HA	0.145	0.999	0.142	1.00	0.993
		30-100 kDa HA	0.134	0.999	0.128	1.01	0.994
		10-30 kDa HA	0.124	0.998	0.119	1.01	0.983
		3-10 kDa HA	0.091	0.999	0.097	0.955	0.994
		< 3k Da HA	0.065	0.999	0.072	0.957	0.999
11		pristine HA	0.083	0.999	0.088	0.960	0.985
		> 100 kDa HA	0.088	0.999	0.090	0.984	0.996
		30-100 kDa HA	0.081	0.999	0.083	0.985	0.992
		10-30 kDa HA	0.076	0.999	0.073	1.02	0.990
		3-10 kDa HA	0.049	0.999	0.061	0.884	0.986
		< 3k Da HA	0.037	0.995	0.046	0.923	0.966
6	10	pristine HA	0.126	0.999	0.121	1.01	0.992
		> 100 kDa HA	0.134	0.999	0.134	0.998	0.992
		30-100 kDa HA	0.119	0.999	0.127	0.954	0.981
		10-30 kDa HA	0.105	0.999	0.099	1.00	0.972
		3-10 kDa HA	0.070	0.999	0.068	1.00	0.994
		< 3k Da HA	0.047	0.999	0.048	0.981	0.996
6	100	pristine HA	0.116	0.999	0.101	1.06	0.997
		> 100 kDa HA	0.126	0.999	0.129	0.987	0.998
		30-100 kDa HA	0.111	0.999	0.115	0.973	0.993
		10-30 kDa HA	0.090	0.998	0.09	0.981	0.982
		3-10 kDa HA	0.062	0.999	0.064	0.954	0.959
		< 3k Da HA	0.042	0.999	0.043	0.972	0.957

S3. Supplementary Figures

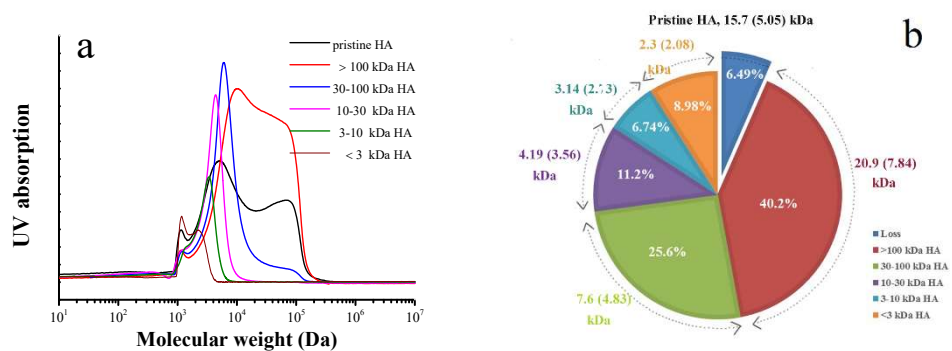


Fig. S1 HPSEC graphs (a) and weight/number-averaged molecular weight and mass composition (b) of the pristine and MW-fractionated HAs.

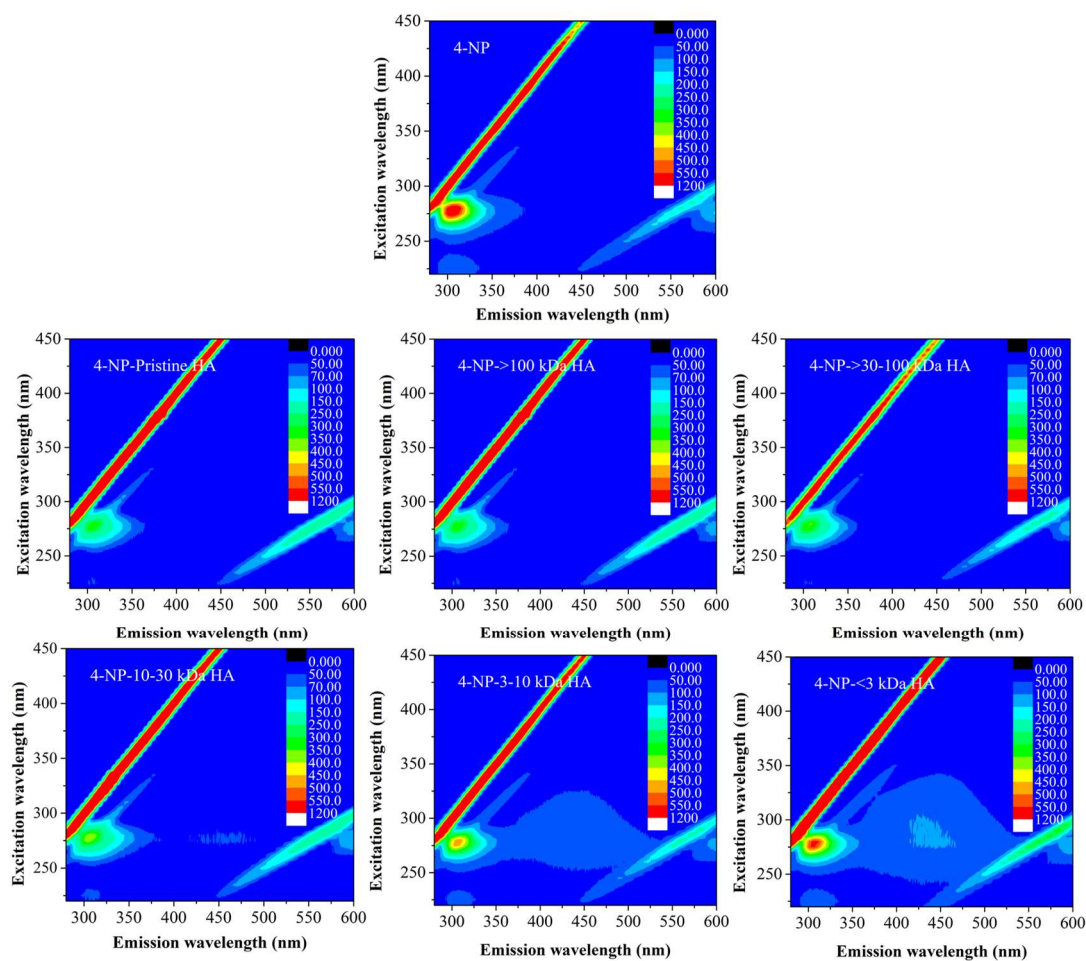


Fig S2. The fluorescence EEM spectra of 4-NP without and with 1 mg C/L pristine- and MW-fractionated HAs; T = 298 K; pH =6.0, 1mol/L NaNO₃.

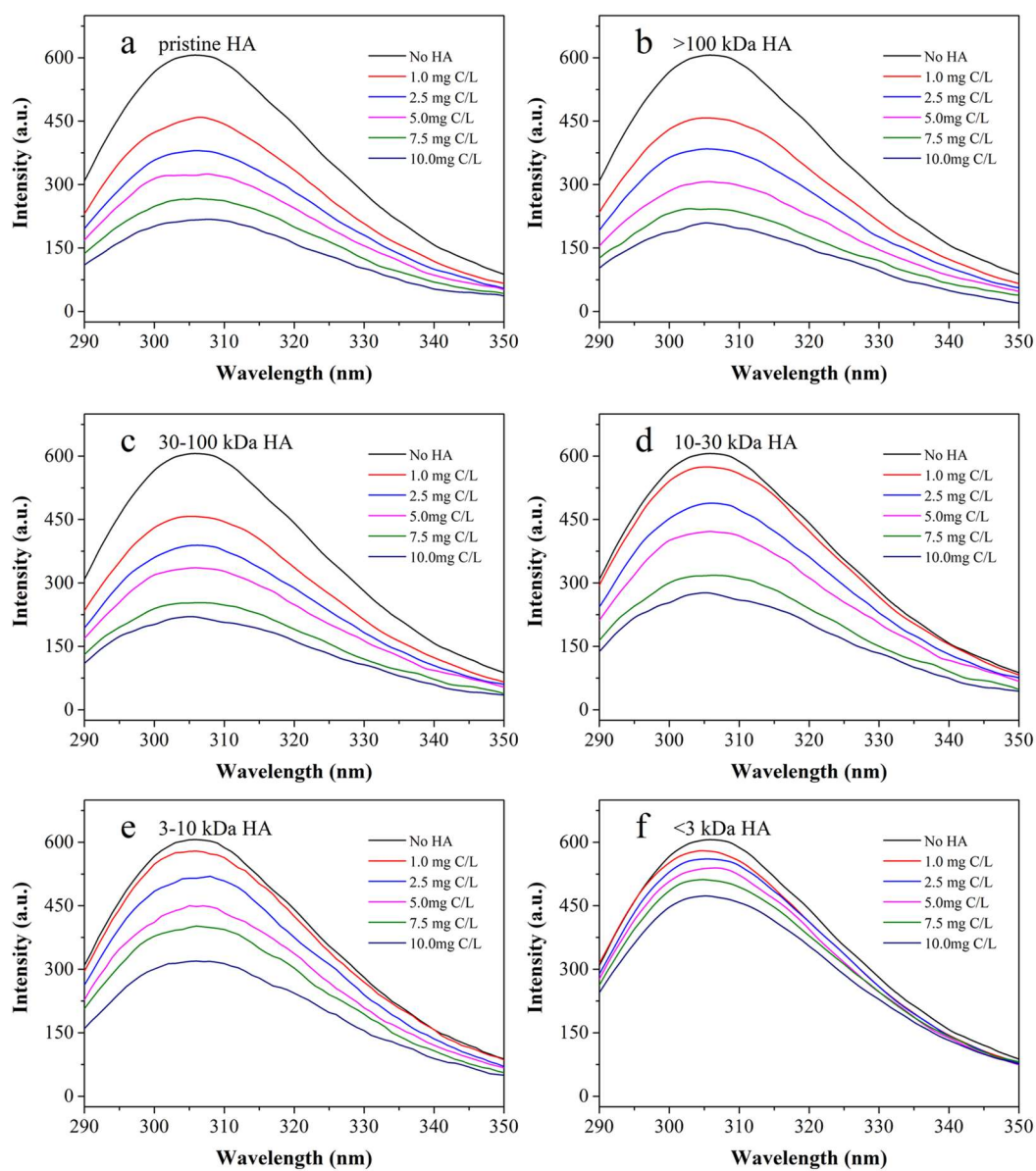


Fig. S3. Corrected fluorescence emission spectra of the 4-NP-HAs systems. The concentration of 4-NP was 1 mg/L; Ex = 280 nm; T = 298 K; pH = 6.0; 1mol/L NaNO₃.

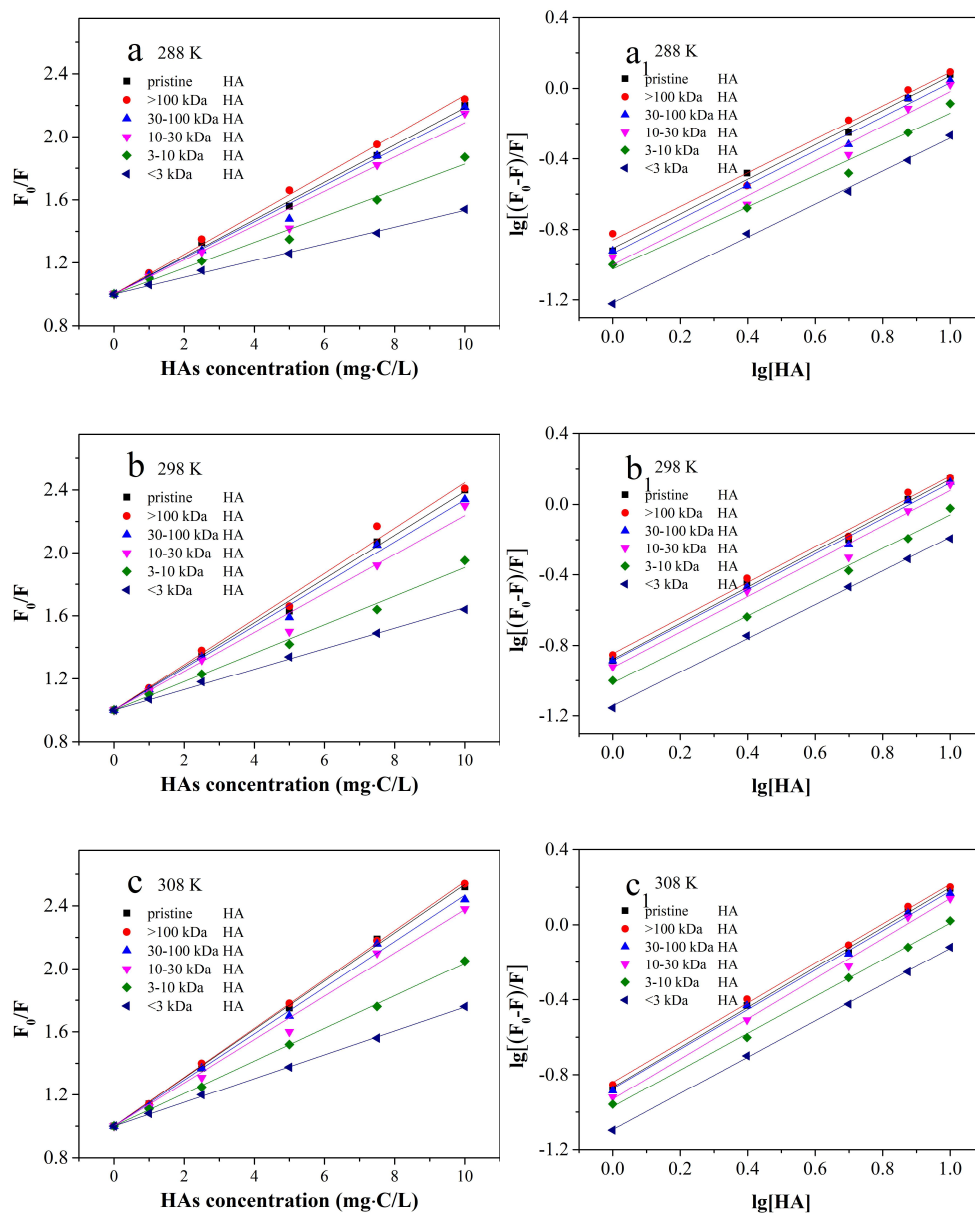


Fig. S4 Stern–Volmer (a-c) and Site-binding (a_1 - c_1) equation plots of 4-NP for HAs at 288K, 298K and 308 K; pH =6.0; 1mol/L NaNO₃.

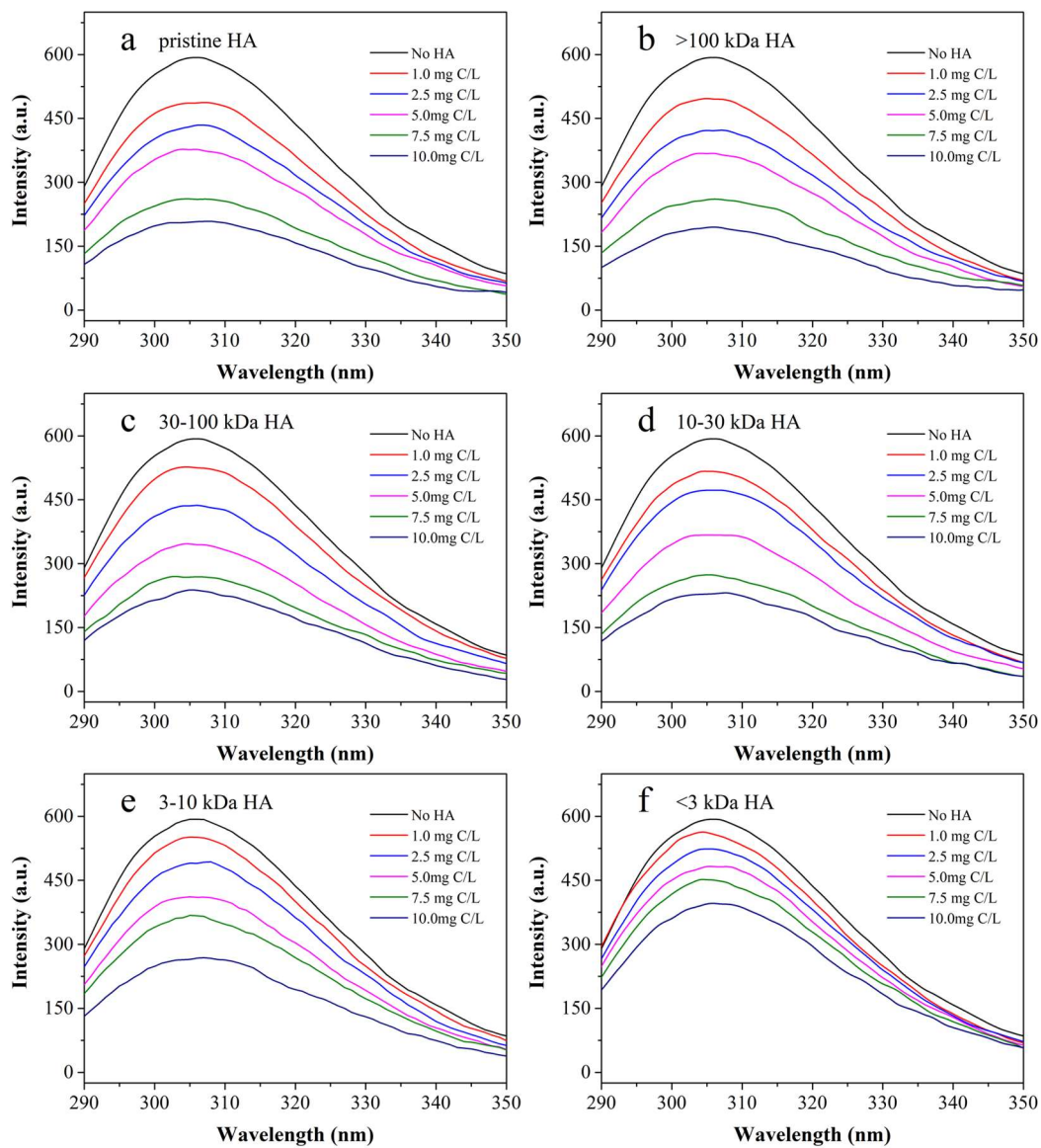


Fig. S5. Corrected fluorescence emission spectra of the 4-NP-HAs systems. The concentration of 4-NP was 1 mg/L; Ex = 280 nm; T = 298 K; pH = 3.0; 1 mol/L NaNO₃.

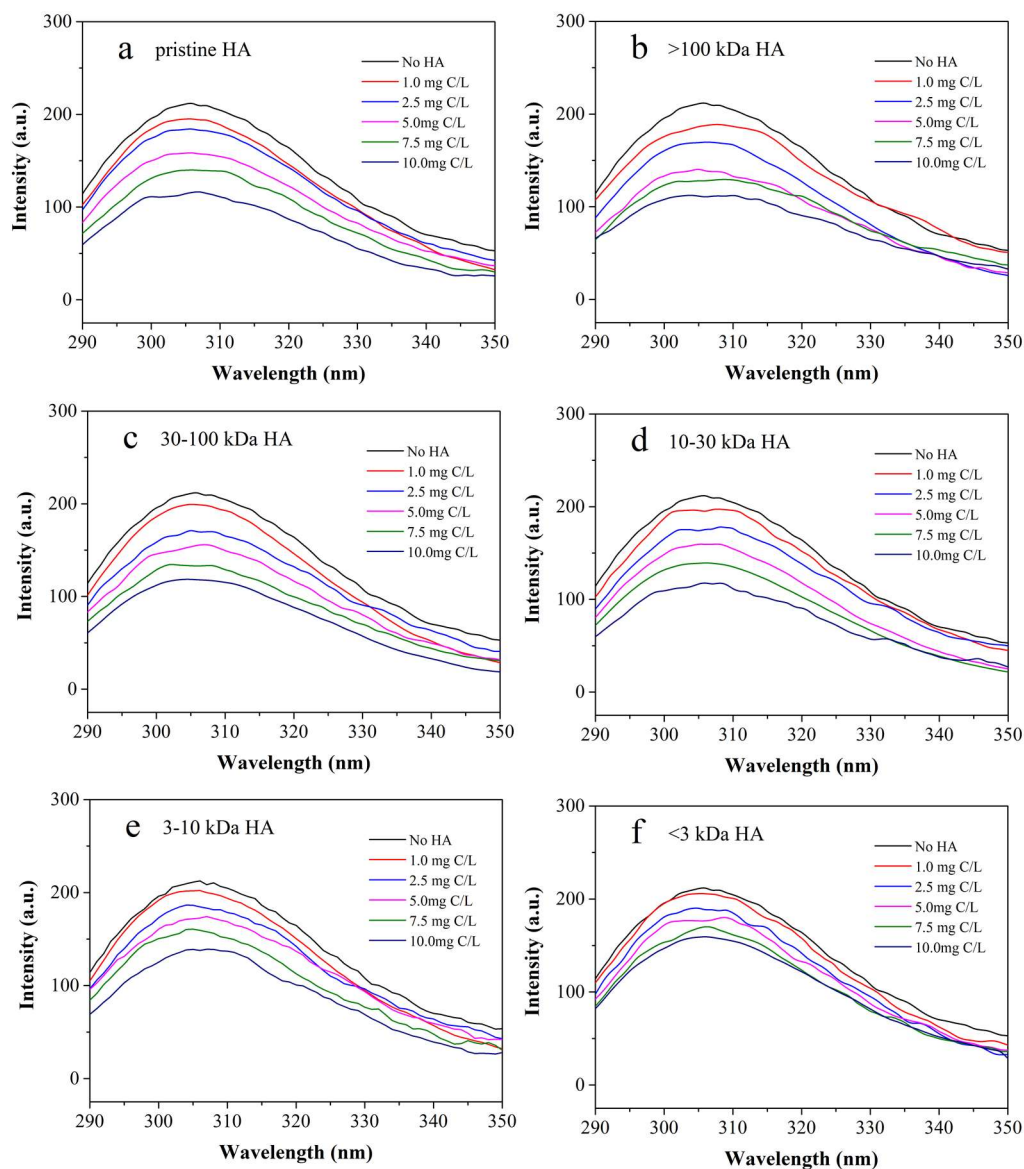


Fig. S6. Corrected fluorescence emission spectra of the 4-NP-HAs systems. The concentration of 4-NP was 1 mg/L; $E_x = 280 \text{ nm}$; $T = 298 \text{ K}$; $\text{pH} = 11.0$; 1 mol/L NaNO_3 .

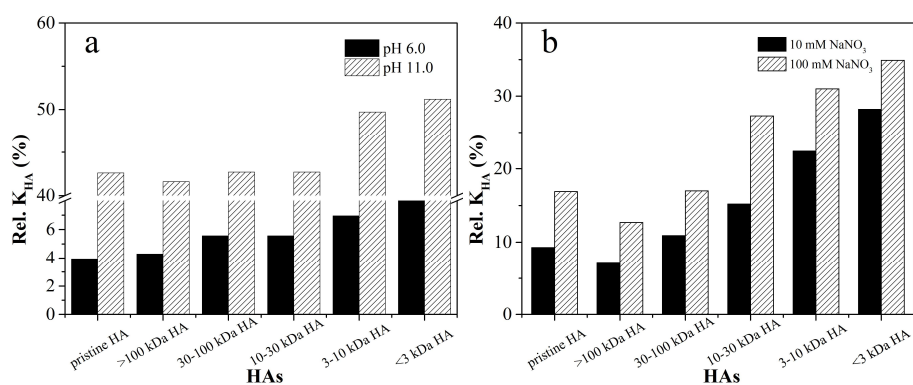


Fig. S7 The relative reduction of K_{HA} for MW-fractionated HAs with increasing pH ($\text{Rel.}K_{HA} = (K_{HA, \text{pH}3} - K_{HA}) / K_{HA, \text{pH}3} \times 100\%$) and NaNO_3 concentration ($\text{Rel.}K_{HA} = (K_{HA, 1 \text{ mM}} - K_{HA}) / K_{HA, 1 \text{ mM}} \times 100\%$); $T = 298 \text{ K}$.

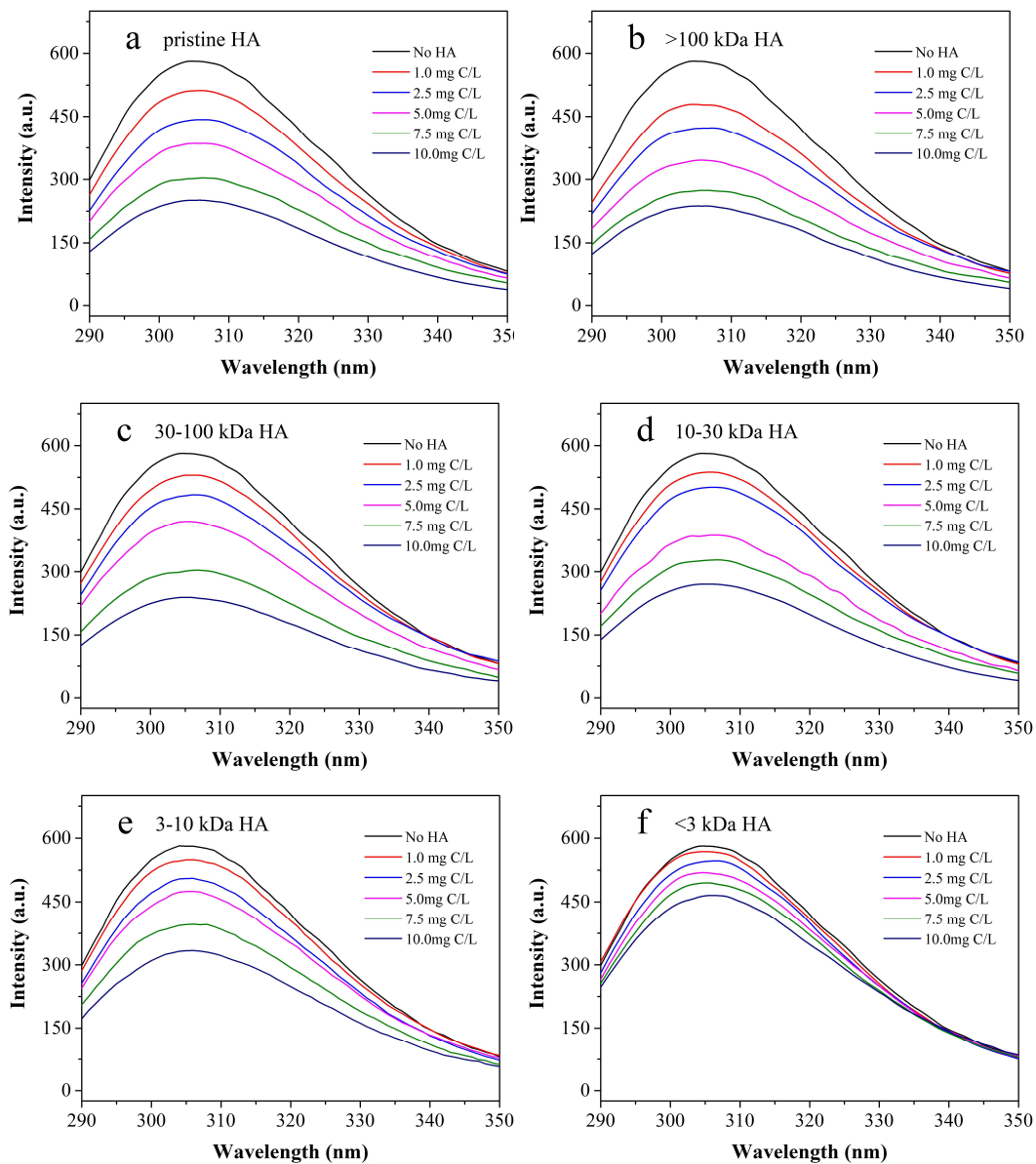


Fig.

Fig. S8. Corrected fluorescence emission spectra of the 4-NP-HAs systems. The concentration of 4-NP was 1 mg/L; Ex = 280 nm; T = 298 K; pH = 6.0; 10 mol/L NaNO₃.

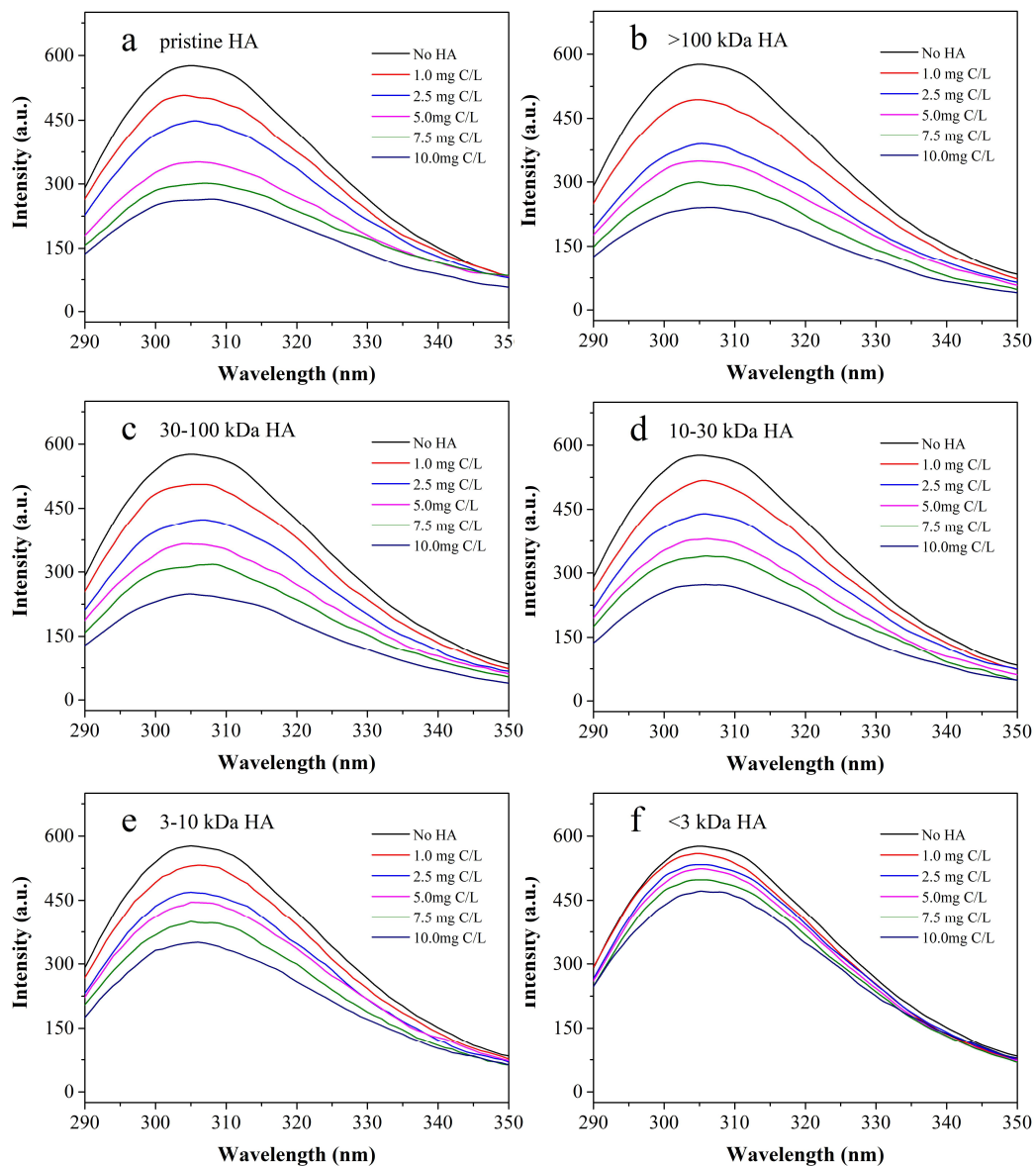


Fig. S9. Corrected fluorescence emission spectra of the 4-NP-HAs systems. The concentration of 4-NP was 1 mg/L; Ex = 280 nm; T = 298 K; pH = 6.0; 100mol/L NaNO₃.

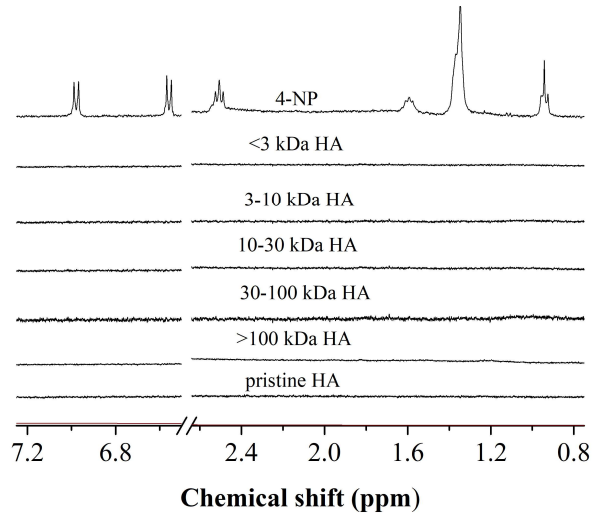


Fig. S10 ^1H NMR spectra of 4-NP and 60 μg C/L pristine- and MW-fractionated HAs.

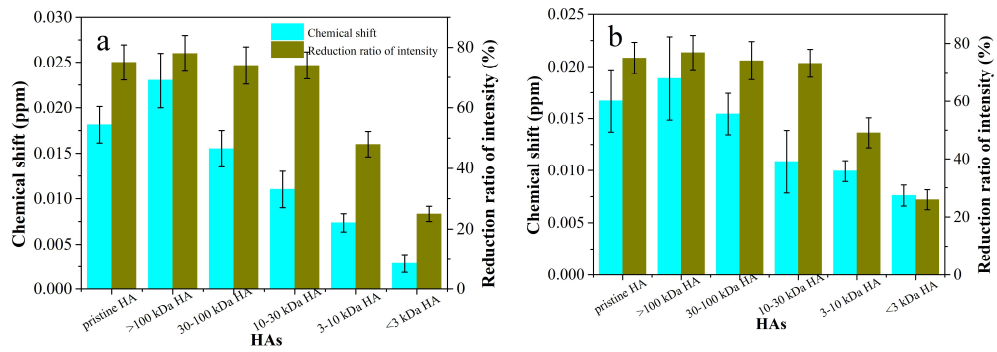


Fig. S11 Changes of H3, H4 (a) and H2, H5 (b) in chemical shift ($\Delta\delta$) and reduction ratio of intensity (%) in different 4-NP-HAs systems. The error bars are representative of the standard deviation of the triplicates.