Supporting information for
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A tailor-made nucleoside-based colourimetric probe of formic acid

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Experimental methods

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General

Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. Column chromatography was carried out with silica gel Si60, mesh size 0.040-0.063 mm (Merck, Darmstadt, Germany). Melting points were determined with a Sanyo-Gallencamp capillary apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, with a Bruker Avance DRX 300 MHz spectrometer, using deuterated chloroform ($CDCl_3$) as solvent. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in ppm and are referenced to $CDCl_3$ signals (7.2 and 77.2 ppm, respectively). The coupling constants J are given in Hz. The one-bond multiplicity of carbon atoms was determined by DEPT experiments. High-resolution mass spectral data were obtained on a VG Autospec, TRIO 1000 (Fisons) instrument. High-resolution mass spectral data were obtained on a VG Autospec, TRIO 1000 (Fisons) instrument. IR spectrum was recorded in solid on a Nicolet iS10 FT-IR spectrometer. Electron impact (EI) at 70 eV was used as ionisation mode in mass spectra. Centrifugation was carried out in an Eppendorf Centrifuge 5804 R. The absorption spectra were obtained with a spectrophotometer Agilent 8453 (UV-Vis Software Chem Station). Measurements were taken at room temperature using quartz cells 4cm^3. TEM images were taken with a 100 kV transmission electron microscope JEM-1010 (JEOL), with a digital camera Mega View III and the image adquisition software was "Analysis"; AuNP samples were deposited on carbon films 24 hours prior to measurement in each of the means of dispersion and dried in a vacuum. The diameter of the nanoparticles was determined by ImageJ, in nanometers. Statistical analysis was obtained by measuring the diameter value of 500 nanoparticles. The structure of all the compounds was determined by analytical and spectroscopic methods and by comparison with data of the compounds reported in literature.

Synthesis of the HS-IN ligand.

5´-amido-5´-deoxy-2´,3´-O-isopropylideneinosine was synthesized according to a reported procedures.[1, 2] The NMR spectra of the herein prepared sample are identical to reported data.

5´-(11-mercaptoundecanamide)-5´-deoxy-2´,3´-O-isopropylideneinosine (**HS-IN):** 5'-amino-5´-deoxy-2´,3´-*O*-isopropylideninosine[2] (150 mg, 0.49 mmol), 11-mercaptoundecanoic acid (112 mg, 0.49 mmol*)* and 1-ethyl-3-(3-(dimethylamino)-propyl) carbodiimide (EDC) (112.5 mg*, 0.*59 mmol) were dissolved in dry pyridine (2 ml). The mixture was stirred at room temperature for 3 h, quenched with deionized water (3 ml) and concentrated to dryness. The crude reaction was dissolved in CH_2Cl_2-MeOH (9.6:0.4 v/v) and filtered over silica gel. The filtrated was concentrated under reduced pressure and the residue was purified by chromatography on silica gel (CH_2Cl_2-MeOH 25:1 v/v) to provide the SH-IN ligand (123 mg, 72%) as a white solid. M.p.65 ºC-66 ºC . $[\alpha]_D^{20}$ -60.9 (*c* 0.075, CH_2Cl_2); IR: ν_{max} : 2923, 2851, 1685, 1547, 1373, 1210, 1093, 1073, 686, 789, 695 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.15-1.27 (m, 16H), 1.49-1.54 (m, 7H), 2.21 (t, *J*= 6 Hz, 2H), 2.41 (q, *J*= 6 Hz, 2H), 3.42-3.46 (m, 1H), 3.76-3.81 (m, 1H), 4.37-4.38 (m, 1H), 4.82-4.84 (m, 1H), 5.22-5.25 (m, 1H), 5.85 (d, *J*= 3 Hz, 1H), 7.89 (s, 1H), 8.28 (s, 1H). ^{13}C NMR ($CDCl_3$): δ = 24.78 (t), 25.46 (q), 25.87 (t), 27.53 (q), 28.78 (t), 29.18 (t), 29.18 (t), 29.53 (t), 29.60 (t), 34.16 (t), 36.77 (t), 41.10 (t), 43.45 (t), 81.85 (d), 83.43 (d), 84.64 (d), 91.93 (d), 115.10 (s), 126.33 (s), 140.30 (d), 145.69 (s),148.20 (s), 158.89 (s) 173.95 (s). HMRS (EI) calculated for $C_{24}H_{37}N_5O_5S$ $[M+H]^+$ 508.2576; found 508.2588.

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[1] F. Liu, D. Austin, *J. Org. Chem.,* **2001**, 66 , 8643.

[2] P. Ciuffreda, A. Loseto and E. Santaniello, *Tetrahedron,* **2002**, 58, 5767.

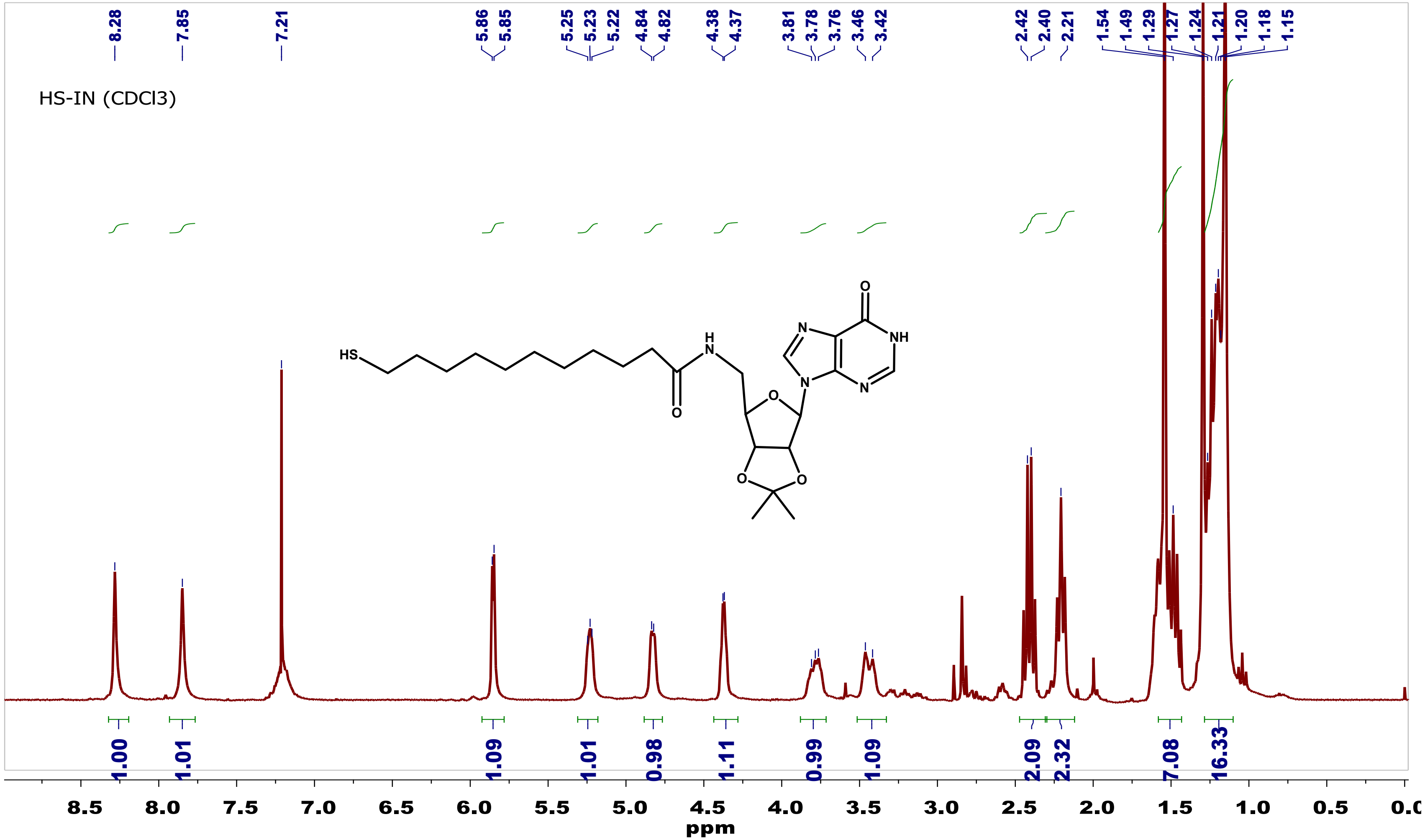

Figure S1. ^{1}H-NMR of HS-IN in $CDCl_3$.

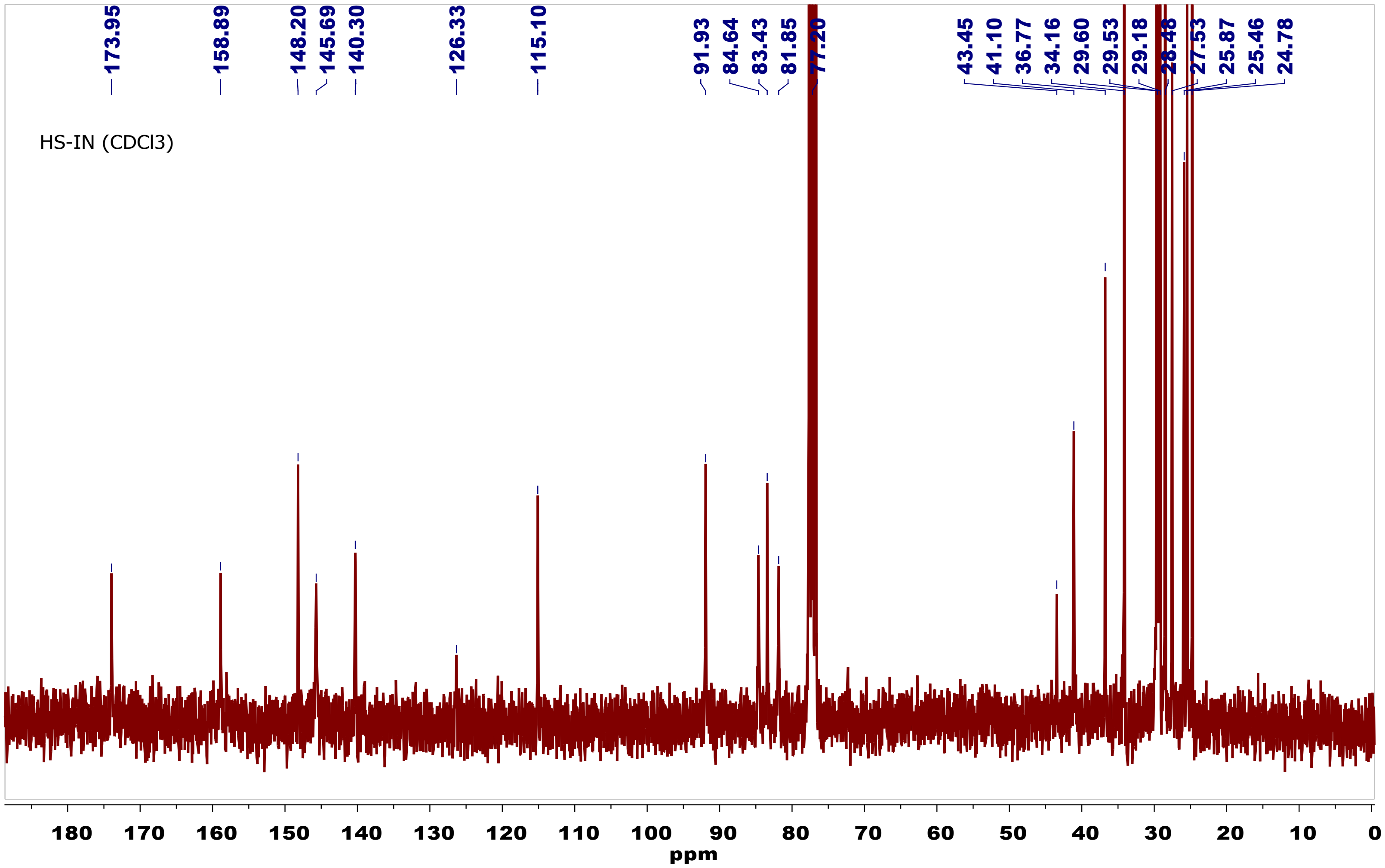

Figure S2. ^{13}C-NMR of HS-IN in $CDCl_3$

Synthesis of gold nanoparticles capped with oleylamine (Au@OA)

They were synthesized according to a reported procedure.[3]

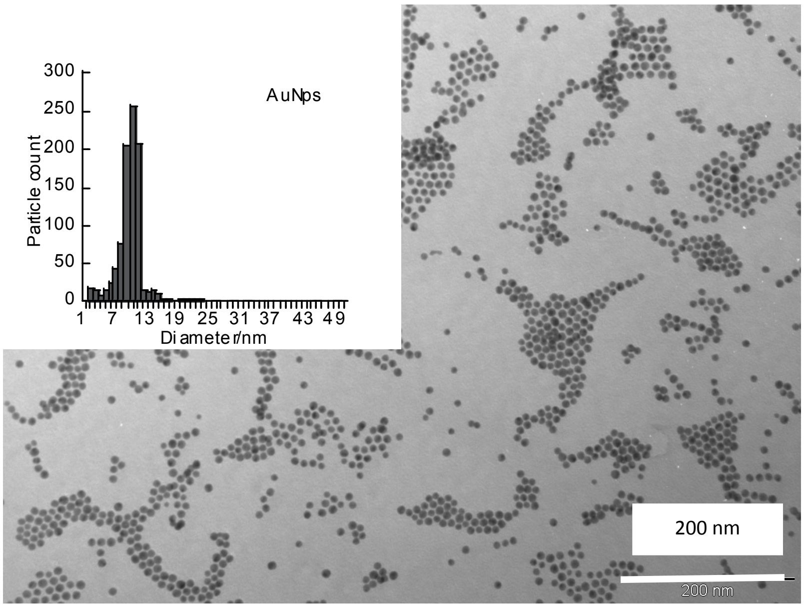

Figure S3: TEM image (scale bar de 200 nm) of Au@OA in $CHCl_3$, with an average core diameter of 10.0±0.4 nm

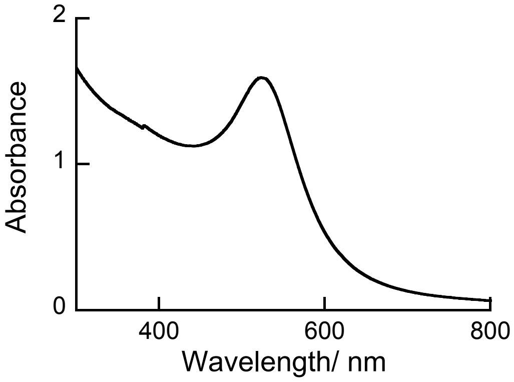

Figure S4: UV-Visible absorption spectrum of Au@OA in chloroform, exhibiting the typical lasmon band at λ_{max} 525 nm.

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[3] X., Lu, H.Y.,Tuan, B. A., Korgel, Y., Xia, *Chem. Eur. J.* **2008**, *14*, 1584.

Synthesis of the inosine-capped AuNPs (Au@S-IN).

A general procedure was used for the synthesis. Au@OA (0.8 mg) was added to a solution of SH-IN (0.04 mmol) in chloroform (2 mL) and the mixture was shaken for 24 h. The NPs were recovered by centrifugation (8500 rpm) and washed several times with acetone, and then they were re-dispersed in chloroform.

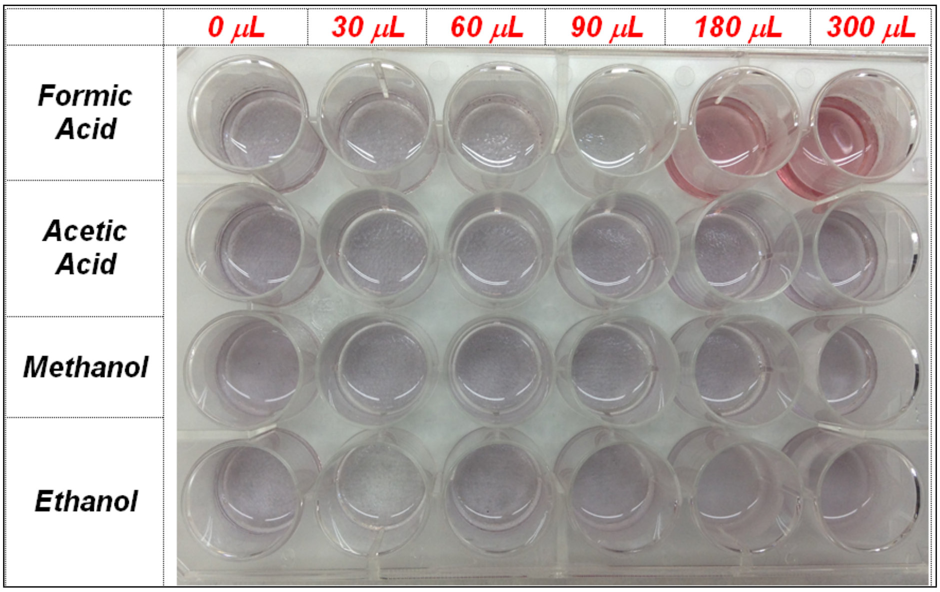
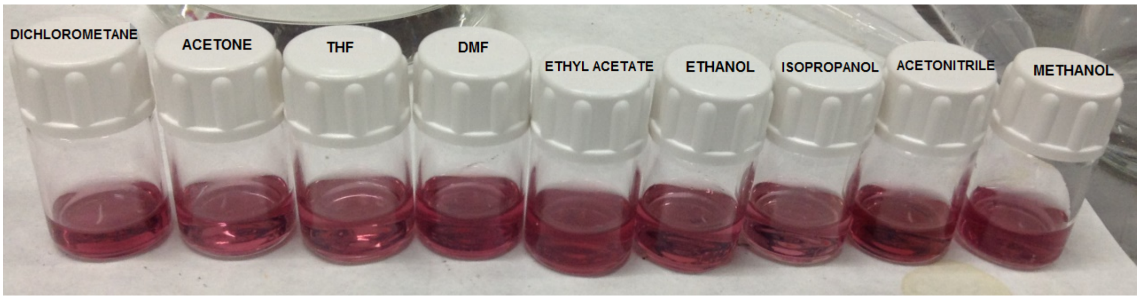


Figure S5. Image showing the effect of the addition of increasing volumes of light alcohols and carboxylic acids to $CHCl_3$ solutions of Au@S-IN.

Dispersibility analysis of Au@IN nanohybrids.

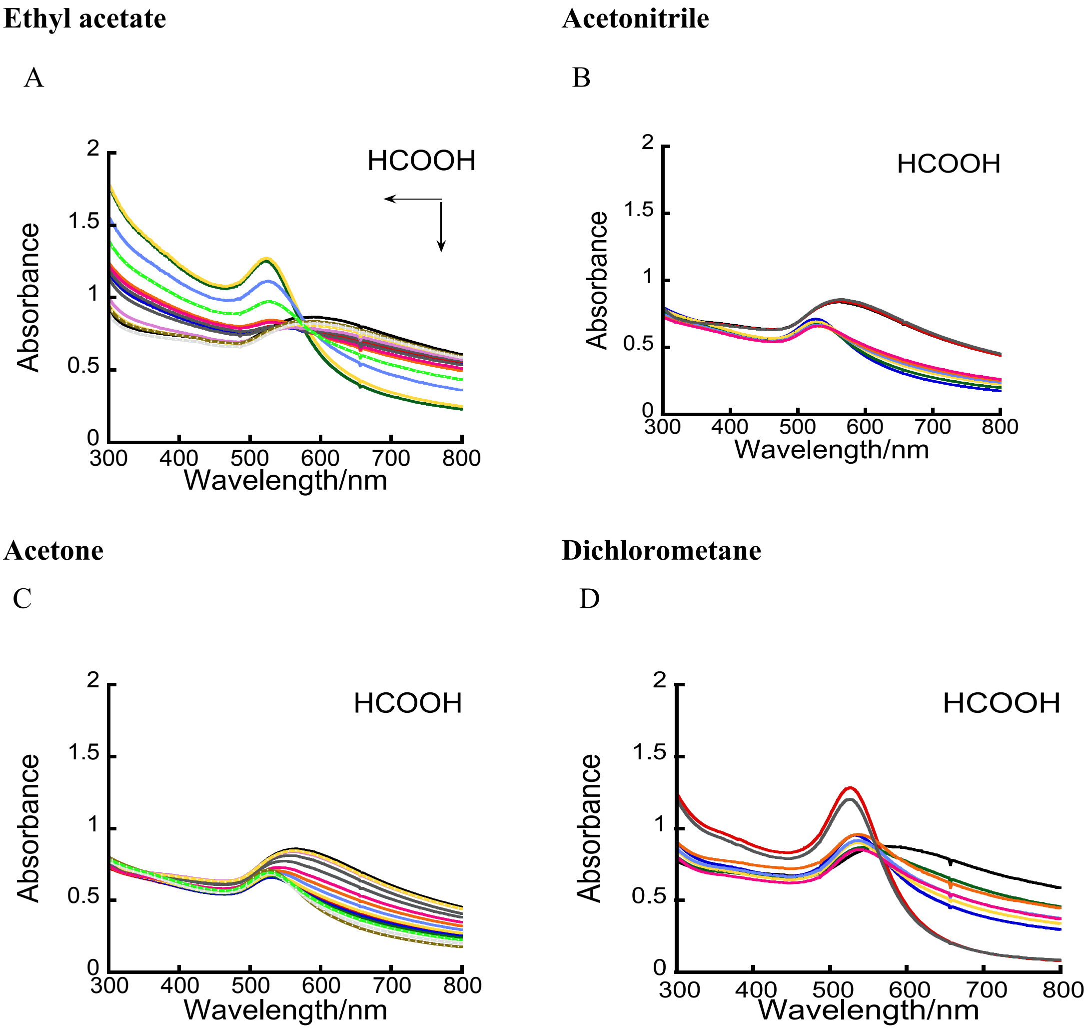
Methanol	Dispersible
Ethanol	Dispersible
Isopropanol	Dispersible
DMF	Dispersible
Acetonitrile	Dispersible
Ethyl acetate	Dispersible
Acetone	Dispersible
THF	Dispersible
Toluene	Non-Dispersible
Ciclohexano	Non-Dispersible
Dichloromethane	Dispersible
Hexane	Non-Dispersible
Chloroform	Dispersible
Diethyl éter	Non-Dispersible
Tetrachloromethane	Non-Dispersible



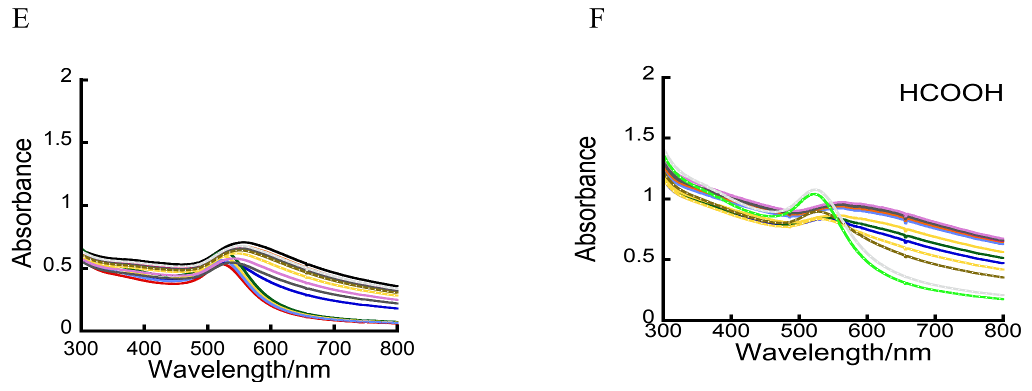
General procedure for the colourimetric sensing assays.

The signalling of the colourimetric probe is based on the colour change of colloidal solution of the AuNPs; the blue colour was associated with aggregated nanoparticles and the red colour was associated with non-aggregated nanoparticles. Acid aliquots were added to a solution of

Au@S-IN (0.8-1.2 mg) dispersed in the organic solvent (1 mL). The absorption spectrum of the sample was taken in less of 1 min after each addition.



Isopropanol **Methanol**



THF

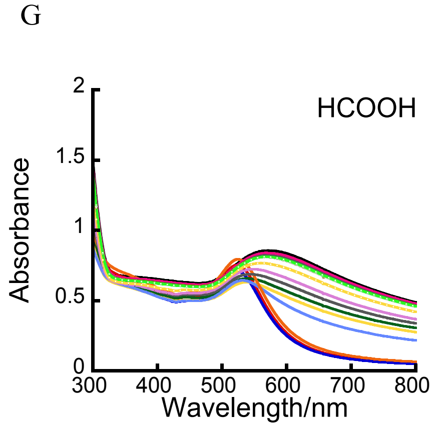


Figure S6. UV-Visible absorption spectra of Au@S-IN aggregates in chloroform in the absence and in the presence of formic acid; the arrows indicate the absorbance trend with increasing [HCOOH];A:[0-25.2M],B:[0-9.3M],C:[0-15.9M],D:[0-7.9M],E:[0-21.2-M],F:[0-21.2M],G[0-23.8M] .

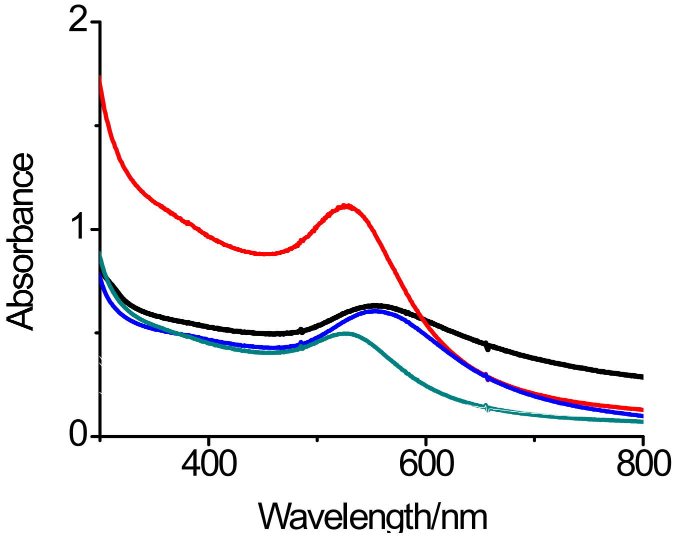


Figure S7. UV-Vis absorption spectra of Au@S-IN showing the assay was reversible; (i) aggregates of Au@S-IN nanoparticles in 1 mL of chloroform (black); ii) de-agglomeration upon addition of 0.6 mL of formic acid ([HCOOH] = 9.3 M, red), iii) again followed by agglomeration of the nanoparticles after addition of 1.6 mL of chloroform ([HCOOH] = 4.8 M, dark blue), and iv) subsequent de-aggregation of the nanoparticles after addition of 1.6 mL of formic acid ([HCOOH] = 9.3 M, light blue).

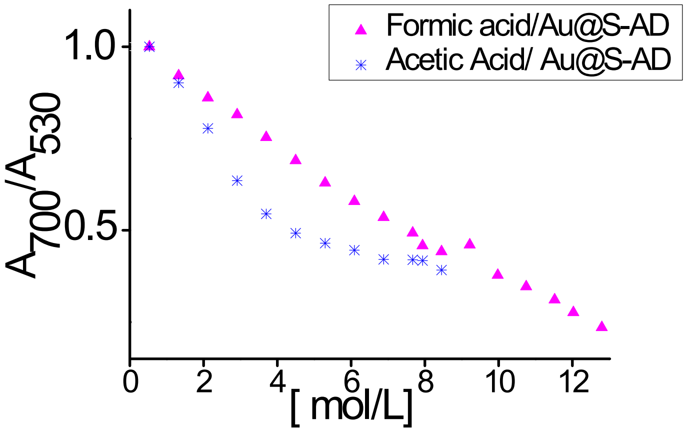
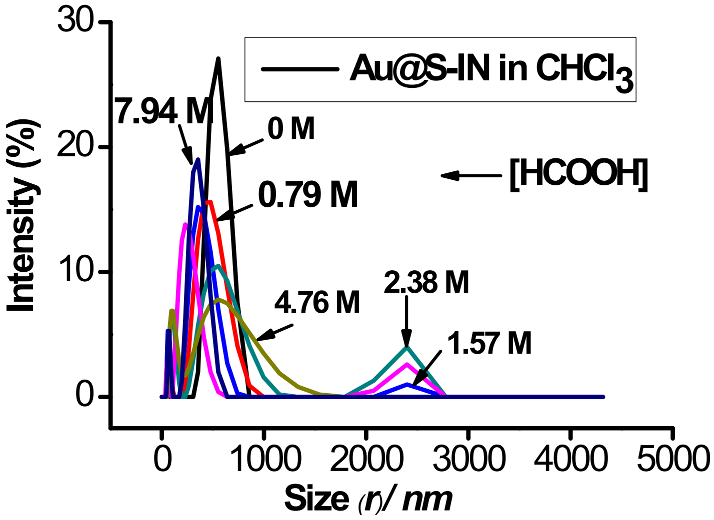


Figure S8. Plots of the A_{700}/A_{530} ratio vs [HCO_2H] and [H_3CCO_2H] for Au@S-AD aggregates in chloroform.



Figue S9. Dynamic light scattering spectra of Au@S-IN in 1 mL of chloroform compared with those obtained after addition of increasing concentrations of formic acid; intensity vs. size.