"Drawing" Upconversion Nanophosphors into Water through Host-Guest Interaction

Qian Liu, Chunyan Li, Tianshe Yang, Tao Yi* and Fuyou Li*

E-mail: fyli@fudan.edu.cn,

Department of chemistry, Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China

General Methods and Materials:

All starting materials were obtained from commercial supplies and used as received. Rare earth oxides Y_2O_3 (99.999%), Yb_2O_3 (99.999%), Er_2O_3 (99.999%), Ce_2O_3 (99.999%), and Tb_2O_3 (99.999%) were purchased from Shanghai Yuelong New Materials Co. Ltd. Oleyl amine (**OM**) (>90%) and 1-octadecane (**ODE**) (>90 %) were purchased from Alfa. Aesar Ltd. 1-adamantaneacetic acid (98%) (**Ad**) were purchased from Aldrich. β-cyclodextrin (**β-CD**) and trifluoroacetic acid (99%) were supplied from Sinopharm Chemical Reagent Coy., Ltd. (Shanghai). All other chemical reagents with analytical grade were used directly without further purification. Deionized water was used throughout. $RE(CF_3COO)_3$ (RE^{3+}=Y^{3+}, Yb^{3+}, Er^{3+}, Ce^{3+}, Tb^{3+}) was prepared according to the method in the literature.[1] 1-Adamantaneacetic sodium was prepared by dissolving the 1-adamantaneacetic acid and sodium hydroxide at elevated temperature.

Characterization: Powder X-ray diffraction (XRD) measurements were performed on a Bruker D4 diffractometer at a scanning rate of 1°/min in the 2θ range from 10 to 70° (Cu Kα radiation, λ = 1.54056 Å). The size and morphology of UCNPs were determined at 200 kV with a JEOL JEM-2010 low to high resolution transmission electron microscope (HR-TEM). These as-prepared samples were dispersed in cyclohexane and dropped on the surface of a copper grid for TEM test. ^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). Fourier transform infrared (FT-IR) spectra were performed using an IRPRESTIGE-21 spectroscope

Supplementary Material (ESI) for Chemical Communications

(Shimadzu) with KBr pellets. The wave number range recorded was 400-4000 cm^{-1}. Thermogravimetric analysis (TGA) curves were recorded on a DTG-60H (Shimadzu) at a heating rate of 10 °C/min. The upconversion luminescence emission spectra were recorded on Edinburgh LFS-920 instrument, but using an external 0-2 W adjustable 980 nm semiconductor laser (Beijing Hi-Tech Optoelectronic Co., China) with an optic fiber accessory as the excitation source, instead of the Xeon source in the spectrophotometer. The images of upconversion luminescence were obtained digitally on a Nikon multiple CCD Camera.

Synthesis of UCNPs-Ad: Thermal decomposition procedure is as follow:[2] to a three-necked flask of 17.5 mL ODE and 2.5 mL OM at room temperature were added given amounts of $Na(CF_3COO)$ (2mmol), $RE(CF_3COO)_3$ (78%mol Y, 20%mol Yb, 2%mol Er, total amount: 1 mmol) and 1-adamantaneacetic sodium (7 mmol). The resulting mixture was heated to 110 °C with constant stirring to remove water and oxygen. After 30 min, the solution was then heated to 320 °C at a rate of 20 K min^{-1} and the temperature was maintained for 1 hour under an Ar atmosphere. When the reaction was completed, an excess amount of ethanol was poured into the solution at room temperature. The resultant mixture was centrifugally separated, and the products were collected. The as-precipitated nanocrystals were washed several times with ethanol and dried in vacuum overnight. All of these as-prepared nanocrystals could be easily redispersed in various nonpolar organic solvents such as cyclohexane, toluene, and chloroform.

Synthesis of DCNPs-Ad: The synthetic procedure was the same as that used to synthesize UCNPs-Ad, except that $RE(CF_3COO)_3$ (80%mol Y,15%mol Ce,5%mol Tb) were taken as the precursors, replacing $RE(CF_3COO)_3$ (78%mol Y, 20%mol Yb, 2%mol Er).

Conversion of Hydrophobic UCNPs-Ad into Hydrophilic UCNPs-Ad/β-CD: The as-prepared UCNPs-Ad (100 mg) were dispersed in 15 mL of a mixture of ethanol and H_2O (2:1, v/v), and then 10 mL water solution containing β-CD (10 mg) was added as a host reagent, stirring 20 s at room temperature. The resultant mixture was centrifugally separated, and the products were collected. The product was washed alternately with deionized water and ethanol for three times, and stored either in deionized water or ethanol.

Conversion of Hydrophobic DCNPs-Ad into Hydrophilic DCNPs-Ad/β-CD: The synthetic

procedure of $NaYF_4$: 15 mol%Ce, 5 mol%Tb was the same as that used to synthesize UCNPs-Ad/β-CD, except that UCNPs-Ad was replaced by DCNPs-Ad.

Cell Culture: A human nasopharyngeal epidermal carcinoma cell line (KB cell) was provided by the Institute of Biochemistry and Cell Biology, SIBS, CAS (China). Cells were grown in RPMI 1640 (Roswell Park Memorial Institute's medium) supplemented with 10 % FBS (fetal bovine serum) at 37 °C and 5% CO_2. Cells (5×10^8 /L) were plated on 14 mm glass cover-slips under 100% humidity condition and allowed to adhere for 24 h.

Cytotoxicity of UCNPs-Ad/β-CD: In vitro cytotoxicity was measured by performing methyl thiazolyl tetrazolium (MTT) assays on the KB cells. Cells were seeded into a 96-well cell culture plate at 5×10^4 / well, under 100% humidity, and were cultured at 37 °C and 5% CO_2 for 24 h; different concentrations of UCNPs-Ad/β-CD (0, 200, 400, and 800 μg/mL, diluted in RPMI 1640) were then added to the wells. The cells were subsequently incubated for 4, 12, 24 and 48 h at 37 °C under 5% CO_2. Thereafter, MTT (10 μL; 5 mg/mL) was added to each well and the plate was incubated for an additional 4 h at 37 °C under 5% CO_2. After addition of 100 μL DMSO, the assay plate was allowed to stand at room temperature for 2 h. The OD570 value (Abs.) of each well, with background subtraction at 690 nm, was measured by means of a Tecan Infinite M200 monochromator-based multifunction microplate reader. The following formula was used to calculate the inhibition of cell growth: Cell viability (%) = (mean of Abs. value of treatment group/mean Abs. value of control) × 100%.

Cellular Staining: To ensure complete dispersion of the UCNPs-Ad/β-CD in the serum-free media, their solutions (200 μg/mL) obtained from a stock suspension were shaken to get homogeneous colloidal solution. For single-label imaging, KB cells were stained with 200 μg/ mL UCNPs-Ad/β-CD in a 5% CO_2 incubator at 37 °C for 2 h, cell imaging was then carried out after washing the cells with PBS three times to remove the excess UCNPs-Ad/β-CD.

Confocal Imaging of Living Cells Incubated UCNPs-Ad/β-CD : Confocal imaging of cells was performed with a modified Olympus FV1000 laser scanning upconversion luminescence microscope (LSUCLM) equipped with a continuous-wave (CW) laser at 980 nm (Connet Fiber Optics, China). A 60 × oil-immersion objective lens was used. For the UCNPs-Ad/β-CD, the CW laser at 980 nm provided the excitation, and emission was collected at 540 ± 20 nm.

The video of phase transfer: To conventional observation of phase transfer process of rare-earth nanophosphors from oily to aqueous phase, down-conversion luminescence nanophosphors ($NaYF_4$: 15 mol% Ce,5 mol% Tb) were also used in the video, excited by 254 nm ultraviolet radiation. The concentration is 1 mg/mL in chloroform. The additive is aqueous solution of β-cyclodextrin with concentration of 1 mg/mL. It is just a process of 20-seconds shaking or stirring.

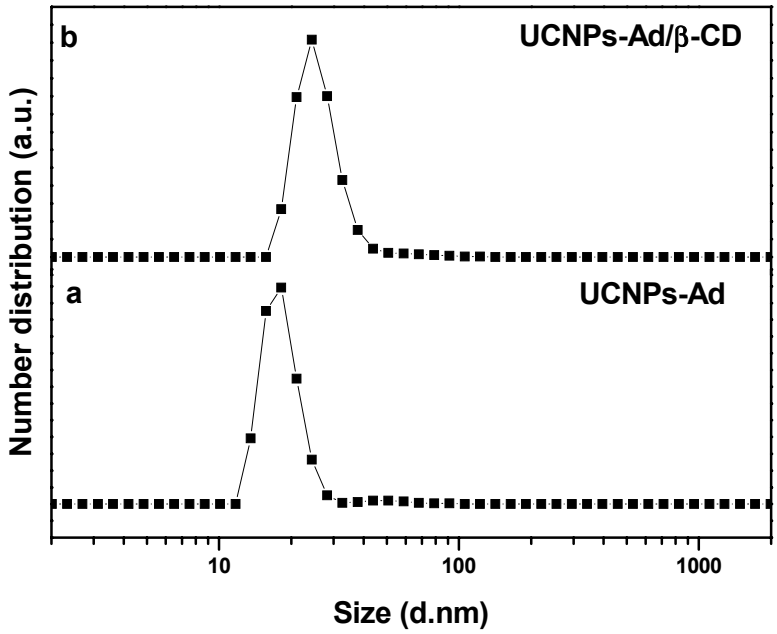

Figure S1. DLS of a) UCNPs-Ad and b) UCNPs-Ad/β-CD samples dissolved in cyclohexane and water, respectively.

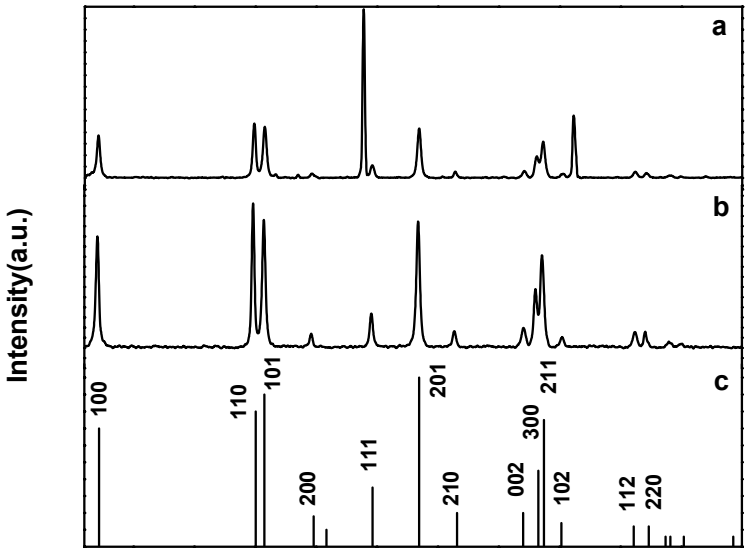

Figure S2. XRD patterns of (a) the as prepared UCNPs-Ad, (b) UCNPs-Ad/β-CD and (c) the standard pattern of Bata (JCPDS card 16-0334) phase of $NaYF_4$. The figure means that these samples have the dominant Beta phase.

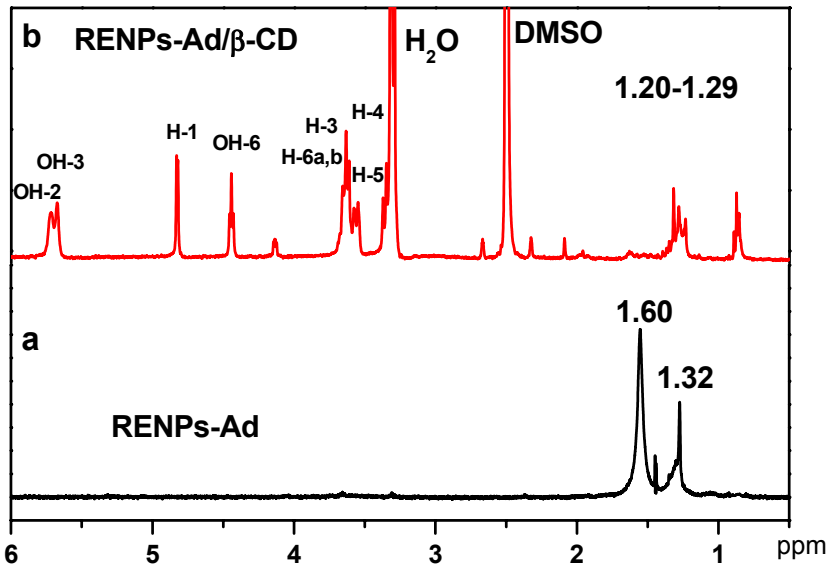

Figure S3. ^{1}H NMR spectra of (a) RENPs-Ad dispersed in $CDCl_3$ and (b) RENPs-Ad/β-CD dispersed in DMSO-d_6.

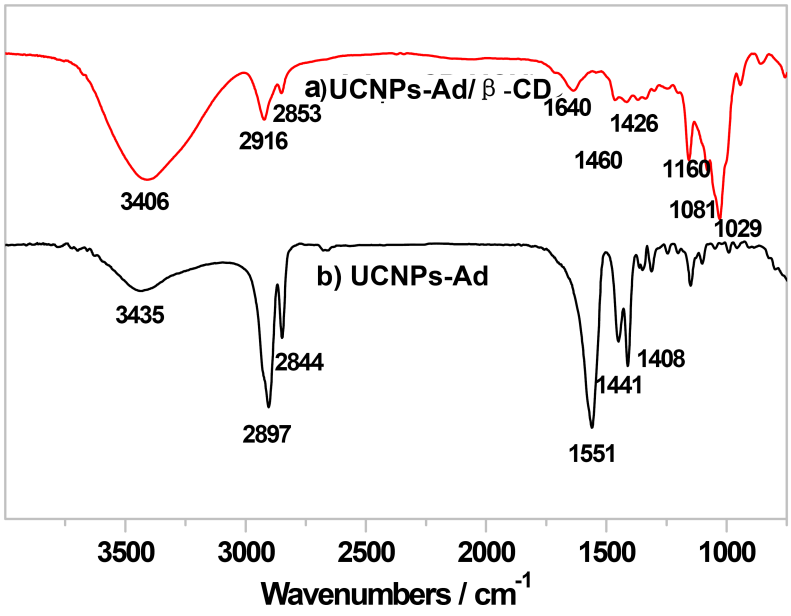

Figure S4. FTIR spectra of the nanoparticles: a) UCNPs-Ad/β-CD; b) UCNPs-Ad

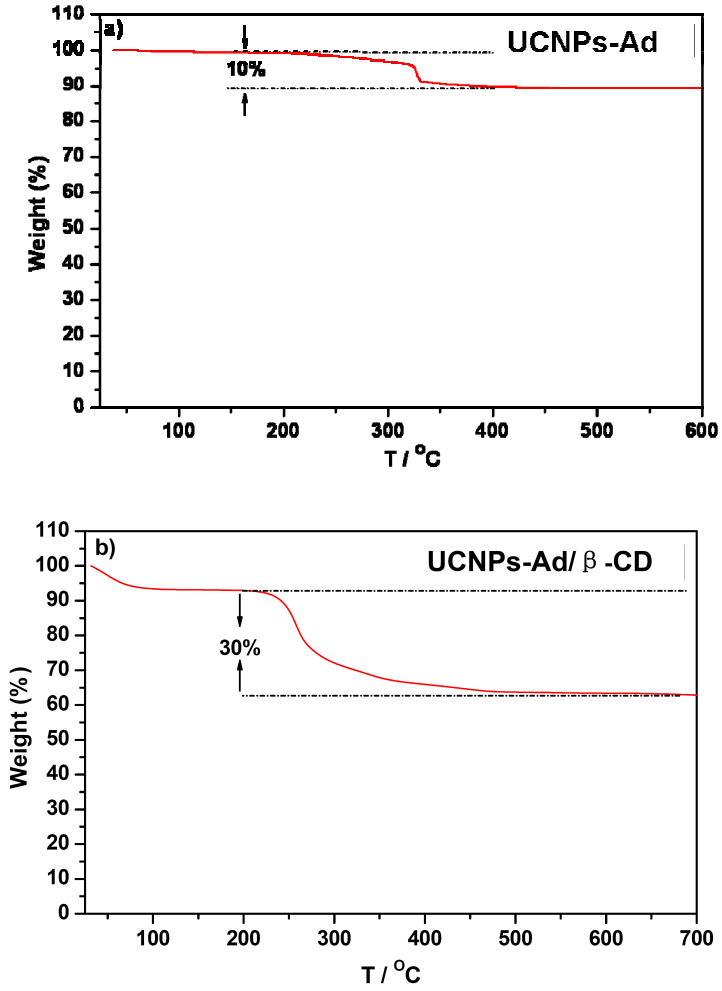

Figure S5. TGA curves of UCNPs-Ad (a) and UCNPs-Ad/β-CD (b).

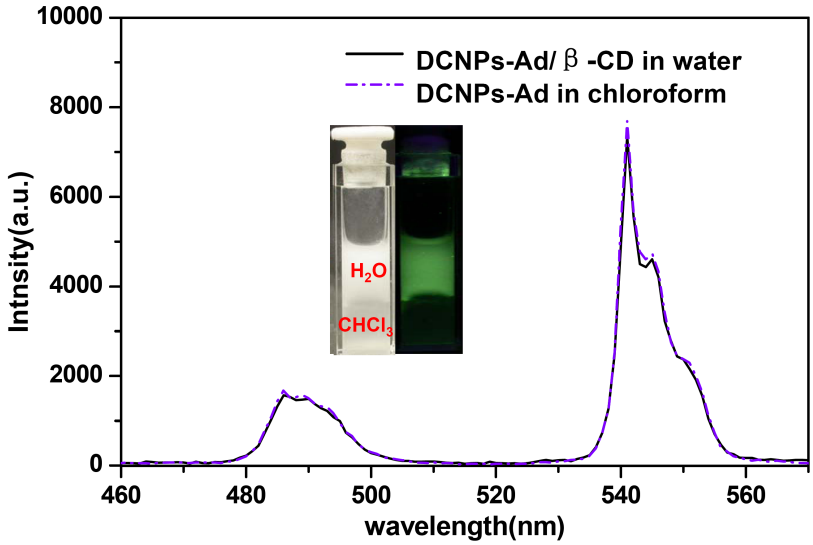

Figure S6. Room-temperature photoluminescence spectra of DCNPs-Ad (1 mg/mL) in chloroform and DCNPs-Ad/β-CD (1 mg/mL) in water. Inset: photos of phase transfer of DCNPs. (λ_{ex}=255 nm),

Figure S7. Bright field of phase transfer of UCNPs.

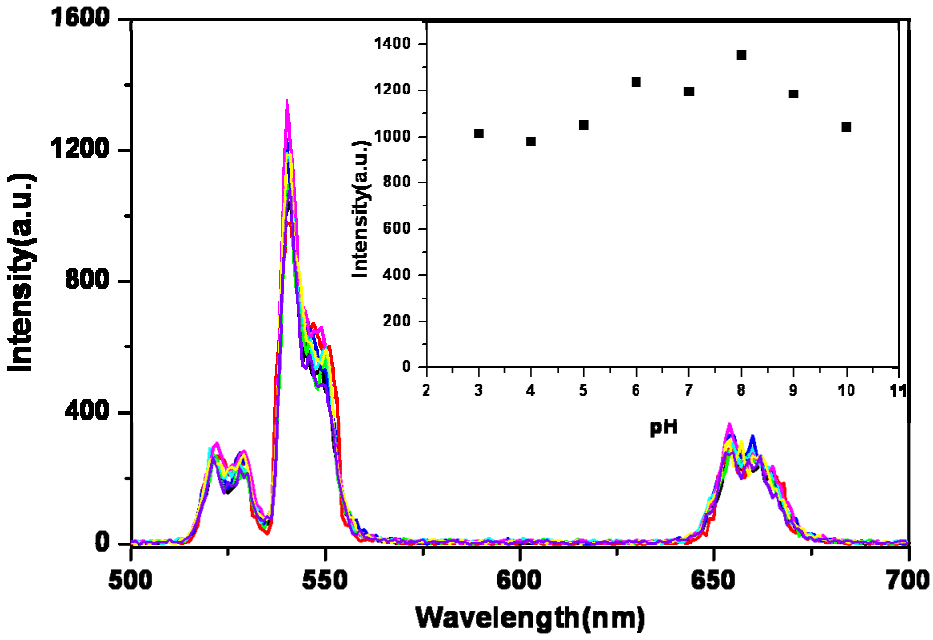

Figure S8. Upconversion luminescence spectra and luminescent intensity at 540 nm (inset) of UCNPs-Ad/β-CD (1 mg/mL) in phosphate buffered saline (PBS) with different pH values (pH = 3 ~ 10). λ_{ex}= CW 980 nm.

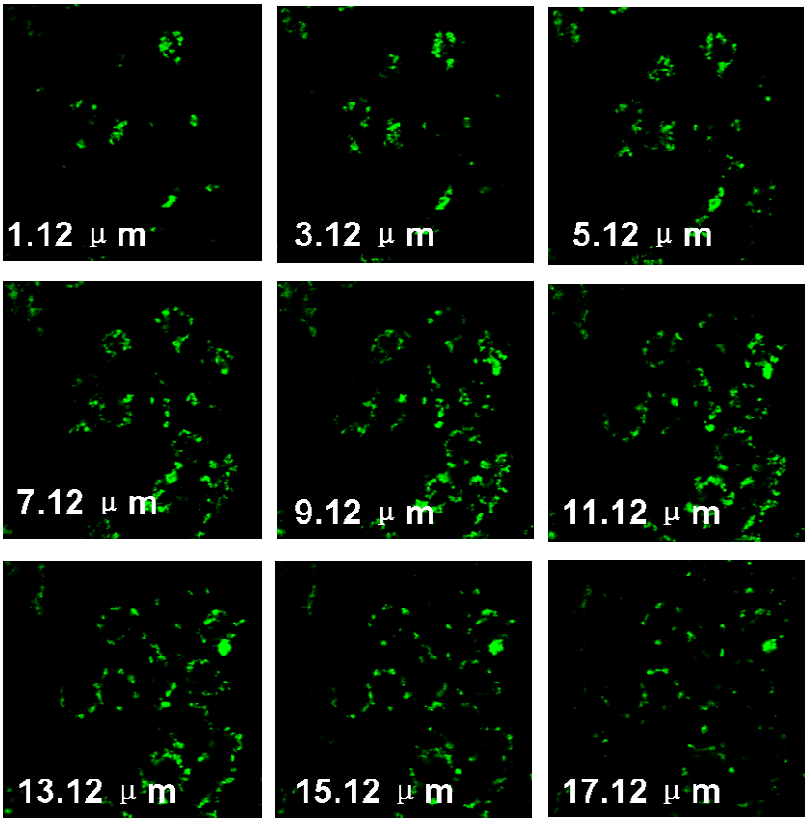

Figure S9. Z-Scan of of cell imaging of KB cells stained with 200 μg/mL UCNPs-Ad/β-CD for 2 h at 37 °C (λ_{ex}= 980 nm, λ_{em} = 540 ± 20 nm).

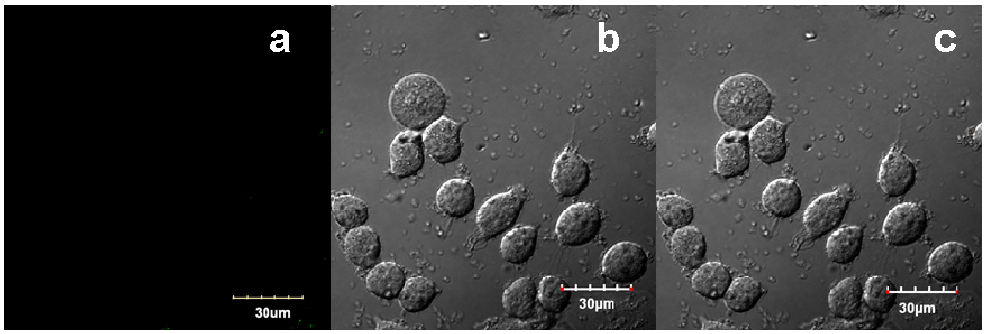

Figure S10. (a) LSUCLM luminescence and (b) bright-field images of KB cells stained with 200 μg/mL UCNPs-Ad/β-CD for 2 h at 4 °C (λ = 980 nm). (c) Overlay of (a) and (b).

References:

1 J. E. Roberts, *J. Am..Chem. Soc.,* 1961, **83**, 1087.

2 H. Mai, Y. Zhang, R. Si, Z. Yan, L. Sun, L. You, C. Yan, *J. Am. Chem. Soc.,* 2006, **128**, 6426.