

Electronic supplementary information (ESI)

## Nanoclay-based sensor composite for facile detection of molecular antioxidants

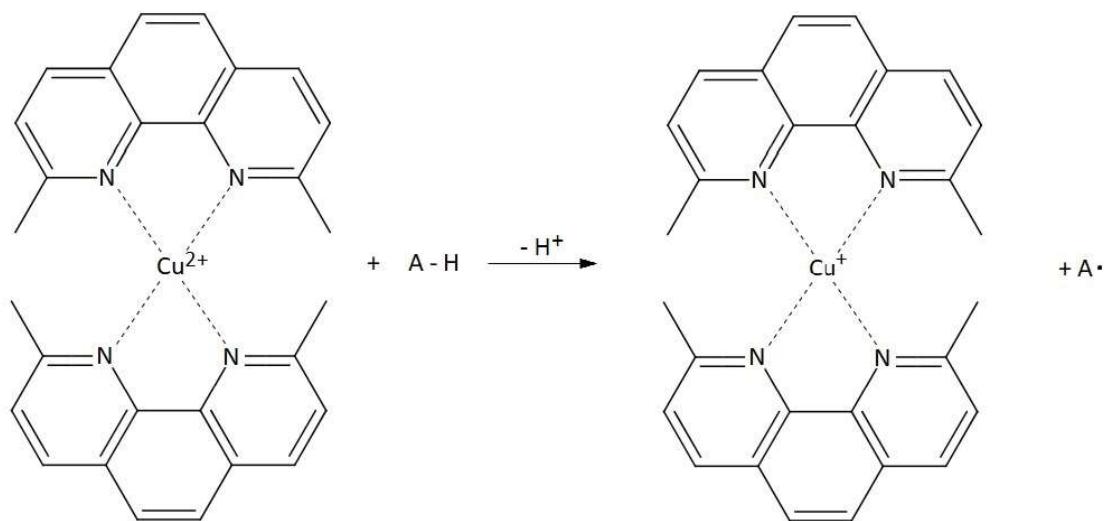
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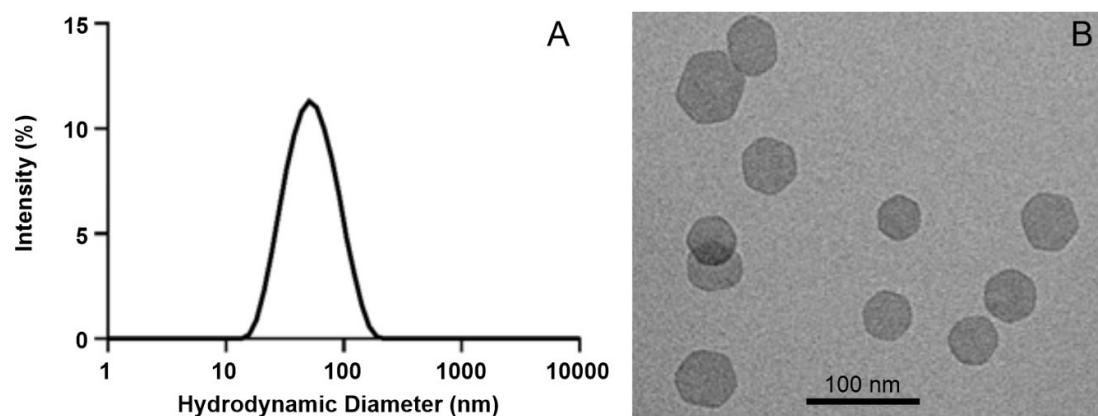
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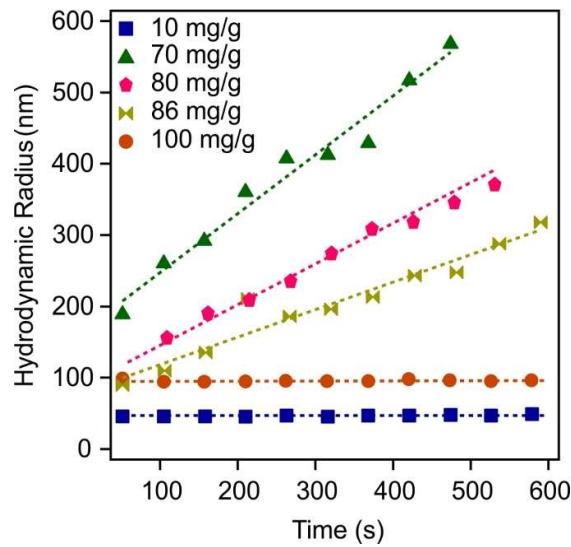
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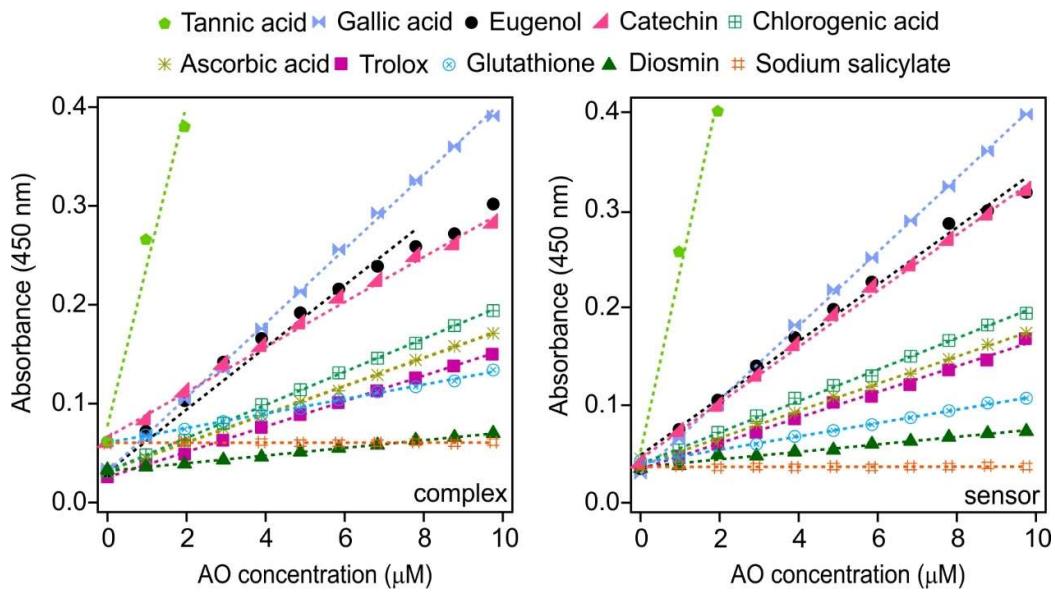
**Scheme S1.** Generic reaction scheme between Cu(Nc)<sub>2</sub> and antioxidants.



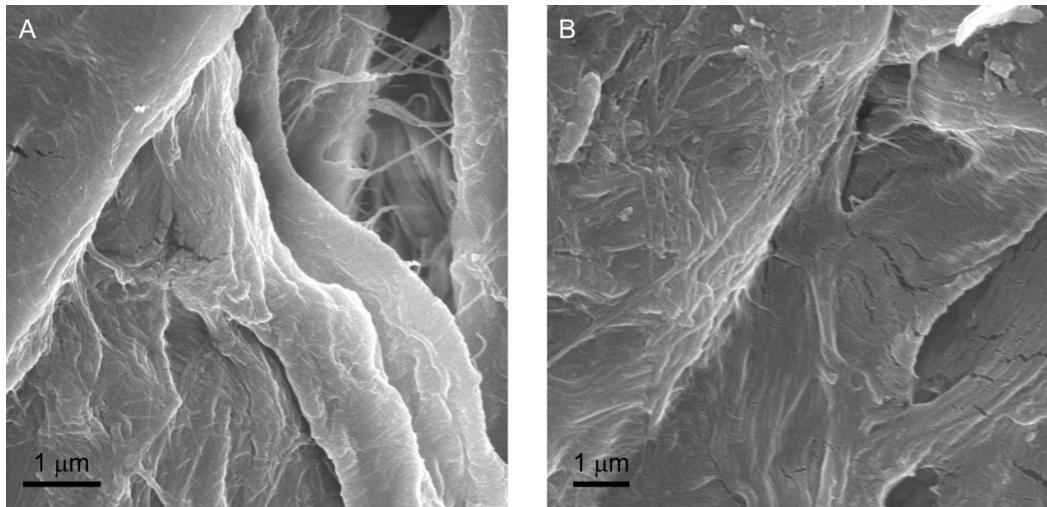
**Fig. S1** The size and morphology of dLDH nanosheets: the particle size distribution (A) and the TEM image (B).



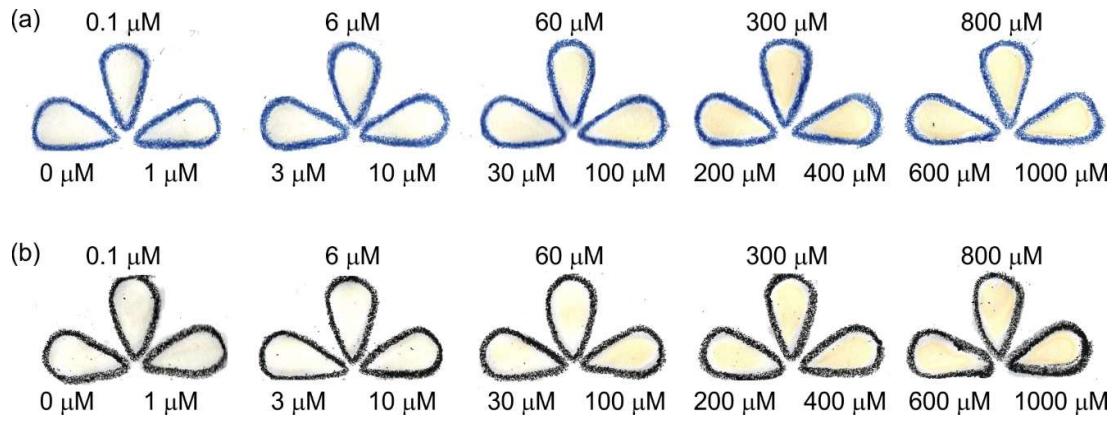
**Fig. S2** Hydrodynamic radius versus time at different NaAlg doses and constant dLDH concentrations at 1 mM ionic strength and pH 9.



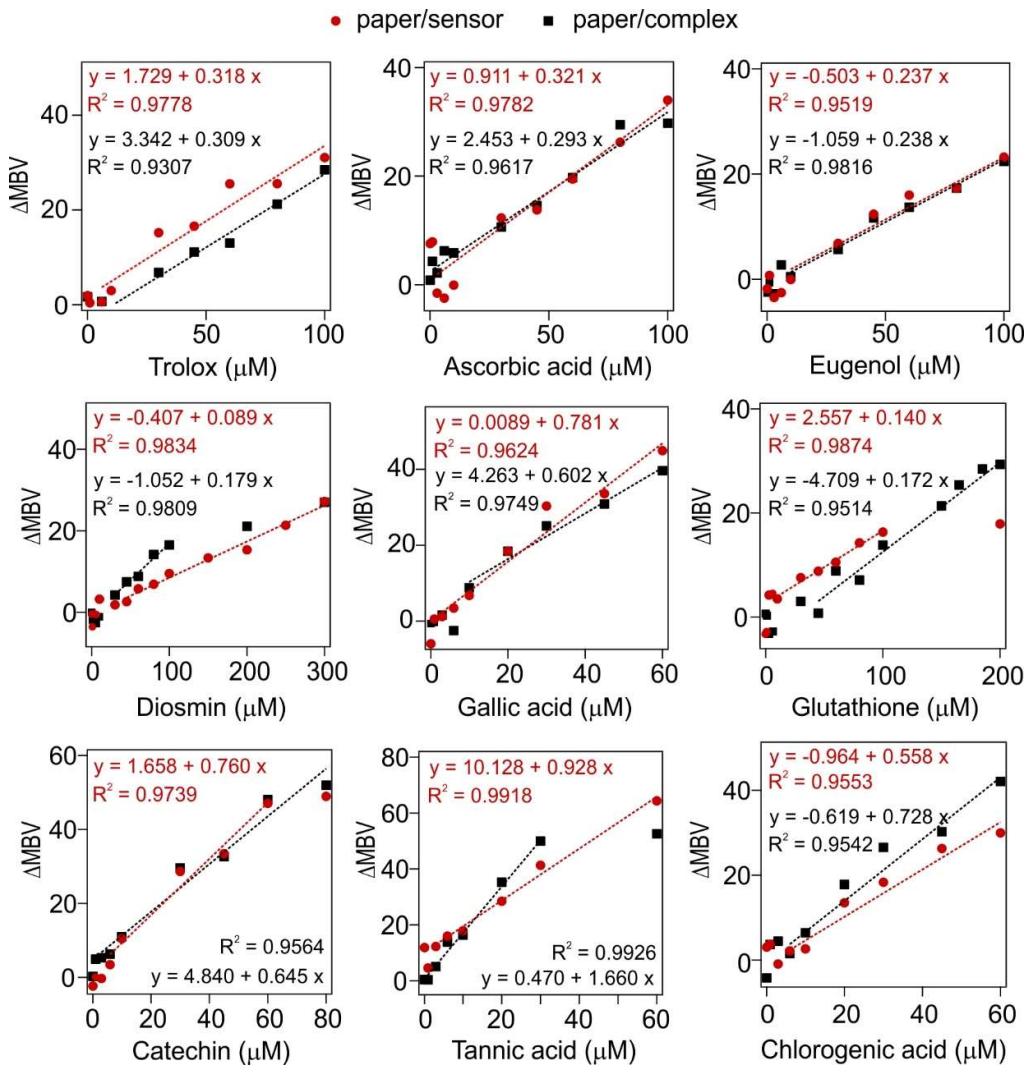
**Fig. S3** Concentration dependent absorbance values measured with different antioxidants.



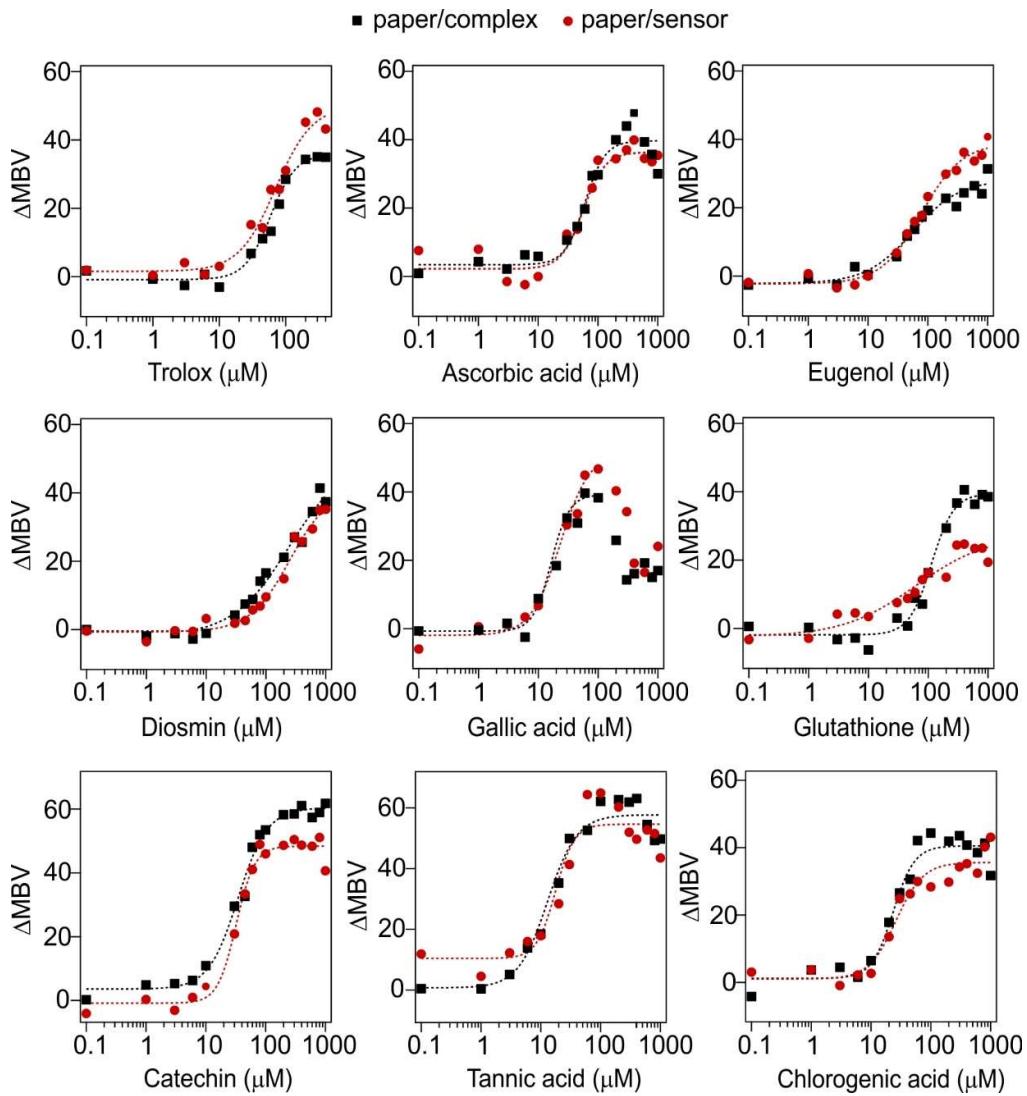
**Fig. S4** SEM image of the paper (A) and P-Cu(Nc)<sub>2</sub> (B).



**Fig. S5** Photos of paper-based sensors after the measurements of the ascorbic acid contents with P-Cu(Nc)<sub>2</sub> (a) and P-dLDH-Alg-Cu(Nc)<sub>2</sub> (b).



**Fig. S6** Calibration curves for different antioxidants. The equations of the fitted lines and the confidence intervals are shown on the graphs. P-Cu(Nc)<sub>2</sub>:paper/complex and P-dLDH-Alg-Cu(Nc)<sub>2</sub>: paper/sensor.



**Fig. S7** Experimental  $\Delta\text{MBV}$  data fitted with Hill equations (dotted lines) for the different antioxidants. P-Cu(Nc)<sub>2</sub>:paper/complex and P-dLDH-Alg-Cu(Nc)<sub>2</sub>: paper/sensor.

**Table S1** Identified Raman bands and their assignments. ( $\nu$ : stretching vibration,  $\delta$ : bending vibration and  $\beta$ : (special) bending mode vibration of water).

Raman shift (cm <sup>-1</sup> )	Assignment	Sample
1095	$\nu$ (COC), $\nu$ (CH)	paper, P-dLDH
1309	$\delta$ (HCO), $\delta$ (HCC)	paper, P-dLDH, P-Cu(Nc) <sub>2</sub> , P-dLDH-Alg-Cu(Nc) <sub>2</sub>
1404 and ~ 1580	$\nu$ (C=C) [aromatic ring]	Cu(Nc) <sub>2</sub> , P-Cu(Nc) <sub>2</sub> , P- dLDH-Alg-Cu(Nc) <sub>2</sub>
1609	$\beta$ (OH)	P-dLDH
~ 2900	$\nu$ (CH), $\nu$ (CH <sub>2</sub> )	paper, P-dLDH, P-Cu(Nc) <sub>2</sub> , P-dLDH-Alg-Cu(Nc) <sub>2</sub>

**Table S2** The structure, TEAC, LOD and linear range of investigated antioxidants.

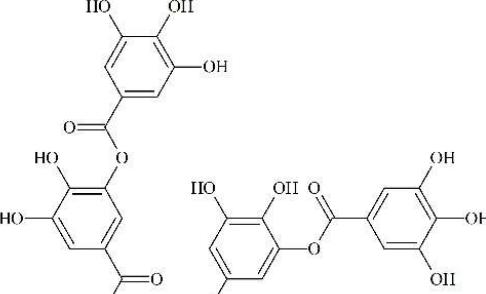
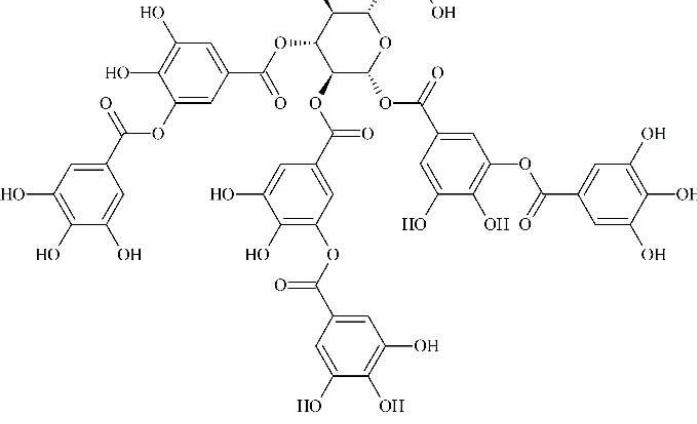
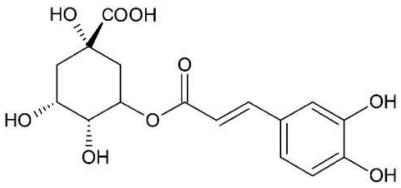
Antioxidant	Structure	TEAC P-Cu(Nc) <sub>2</sub>	LOD P-Cu(Nc) <sub>2</sub>	Linear range P-dLDH-Alg-Cu(Nc) [μM]
Trolox		1	1	42 39 45-100 40-100
Ascorbic acid		0.97	1.25	72 48 80-100 60-100
Eugenol		1.04	0.90	65 59 80-100 65-100

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Diosmin		0.24	0.28	65	124	65-100	150-300
Gallic acid		3.59	3.04	29	18	30-60	20-60
Glutathione		0.52	1.14	146	79	150-200	80-100
Catechin		1.70	2.20	16	10	20-60	10-60

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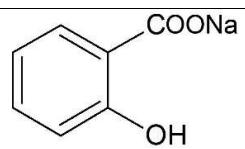
						
Tannic acid		4.52	4.01	15	1	30-60    3-60
Chlorogenic acid		2.51	2.70	31	16	35-60    20-60

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Sodium  
salicylate

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**Table S3** Comparison of antioxidant detection methods

Method	Antioxidants	Properties	Reference
Colorimetric assay based on etching of gold nanorods	Ascorbic acid, tannic acid, ferulic acid	Linear range: 0.4-116.7 $\mu$ M LOD: 0.3-2.3 $\mu$ M	1
Nafion membrane modified by ferric- <i>o</i> -phenanthroline	Caffeic acid, ferulic acid, catechin, gallic acid, quercetin, rutin, rosmarinic acid, ascorbic acid, uric acid, $\alpha$ -tocopherol, bilirubin, glutathione, cysteine, homocysteine	Linear range: 0.46-104.8 $\mu$ M LOD (for trolox): 0.26 $\mu$ M	2
Paper based CuPRAC assay	Gallic acid, vanillic acid, ascorbic acid, caffeic acid	Linear range: 0.5-70 mM LOD: 0.5-1.2 mM	3
CuPRAC based electrochemical sensor	Trolox, ascorbic acid, gallic acid	Linear range: 62-770 $\mu$ M LOD (for trolox): 62.9 $\mu$ M	4
Paper and 3D printed antioxidant sensor based on CeO <sub>2</sub> nanoparticles	Vanillic acid, ascorbic acid, trolox, quercetin, ellagic acid, ferulic acid	Linear range: 2-500 $\mu$ M LOD: 9-32 $\mu$ M	5

Functionalized paper by dLDH particles	Trolox, ascorbic acid, eugenol, diosmin, gallic acid, glutathione, catechin, tannic acid, chlorogenic acid, sodium salycilate	Linear range: 3-300 $\mu\text{M}$	This work
		LOD: 1-146 $\mu\text{M}$	

## References

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- 5 A. Othman, L. Norton, A. S. Finny and S. Andreeescu, *Talanta*, 2020, **208**, 120473.