Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Electronic supplementary information

Nano-goethite-mediated transformation of anthracene derivatives under low moisture conditions

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Contents:

18 pages, 9 figures, 5 tables

S1. Supplemental methods

Nao-goethite synthesis

The Goe-03 nano-goethite sample was synthesized as follows. Five mL of 5 M KOH was mixed with 250 mL of 0.1 M $Fe(NO_3)_3 \cdot 9H_2O$ in a beaker under magnetic stirring. The mixture was aged at 60 °C for 70 h. Next, the cooled mixture was transferred into a dialysis tube (MD34 (7000)), which was then placed into a 2-L beaker filled with ultrapure water. The ultrapure water was replaced 10 times each day until the conductivity was less than 1.0 $\mu S \cdot cm^{-1}$. The product was dried at 80 °C for 4 h, and then at 50 °C for 2 h.

The Goe-02 nano-goethite sample was synthesized by reacting 30 mL of 0.5 M $Fe(NO_3)_3 \cdot 9H_2O$ with 125 mL of 2.5 M KOH, followed by aging at 60 °C for 100 h. The aged suspension was washed as abovementioned and then dried at 40 °C overnight to obtain the final product.

The Goe-01 nano-goethite sample was synthesized by adding rapidly 180 mL of 5 M KOH to 100 mL of 1 M $Fe(NO_3)_3 \cdot 9H_2O$ under magnetic stirring, followed by immediate dilution of to 2 L with ultrapure water and subsequent aging at 70 ℃ for 60 h. The aged suspension was washed and dried as abovementioned.

Nao-goethite characterization

Specific surface areas of the nano-goethite samples were measured by the Brunauer-Emmett-Teller (BET) gas adsorption isotherms with water vapor using a surface area and porosimetry analyzer (Micromeritics ASAP 2460). The water vapor adsorption curves and gravimetric water content for each sample at 20 °C were obtained at vapor pressure of P/P_0=0–0.1. X-ray diffraction (XRD) analysis was performed using a Bruker Discover diffractometer operating at 40 kV and 40 mA with Cu Kα radiation (α = 1.54 Å) in a 2θ range from 5° to 80° at a scan rate of 0.05°/s. The morphological features of nano-goethite were observed using a transmission electron microscope system (JEM-2100; JEOL, Tokyo, Japan) at 200KV. The nano-goethite were mixed with KBr on a mass ratio of 1:100 before analysis using a FTIR spectrometer (Nicolet NEXUS870; Thermo Scientific).

Electron paramagnetic resonance (EPR) measurements

All samples were analyzed at room temperature with an X-band microwave frequency of 9.81 GHz, and microwave power of 20.0 mW. The instrument and operating parameters were set as follows: at center field, 3503 G; sweep width, 200 G; resolution of 1024 points; receiver gain of 3.17×10^3; modulation frequency of 100 kHz; modulation amplitude, 1 G; time constant, 39.06 ms; sweep time, 40.00 s.

Calculation of water film coverage

The theoretical length of three sides in a water molecule were calculated as 3.97, 3.27 and 3.04 Å, and three van der Waals molecular surface area are 9.95, 12.06 and 12.99 Å^2. Thus, the total areas of water molecules in 1.0 g of goethite were 160–209, 223–291, 283–369, 483–621 m^2 at 4.8%, 6.7, 8.5% and 14.5% water content. According to the BET specific surface area (138 m^2/g) of nano-goethite (Goe-03), it is roughly estimated that mono-layer water film may form on the surface of nano-goethite with

4.8% and 6.7% water content. By contrast, at 8.5% and 14.5% water content multi-layer water film may cover the surface of nano-goethite.

S2. Supplemental Results

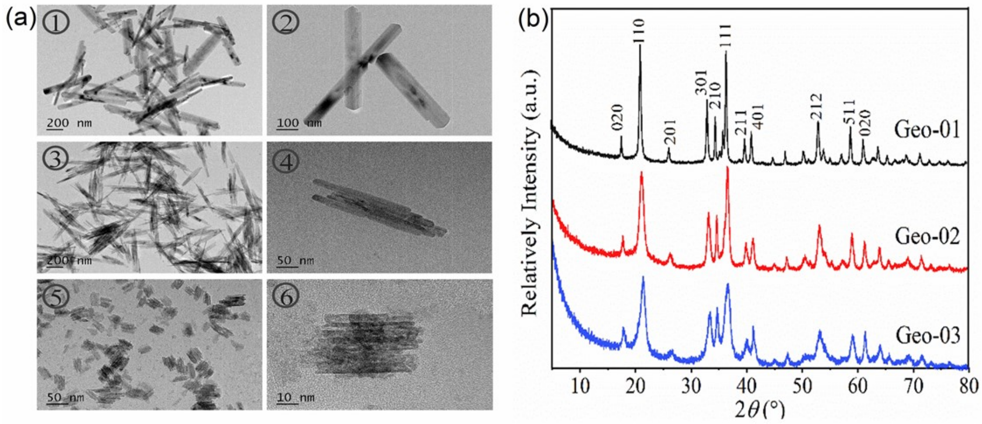

Fig. S1 (a) TEM images showing aggregation of goethite nanorods in 87.0 nm (①, ②) Geo-01 sample, (③, ④) 22.7 nm Geo-02 sample, (⑤, ⑥) 11.1 nm Geo-03 sample. (b) XRD patterns of nano-goethite samples of different sizes.

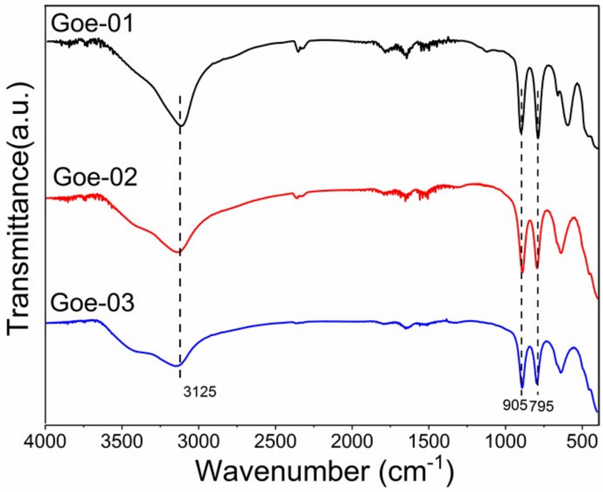

Fig. S2 FITR spectra of nano-goethite samples of different sizes.

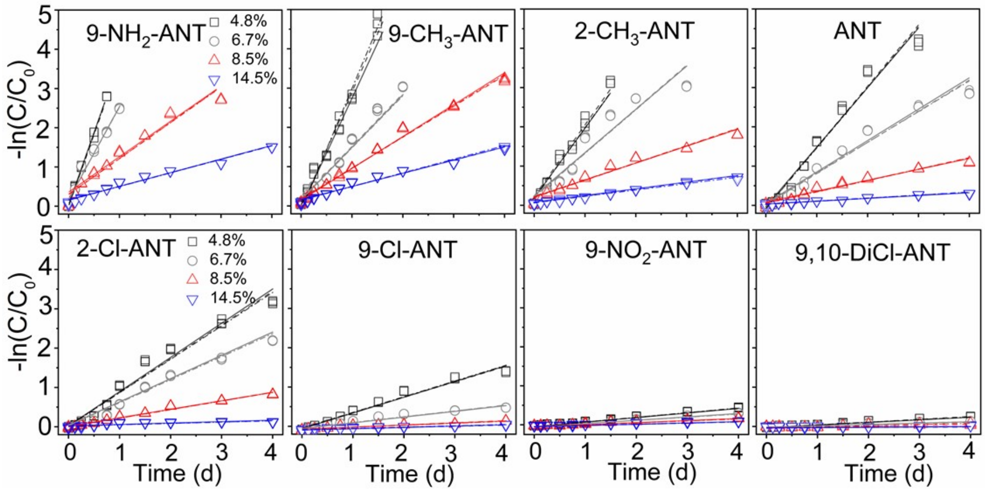

Fig. S3 Transformation kinetics of ANT and ANT derivatives on nano-goethite (Goe-03) at different water content and 20 ℃. The kinetic data were fitted to the first-order kinetic model, and the fitting parameters are summarized in Table S3.

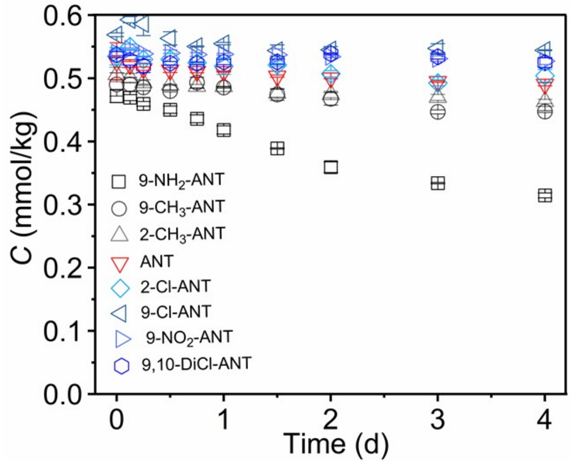

Fig. S4 Transformation of ANT and ANT derivatives on silica powder with 0.6% water content at 10% relatively humidity and 20 ℃.

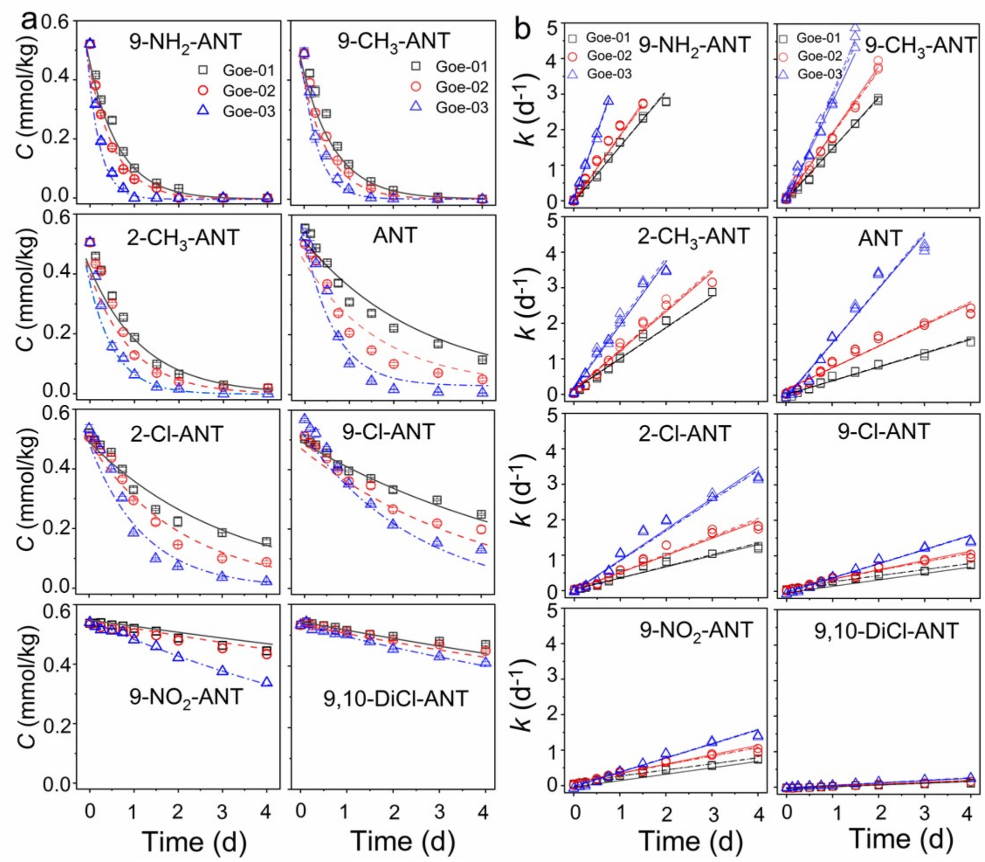

Fig. S5 (a) Transformation kinetics of 0.5 mmol/kg ANT and ANT derivatives on Goe-01, Goe-02, and Goe-03 nano-goethite samples with water content of 2.3%, 3.1%, and 4.8%, respectively. (b) The transformation kinetics were fitted to the first-order kinetic model, and the fitting parameters are summarized in Table S4.

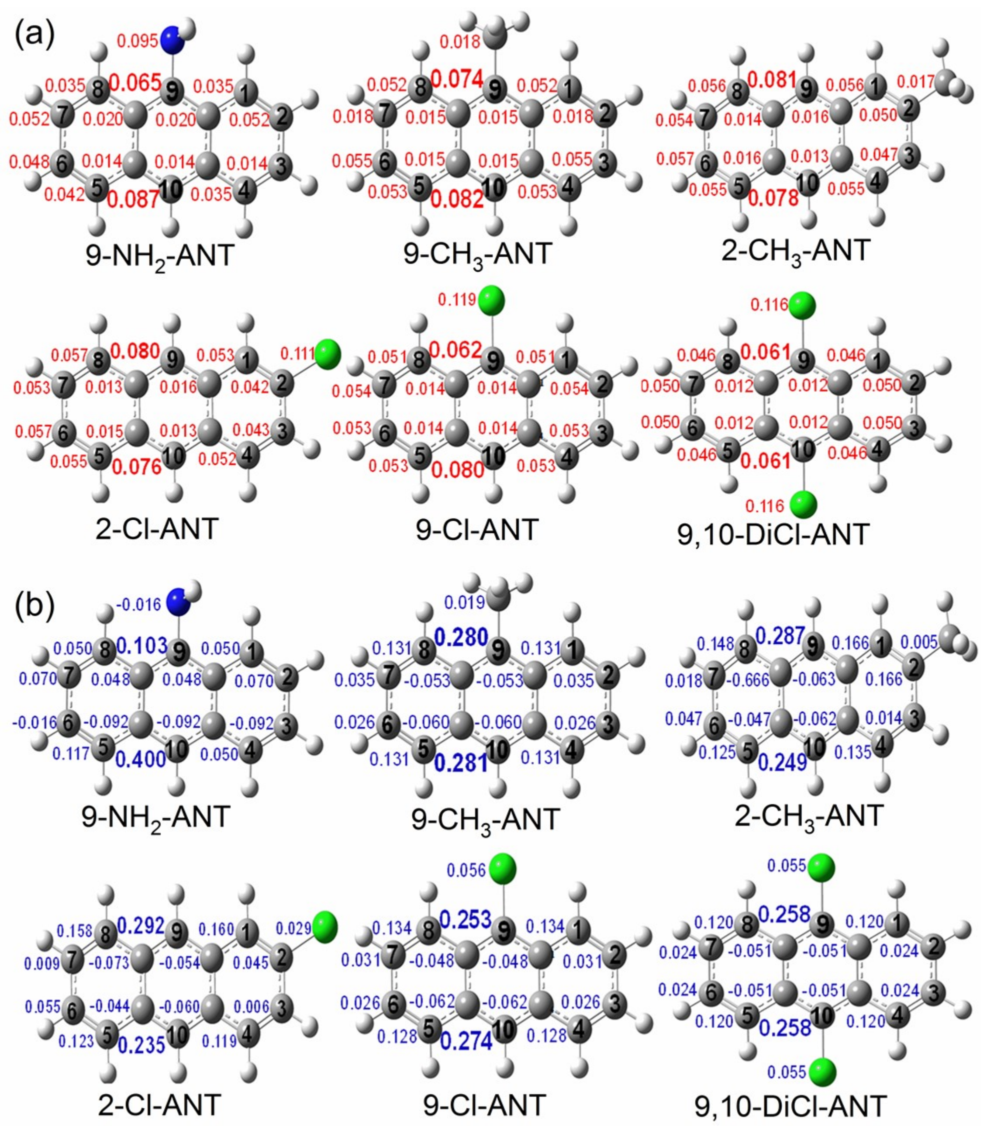

Fig. S6 (a) Fukui functions of 9-NH_2-ANT, 9-CH_3-ANT, 2-CH_3-ANT, 2-Cl-ANT, 9-Cl-ANT and 9,10-DiCl-ANT. (b) Mulliken atomic spin densities of 9-NH_2-ANT, 9-CH_3-ANT, 2-CH_3-ANT, 2-Cl-ANT, 9-Cl-ANT and 9,10-DiCl-ANT.

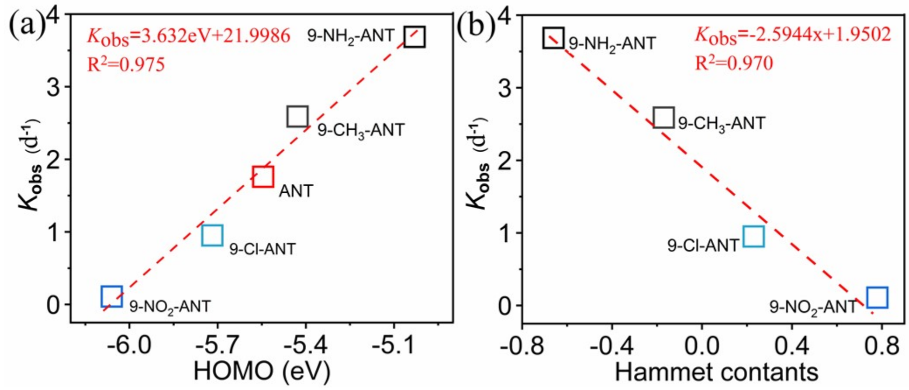

Fig. S7 (a) The first-order rate constants of 9-NH_2-ANT, 9-CH_3-ANT, ANT, 9-Cl-ANT, and 9-NO_2-ANT as function of HOMO energy. (b) The first-order rate constants of 9-NH_2-ANT, 9-CH_3-ANT, 9-Cl-ANT, and 9-NO_2-ANT as function of Hammett constants of their substitution groups.

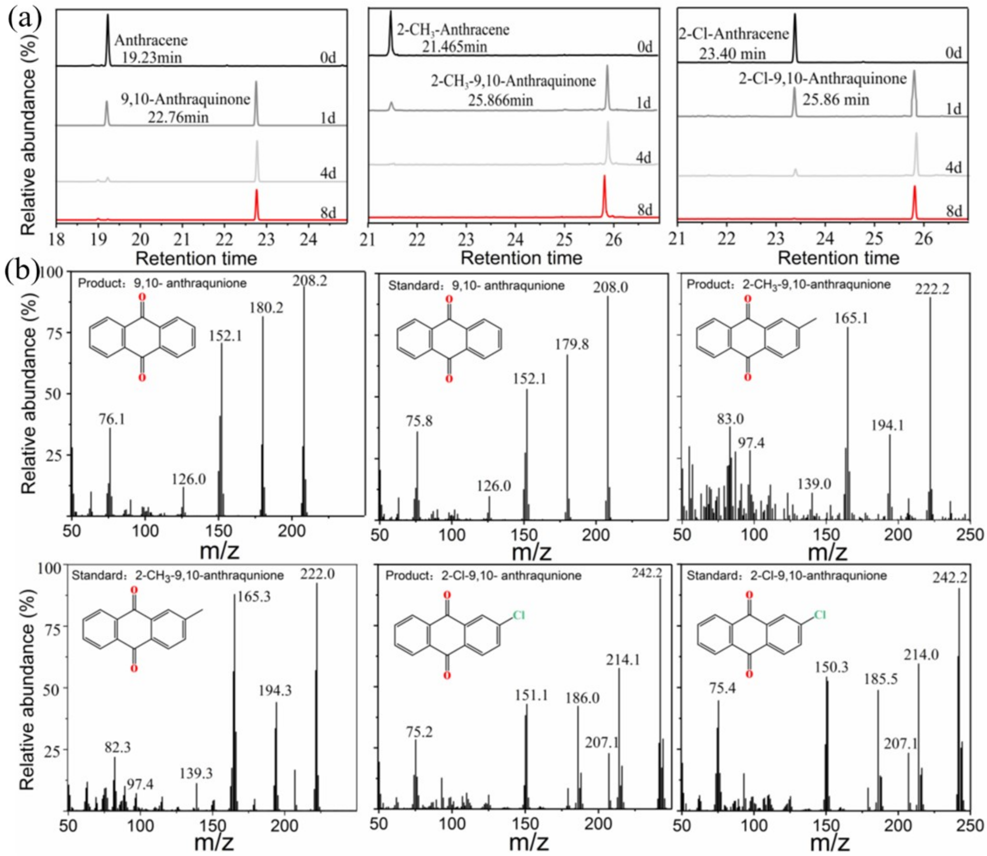

Fig. S8 (a) GC-MS chromatograms of 1:1 acetone/dichlormethane extract of Goethite/ANT, 2-Cl-ANT, 2-CH_3-ANT reaction mixture after 1 d, 4 d, and 8 d. (b) GC-MS chromatograms of transformation products (9,10-anthraquinone, 2-Cl-9,10-anthraquinone, 2-CH_3-9,10-anthraqunione).

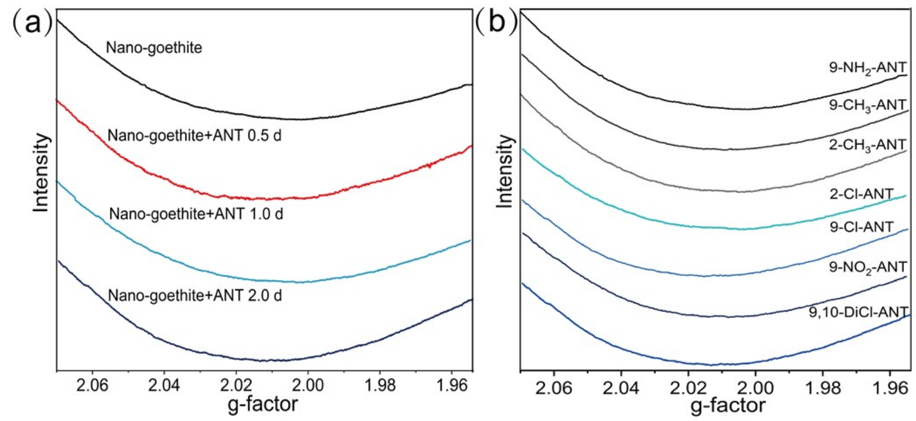

Fig. S9 EPR spectra of original nano-goethite and nano-goethite reacted with ANT for 0.5, 1, and 2 d, and with ANT derivatives for 1 d.

Table S1. Physical and chemical properties of ANT, ANT derivatives and transformation products.

Compounds	Formulae	Boiling point (°C)	LogK_{ow}	Vapor pressure (mmHg)	Solubility (mg L^{-1})
9-aminoanthracene	$C_{14}H_{11}N$	402.2±14.0	3.43	4.05E^{-006}	4.3430
9-methylanthracene	$C_{15}H_{12}$	347.2±0.0	5.07	4.00E^{-05}	0.2610
2-methylanthracene	$C_{15}H_{12}$	353.5±9.0	5.00	5.34E^{-06}	0.0213
anthracene	$C_{14}H_{10}$	337.4±9.0	4.45	6.53E^{-06}	0.0434
2-chloroanthracene	$C_{14}H_9Cl$	370.1±11.0	4.99	2.56E^{-005}	0.1601
9-chloroanthracene	$C_{14}H_9Cl$	370.1±11.0	4.99	2.56E^{-005}	0.1601
9-nitroanthracene	$C_{14}H_9NO_2$	402.9±14.0	1.96	5.09E^{-014}	53.5100
9,10-dichloroanthracene	$C_{14}H_8Cl_2$	401.3±18.0	5.63	6.20E^{-006}	0.0294
9,10-anthraquinone	$C_{14}H_8O_2$	377.0±12.0	3.39	1.16E^{-007}	3.9230
2-methyl-9,10-anthraquinone	$C_{16}H_{12}O_2$	415.4±35.0	4.37	2.67E^{-006}	0.4049
2-chloro-9,10-anthraquinone	$C_{14}H_7ClO_2$	425.7±34.0	3.99	2.36E^{-006}	0.7905

Note: the boiling point, logK_{ow}, vapor pressure, and solubility values for ANT, ANT derivatives and degradation products were form http://www.chemspider.com/.

Table S2. The recovery percentage, relative standard deviation (RSD), and detection limits of ANT and ANT derivatives for the extraction and analytical methods in this study.

Compounds	0.50 mmol/kg		0.05 mmol/kg		Detection limit
	Recovery %	RSD	Recovery %	RSD	ug/L
9-NH_2-ANT	97.37	5.80	96.62	1.74	0.53
9-CH_3-ANT	96.13	3.34	96.61	2.89	0.12
2-CH_3-ANT	99.19	2.01	96.19	1.82	0.05
ANT	100.98	4.53	98.29	4.09	0.15
2-Cl-ANT	100.78	2.00	98.33	3.57	0.19
9-Cl-ANT	99.69	1.83	98.96	1.42	0.26
9-NO_2-ANT	105.90	0.66	97.50	1.55	0.21
9,10-DiCl-ANT	104.43	1.42	96.9	1.80	0.40
9,10-anthraquinone	97.92	2.42	97.35	5.64	2.00
2-CH_3-9,10-anthraquinone	97.99	2.50	96.83	6.11	2.71
2-Cl-9,10-anthraquinone	98.04	1.78	96.19	4.56	2.24

Table S3. The fitted first-order kinetic parameters of ANT and ANT derivatives on nano-goethite (Goe-03) at different water content.

The mean is the average value of the fitted first-order kinetic parameters, and SD is the standard deviation from the triplicate experiments.

Compounds	4.8%				6.7%				8.5%				14.5%			
	k/d^{-1}		R^2		k/d^{-1}		R^2		k/d^{-1}		R^2		k/d^{-1}		R^2	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
9-NH_2-ANT	3.681	0.034	0.998	0.001	1.815	0.008	0.976	0.0004	0.907	0.008	0.985	0.001	0.346	0.003	0.975	0.002
9-CH_3-ANT	2.941	0.152	0.986	0.005	1.335	0.009	0.991	0.002	0.796	0.013	0.991	0.002	0.339	0.008	0.977	0.009
2-CH_3-ANT	1.802	0.018	0.979	0.006	1.113	0.008	0.925	0.001	0.436	0.005	0.964	0.003	0.169	0.006	0.993	0.006
ANT	1.536	0.021	0.972	0.009	0.791	0.008	0.971	0.005	0.285	0.007	0.962	0.006	0.075	0.004	0.948	0.026
2-Cl-ANT	0.858	0.009	0.969	0.002	0.588	0.004	0.982	0.001	0.217	0.002	0.980	0.003	0.050	0.005	0.886	0.015
9-Cl-ANT	0.397	0.004	0.975	0.005	0.147	0.003	0.946	0.010	0.052	0.002	0.902	0.049	0.036	0.002	0.887	0.042
9-NO_2-ANT	0.119	0.001	0.993	0.002	0.085	0.003	0.996	0.002	0.051	0.002	0.964	0.012	0.031	0.002	0.936	0.023
9,10-DiCl-ANT	0.069	0.004	0.983	0.009	0.034	0.002	0.962	0.022	0.027	0.007	0.879	0.024	0.014	0.004	0.841	0.066

Table S4. The fitted first-order kinetic parameters of ANT and ANT derivatives on Goe-01, and Goe-02 nano-goethite samples at water content of 2.3%, and 3.1%, respectively. The mean is the average value of the fitted first-order kinetic parameters, and SD is the standard deviation from the triplicate experiments.

Compounds	Goe-01				Goe-02			
	k/d^{-1}		R^2		k/d^{-1}		R^2	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
9-NH_2-ANT	1.561	0.024	0.995	0.002	1.875	0.026	0.994	0.004
9-CH_3-ANT	1.425	0.021	0.996	0.002	1.816	0.048	0.996	0.002
2-CH_3-ANT	0.872	0.002	0.979	0.002	1.117	0.015	0.972	0.007
ANT	0.390	0.003	0.980	0.007	0.610	0.010	0.956	0.014
2-Cl-ANT	0.323	0.008	0.950	0.015	0.494	0.012	0.960	0.007
9-Cl-ANT	0.175	0.005	0.982	0.006	0.250	0.012	0.965	0.017
9-NO_2-ANT	0.038	0.002	0.964	0.014	0.046	0.003	0.987	0.005
9,10-DiCl-ANT	0.051	0.002	0.980	0.011	0.053	0.001	0.991	0.005

Table S5. Fitting parameters of Mössbauer spectra of nano-goethite samples before and after reaction with ANT and 9-NO_2-ANT.

Samples	Phase	QS (mm/s)	IS (mm/s)	H (T)	Area (%)
Nano-goethite	Fe(II) Doublet	3.55	1.25	——	2.4
	Fe(III) Sixlet	-0.20	0.26	38.56	97.6
Nano-goethite +ANT	Fe(II) Doublet	3.38	1.41	——	5.2
	Fe(III) Sixlet	-0.27	0.25	38.02	94.8
Nano-goethite +9-NO_2-ANT	Fe(II) Doublet	3.06	1.43	——	4.2
	Fe(III) Sixlet	-0.27	0.25	38.74	95.8

QS: quadrupole splitting; IS: isomer shifts; H: Hyperfine field; Area: relative phase abundance in %.