Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION FOR PHOTOLUMINESCENCE SPECTRA AND QUANTUM YIELDS OF GOLD NANOSPHERE MONOMERS AND DIMERS IN AQUEOUS SUSPENSION

Matthieu Loumaigne,[1,2]‡ Guillaume Laurent,[3] Martinus H. V. Werts[2] and Anne Débarre[1,3*]

[1] Laboratoire Aimé Cotton, CNRS, Univ. Paris-Sud, ENS-Cachan, Université Paris-Saclay, 91405 Orsay Cedex, France

[2] Laboratoire SATIE, CNRS, ENS Rennes, Université Bretagne Loire, Campus de Ker Lann, F-35170 Bruz, France

[3] PPSM, ENS-Cachan, CNRS, Université Paris-Saclay, 94235 Cachan cedex, France

*) e-mail: anne.debarre@lac.u-psud.fr

‡ Present address : Moltech-Anjou, CNRS UMR 6200, University of Angers, 49000 Angers, France

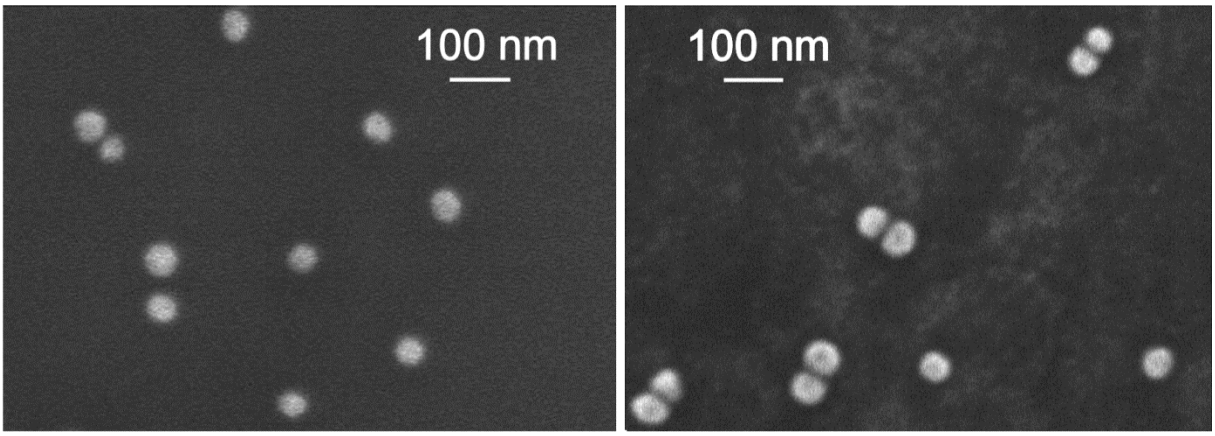

Figure S1 Scanning electron microscopy images of monomers (left) and of the mixture of monomers and dimers (right), both deposited onto a clean silicon substrate from aqueous suspensions. Droplets of the initial solution of monomers (Fig S1 left) and of the mixture of monomers and dimers of gold spheres of 50 nm diameter obtained using the dimerization protocol (see main text) (Fig S1 right) were left on the silicon substrate for 10 mn, then the solutions were removed by spinning at 2000 rpm (Hitachi SEM-FE SU8000, voltage 3 kV).

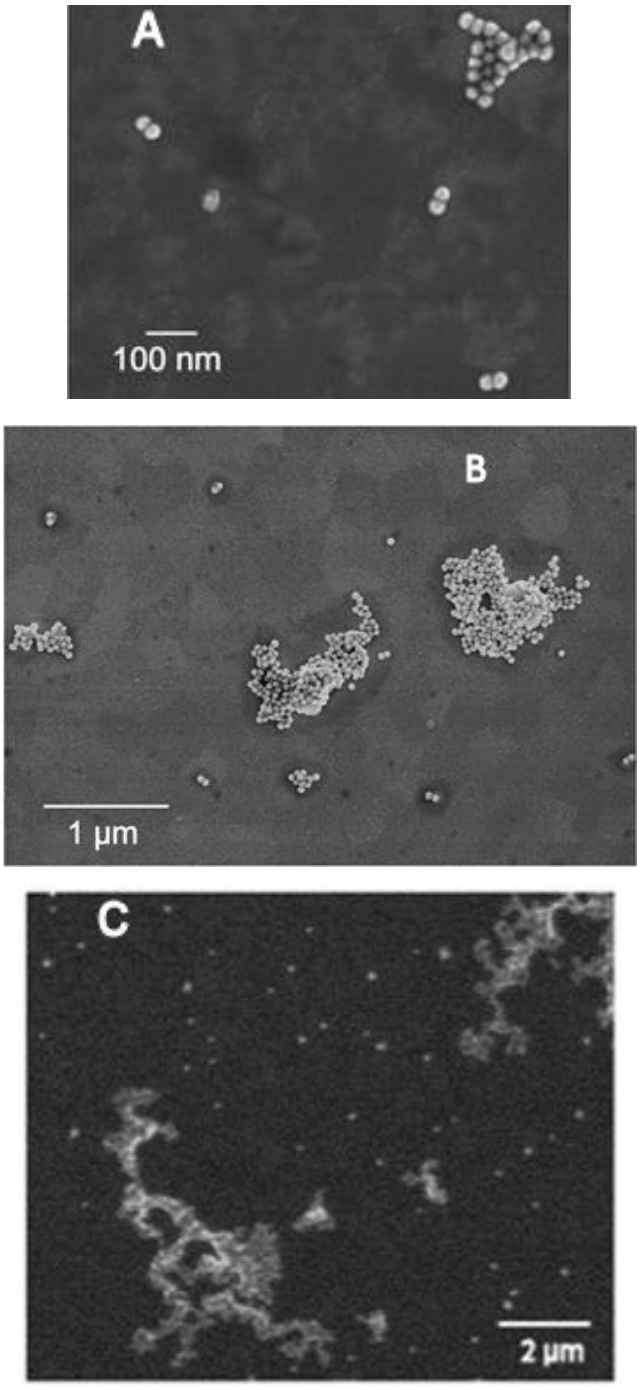

Figure S2 Scanning electron microscopy images of a deposit from a mixture of monomers and dimers (A and B), both deposited onto a clean silicon substrate from aqueous suspensions; and of a deposit of pure monomers on an ITO-coated slide. Quite large aggregates of particles can be observed in the images. In contrast, there are very few small aggregates (trimers, tetramers…), about 4 to 6 trimers, tetramers and pentamers for 100 dimers and monomers. The large aggregates are likely to form on a defect during drying of the solvent (Hitachi SEM-FE SU8000, voltage 3 kV).

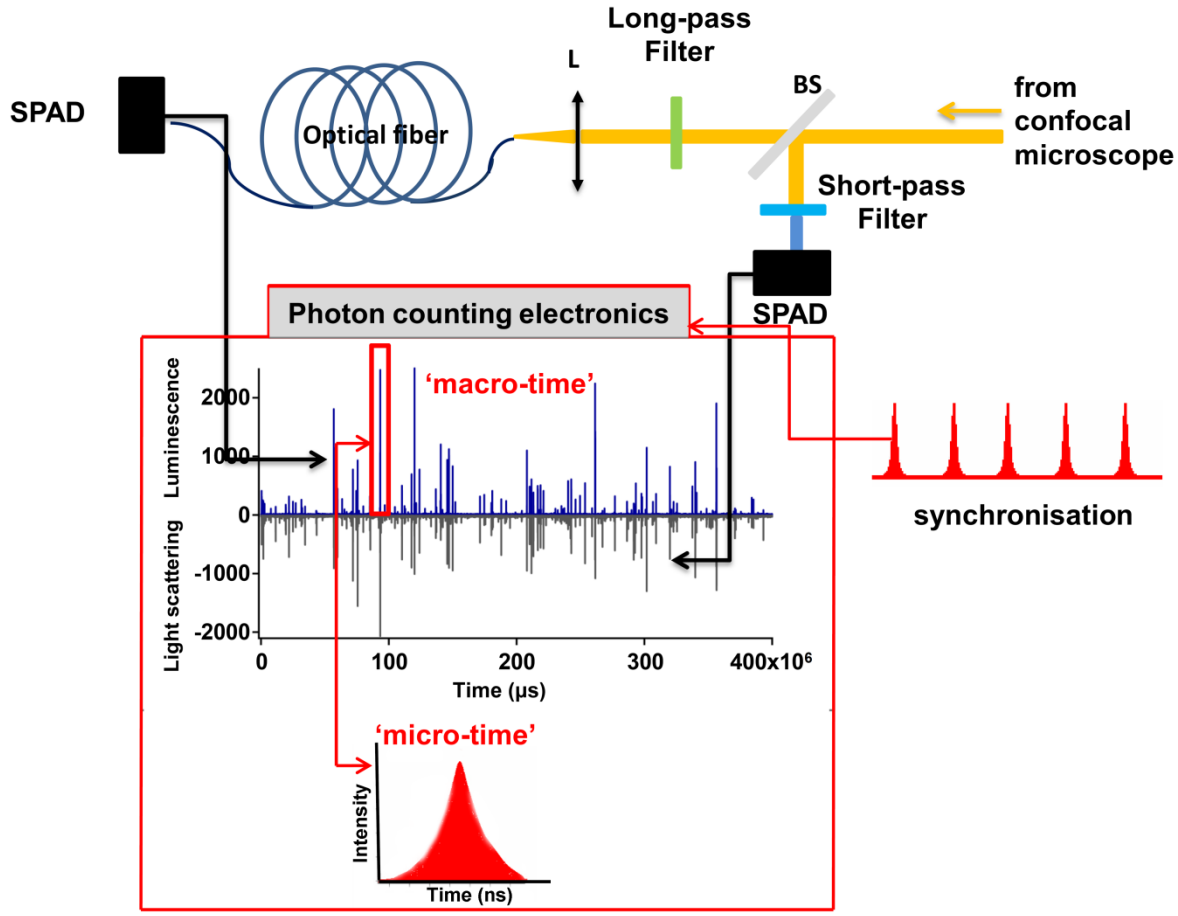

Figure S3 Schematics of the experimental set-up.

The signal emitted by the particles diffusing through the excitation volume of the confocal microscope is split into two channels by a beamsplitter (BS). One of the channels is devoted to spectral analysis and the emitted photons are filtered by a high-pass filter, sent into a long fiber, and detected by a single photon avalanche photodiode (SPAD). The other channel is devoted to light scattering and a low-pass filter selects the photons that are scattered at the excitation wavelength (430 nm). The photon counting electronics record simultaneously arrival times ('macro-times') of the luminescence photons (blue trace) and of the scattered photons (black trace), as well as the time delay between the excitation pulse and the photoelectric detection of each photon ('micro-time'). PTOFS uses the conversion of micro-times (ns) into wavelengths to obtain the spectrum of the bursts, using the time dispersion of different wavelengths in a long (94 meter-long) optical fiber.

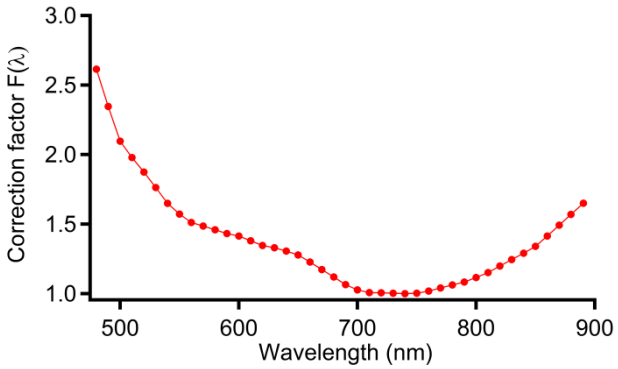

Figure S4. Correction factor F(λ) for the PTOF spectra taking into account the transmission of the optics and SPAD detector quantum efficiency as a function of the wavelength. The corrected PTOF emission spectrum is obtained by multiplying the raw uncorrected spectrum with the correction factor F(λ).

Numerical implementation of the Fraser-Suzuki 'skewed Gaussian' function.

The Fraser-Suzuki function was evaluated numerically using the following Python code. We used the Anaconda Python distribution (2.3.0, 64-bit) with Python 2.7.10 and Numpy 1.9.2. For brevity, we only give the code for the evaluation of the Fraser-Suzuki function as expressed in Eqn. (2) in the main text. It can be readily used in standard curve-fitting routines.

```
# -*- coding: utf-8 -*-

import numpy as np

def _skew_gauss_vec(x, A, x0, w, b):
    """vectorised version of skewed Gaussian, called by skew_gauss
    This function is only called when skew_gauss receives a numpy array
    """
    ndeps = np.finfo(x.dtype.type).eps
    lim0 = 2.*np.sqrt(ndeps)
    # Through experimentation  2*sqrt(machine_epsilon) was found
    # to be a good safe threshold for switching to the b=0 limit
    # at lower thresholds, numerical rounding errors appear
    if (abs(b) <= lim0):
        sg = A * np.exp(-4*np.log(2)*(x-x0)**2/w**2)
    else:
        lnterm = 1.0 + ((2*b*(x-x0))/w)
        sg = np.zeros_like(lnterm)
        sg[lnterm>0] =\
            A * np.exp(-np.log(2)*(np.log(lnterm[lnterm>0])/b)**2)
    return sg

def skew_gauss(x, A, x0, w, b):
    """Fraser-Suzuki skewed Gaussian.

    A: peak height, x0: peak position,
    w: width, b: skewness"""
    if type(x)==np.ndarray:
        sg = _skew_gauss_vec(x, A, x0, w, b)
    else:
        x = float(x)
        ndeps = np.finfo(type(x)).eps
        lim0 = 2.*np.sqrt(ndeps)
        if (abs(b) <= lim0):
            sg = A * np.exp(-4*np.log(2)*(x-x0)**2/w**2)
        else:
            lnterm = 1.0 + ((2*b*(x-x0))/w)
            if (lnterm>0):
                sg = A * np.exp(-np.log(2)*(np.log(lnterm)/b)**2)
            else:
                sg = 0
    return sg

def func(x, A0, xo0, w0, b0, A1, xo1, w1, b1):
    """This function is used for fitting photoluminescence spectra
    of gold nanosphere dimers. It simply calculates the sum of two
    Fraser-Suzuki functions."""
    y = skew_gauss(x, A0, xo0, w0, b0) + skew_gauss(x, A1, xo1, w1, b1)
    return y
```

Absorbance measurements.

The absorption maximum of Rose Bengal in water (0.01 M NaOH) is 549 nm. The absorption at 430 nm is very weak. Consequently, the baseline must be accurately determined. The measurements have been performed on a spectrometer Cary 4000 (Agilent). We have measured the absorption of two solutions of Rose Bengal with a ten-fold difference between the concentrations (Fig. S5). We have verified that the values of the absorbance at 430 nm differ by a factor of 10. This is the case within 10% (0.3574 vs 0.00363).

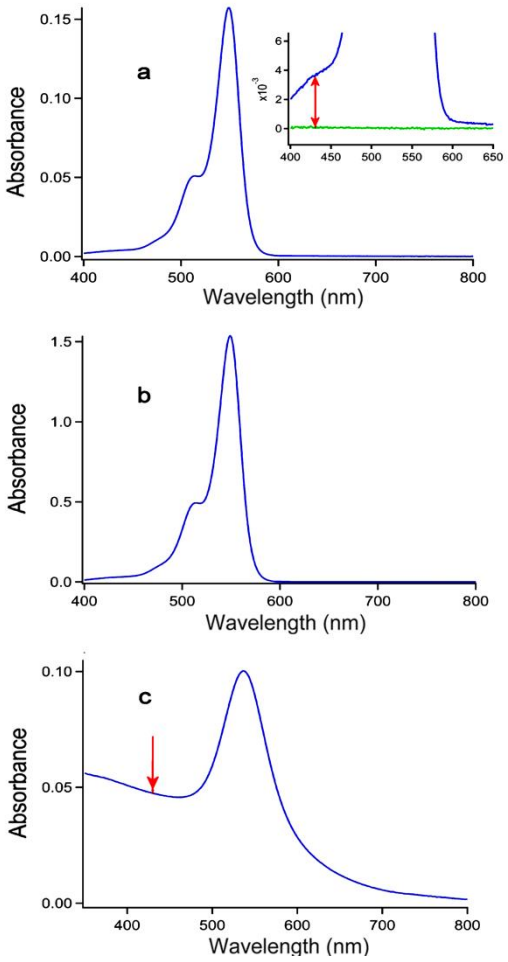

Figure S5. Absorbance spectra of the samples used for measuring photoluminescence quantum yields: solutions of Rose Bengal in 0.01M NaOH (aq) (a+b), and 50 nm gold nanospheres (c). a) solution of Rose Bengal diluted 10 times compared to b). In inset of fig. S5a, zoom of the absorbance curve in the excitation region at 430nm, which is indicated by the red arrow. c) Absorbance spectrum (actually, "extinctance" spectrum) of a solution of gold nanospheres of 50 nm, 10 times diluted compared to the solution of spheres used in the luminescence measurement by PTOFS. The excitation wavelength is indicated by a red arrow.

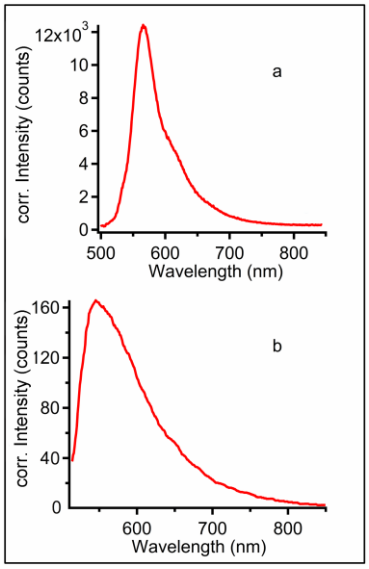

Figure S6. *Corrected PTOF emission spectra* of solutions of Rose Bengal and of 50 nm diameter gold spheres in 0.01M aqueous NaOH. a): Fluorescence of Rose Bengal, same solution than for Fig. S5 a, acquisition time 120s, 0.3 mW, excitation wavelength 430 nm; excitation wavelength 430 nm; b): Luminescence of gold spheres of diameter 50 nm, 10 times more concentrated than the solution used for absorbance measurement of Fig. S5, acquisition time 240s, 0.3 mW, excitation wavelength 430nm, Long-pass filter at 510 nm (Omega optical, 510LP rapid edge).

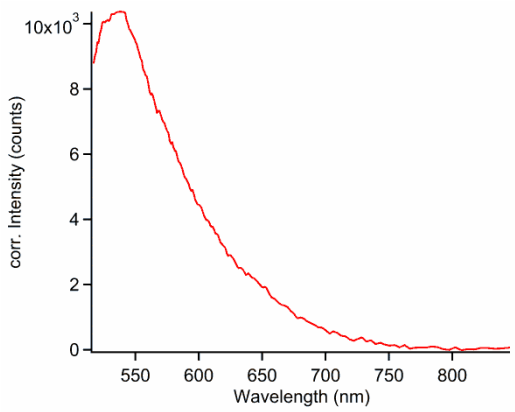

Figure S7. Corrected integrated PTOF ensemble emission spectrum of the monomers of 50 nm diameter gold nanospheres in water (lipoate-stabilised). The peak of the spectrum is 536 nm (±4 nm). Excitation 430 nm, 1.5 mW.

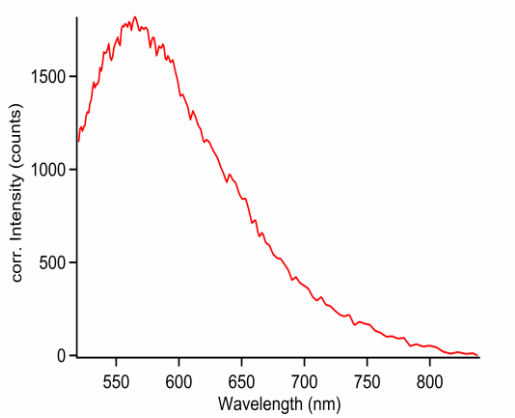

Figure S8. Corrected integrated PTOF ensemble emission spectrum of the monomers of 80 nm diameter gold nanospheres in water (lipoate-stabilised). The peak of the spectrum is 561 nm (±4 nm). Excitation 430 nm, 1.5 mW.

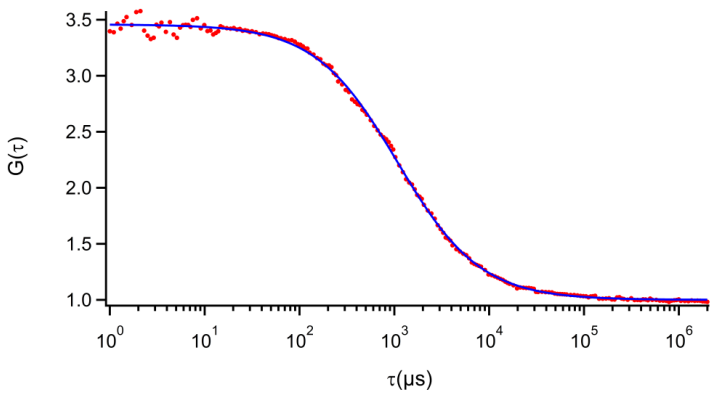

Figure S9. Intensity autocorrelation profile of monomers of 50 nm diameter spherical gold nanoparticles in water (lipoate stabilised). Red dots, experimental data, blue curve fit according to eq. 1 of main text, diffusion time 1140 μs (±20 μs). Excitation 430 nm, 1.5 mW.

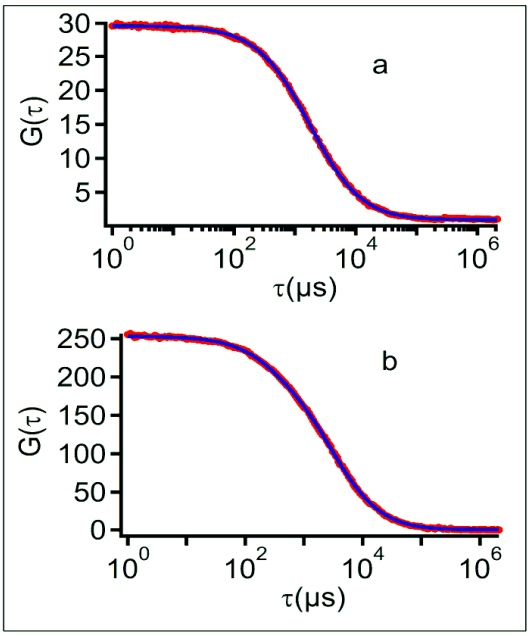

Figure S10. Correlation profiles of the subpopulations of monomers and of gold dimers of spheres of 80 nm diameter gold nanospheres in water. (a) Correlation profile of the monomer subpopulation; red dots, data, blue curve, fit according to eq. 1 of main text. The diffusion time is 1750 μs (±20 μs). (b) Correlation profile of the dimer subpopulation: red dots, data, blue curve, fit. The dimer data can be fitted by a model including a rotation contribution (eq. 2 of main text). The diffusion time is 2800 μs (±20 μs) and the rotation time is 240 (±20 μs). Excitation 430 nm, 1.5 mW.