Electronic Supplementary Information (ESI) for

Highly efficient SERS test strips †

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Experimental

Characterization

The surface morphologies of the samples were measured on a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM) operating at 3.0 keV. The subfiber stucture of the samples were characterized through JEOL-2100F transmission electron microscope (TEM) at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 spectrometer. The distribution of the elements were collected by JSM 7001F Energy Dispersive X-ray Detector (EDX). Surface-enhanced Raman spectra were measured on JOBIN YVON T64000 equipped with a liquid-nitrogen-cooled argon ion laser at 514.5 nm (Spectra-Physics Stabilite 2017) as excitation source (the laser power used was about 40 μW at the samples with an average spot size of 1 μm in diameter). The spectral resolution was 4 cm^{-1} at the excitation wavelength.

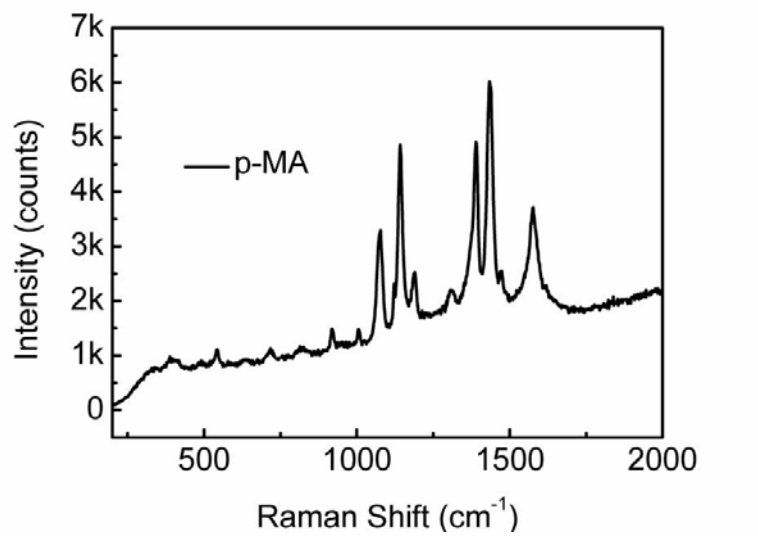

Fig. S1 SERS spectrum of p-Mercaptoaniline (p-MA) with a concentration of 10^{-6} M on the Ag/paper substrate.

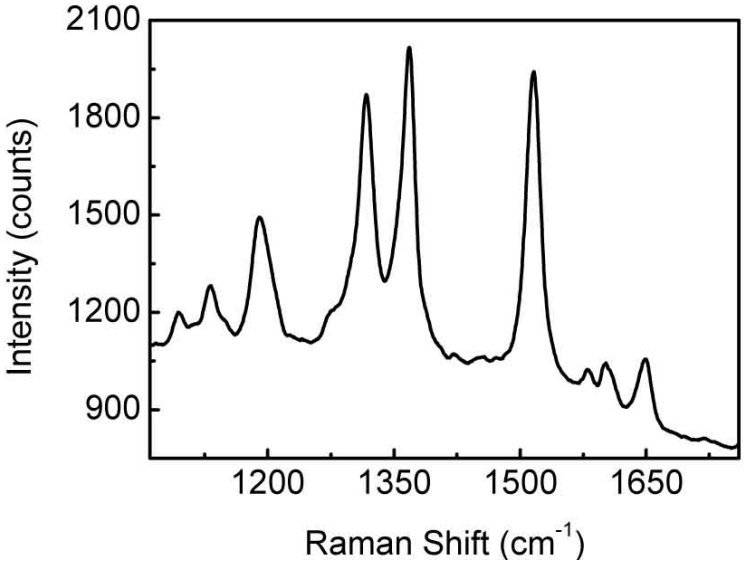

Fig. S2 SERS spectrum of the R6G of 10^{-6}M on Ag/paper, the excitation wavelength is 785 nm.

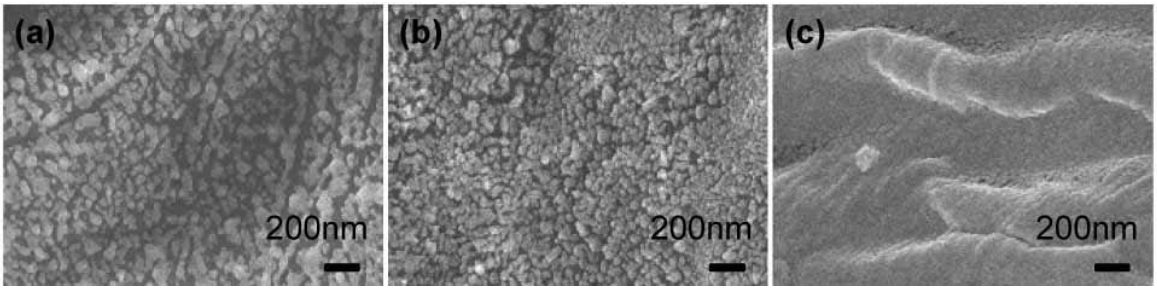

Fig. S3 SEM images of the paper covered with silver of (a) 5nm; (b) 10nm; (c) 20nm.

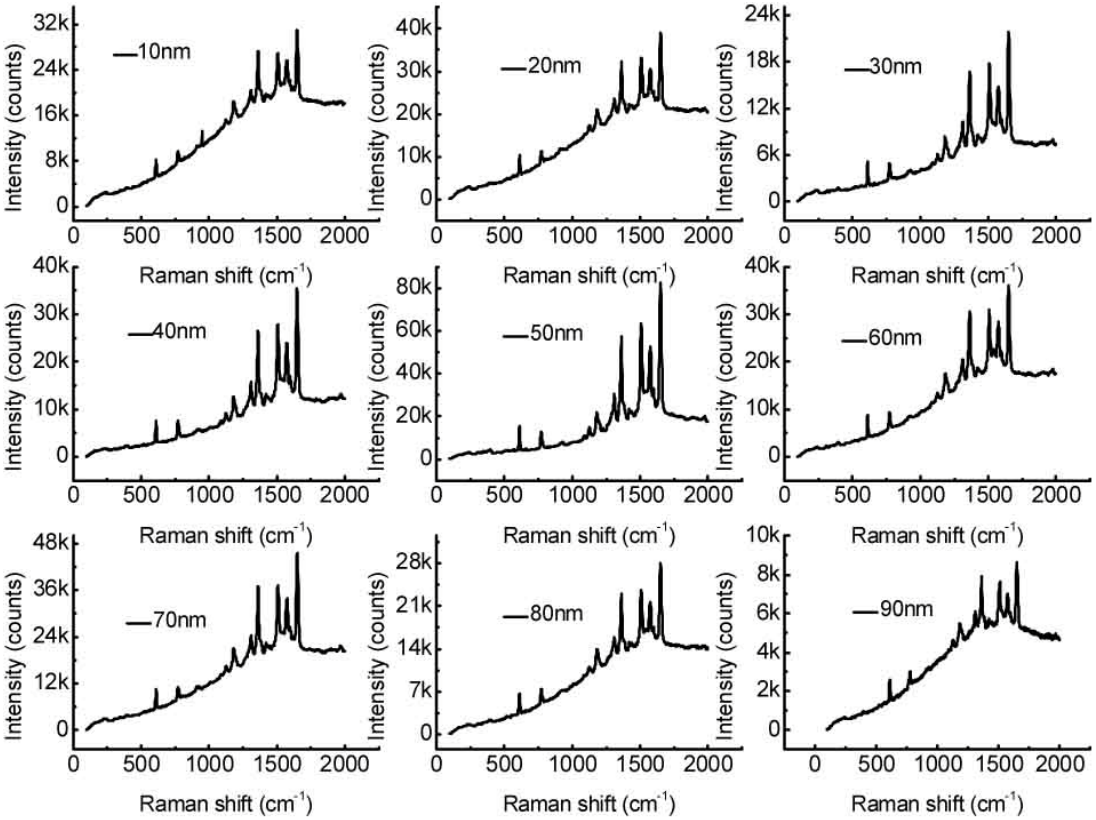

Fig. S4 Raman spectra of paper with silver thickness from 10nm to 90nm.

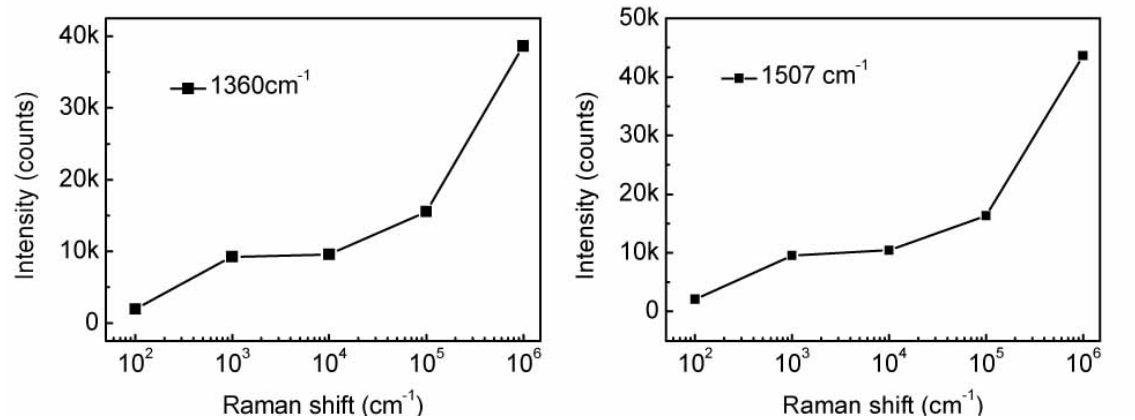

Fig. S5 Semilog plot of the concentration versus 1360 cm^{-1} and 1507 cm^{-1} peak intensity.

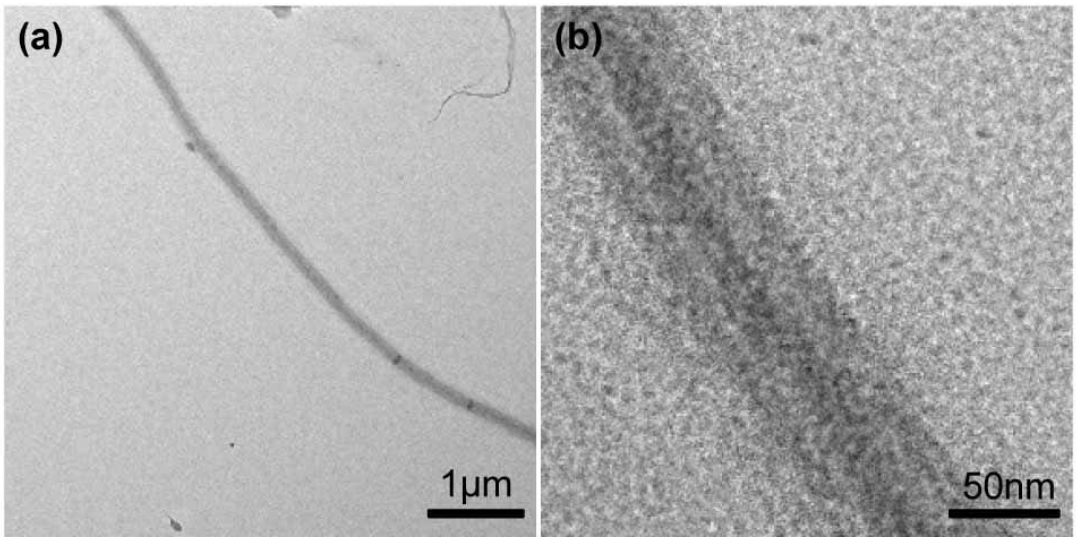

Fig. S6 TEM image of the nanofibrils separated from the printing paper (a) and the magnified image (b).

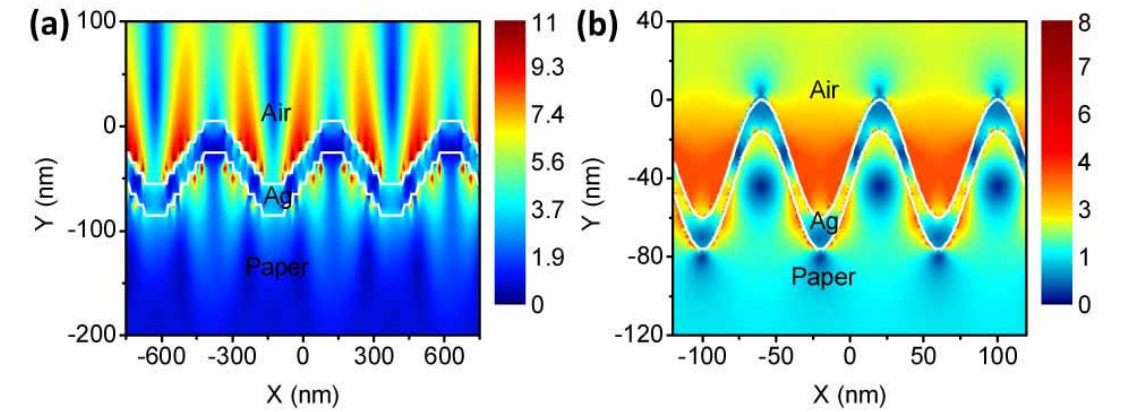

Fig. S7 Electric field component E_X distribution simulations of (a) silver coated wrinkles with intervals of 500nm; (b) silver coated nanofibrils of 80nm width. The incident laser wavelength is 514 nm.

The electricfield component E_X distribution simulations of the regions of silver coated cellulose fibers were implemeted by the FDTD method. In the calculation, the interval of the wrinkles was set at 500nm (Fig. 3a in main text), and height was 100nm (Fig. 3c in main text). The thickness of the coated silver was set to 30 nm corresponding to the experiment. Take the roughness caused by the silver nanoparticles (Fig. 3b in main text) into account, we added some steps upon the silver surface. The incident laser wavelength was 514nm. The calculated result (Fig. S4a) displayed that the electric enhancement could realize 11 which contributed 10^4 enhancement to the SERS signal. We simulated some parallel 80 nm wide nanofibrils coated with silver of 30nm (Fig. S4b), the depth of the gap were 10nm (Fig. 3d in main text). The electric enhancement was 8 which contributed to 400 enhancement to SERS. As there were many other complicated structure consisted in the paper which were not mentioned in the communication, the limit of the detection could reach 10^{-10}M.

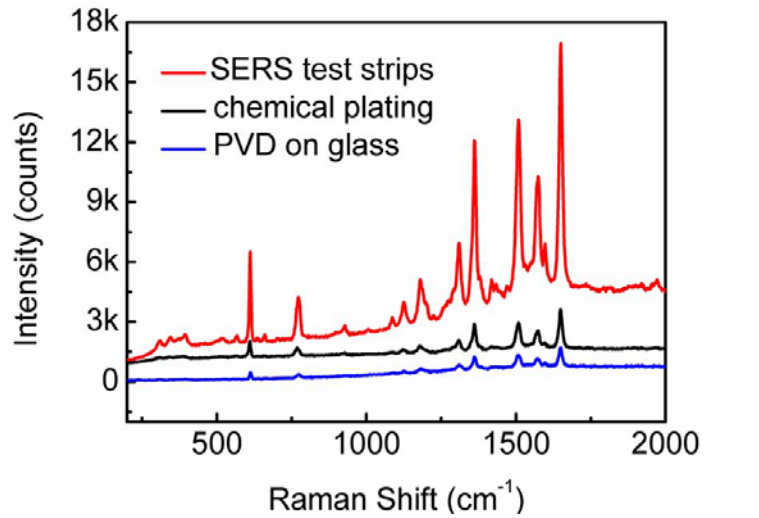

Fig. S8 Comparison of the SERS spectra of R6G of 10^{-6}M on the test strips, chemical silverplanting on glass and the PVD Ag film on glass.

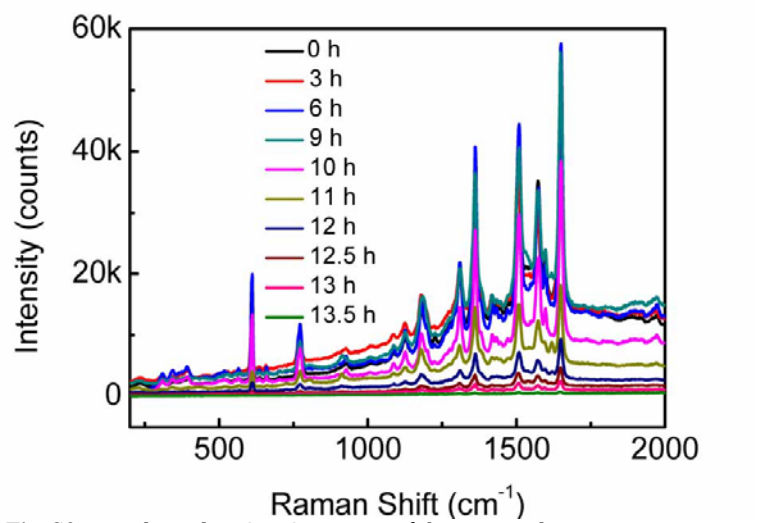

Fig. S9 Time dependent SERS intensity of the new-made test strips.

The SERS activity of the test strips doesn't change obviously in the first 9 hours in use, it decreases gradually from then on, after 13.5 hours the Raman activity of the substrate will decrease significantly.

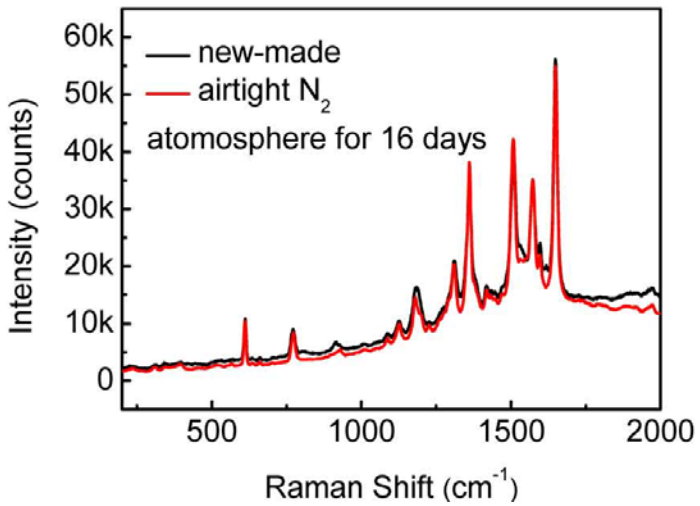

Fig. S10 The SERS spectra of the new-made test strips and that placed in airtight N_2 atomosphere for 16 days.

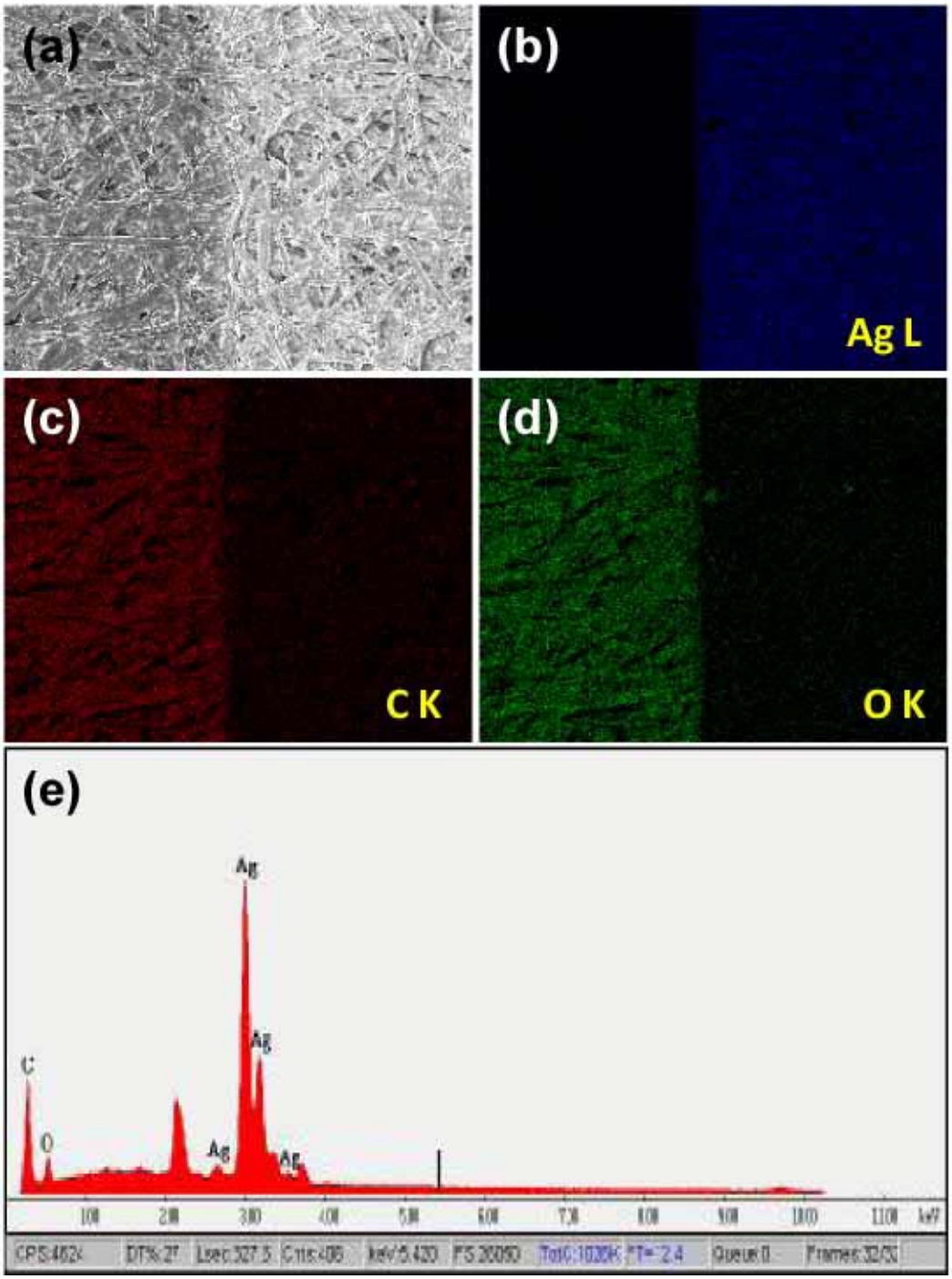

Fig. S 11 (a) SEM image of the boundary of the paper with and without silver coating; the EDX of the (b) Ag maps (c) C maps (d) O maps corresponding to the SEM image; (e) EDX spectrum of the silver coated paper.

Estimation of enhancement factor

Taking p-Mercaptoaniline (p-MA) as test molecules, the enhancement factor (EF) of the samples was estimated, in order of magnitude, by the equation:

$$\mathbf{EF = (I_{SERS}/N_{ads})/(I_{bulk}/N_{bulk})} \quad [s1]$$

Where I_{SERS} and I_{bulk} are the Raman signals at a certain vibration for the p-MA molecules adsorbed on a substrate with SERS effect and solid p-MA molecules, respectively. N_{ads} and N_{bulk} are the numbers of the adsorbed and the solid p-MA molecules within the laser spot, respectively. In our experimental condition for solid p-MA, the probe volume could be considered to be a tube with a waist diameter of ~ 1.0μm and a depth of ~ 20μm. So we can calculate the N_{bulk} value, about 9.4×10^{10}. The N_{ads} can be calculated by dipping definite volume p-MA solution (0.1 nM) on the substrate, estimating the existing area and the amount of molecule in the laser dot can be attained. We estimate the EF value, for the vibration at 1075 cm^{-1}.

$$\mathbf{EF=4\times10^{10}}$$

[s1]Orendorff C J, Gole A, Say T K and Murphy C J, Anal. Chem 2005, 77, 3261-3266.