Electronic Supplementary Information (ESI) for

A Complete Explanation of the Plasmonic Colours of Gold Nanoparticles and of the Bichromatic Effect

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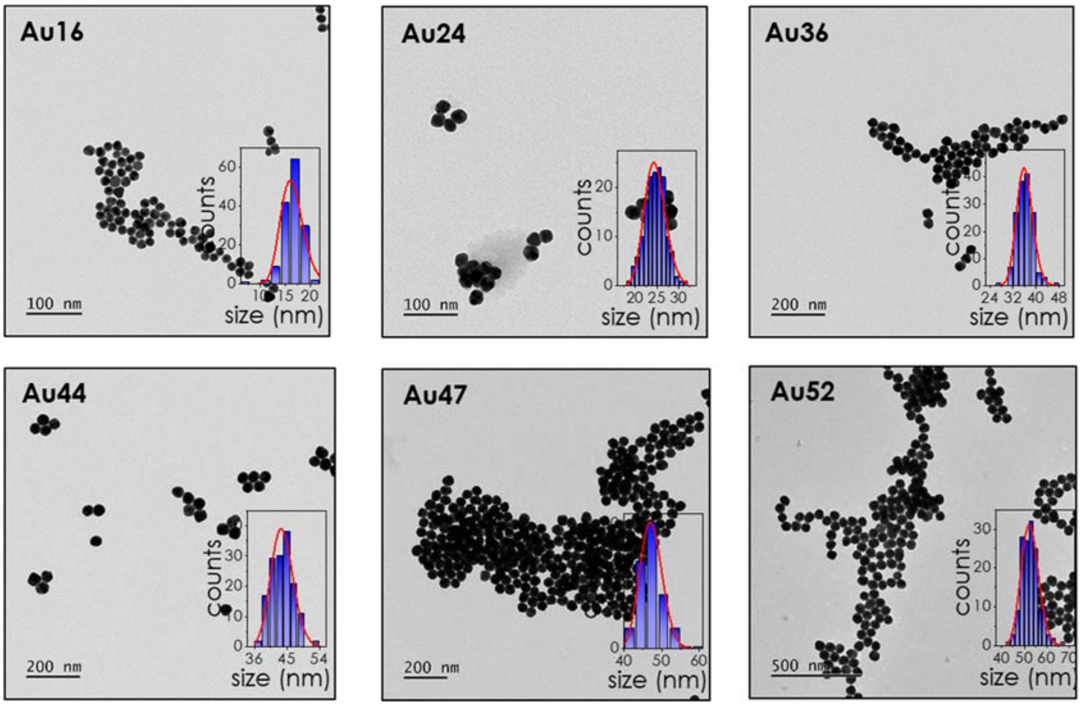
1. TEM images of the twelve samples of the study

After synthesis, each AuNP suspension was analysed with TEM and the nanoparticle diameter was evaluated by measuring the size of at least 200 particles. The corresponding histograms are placed as insets in each TEM image.



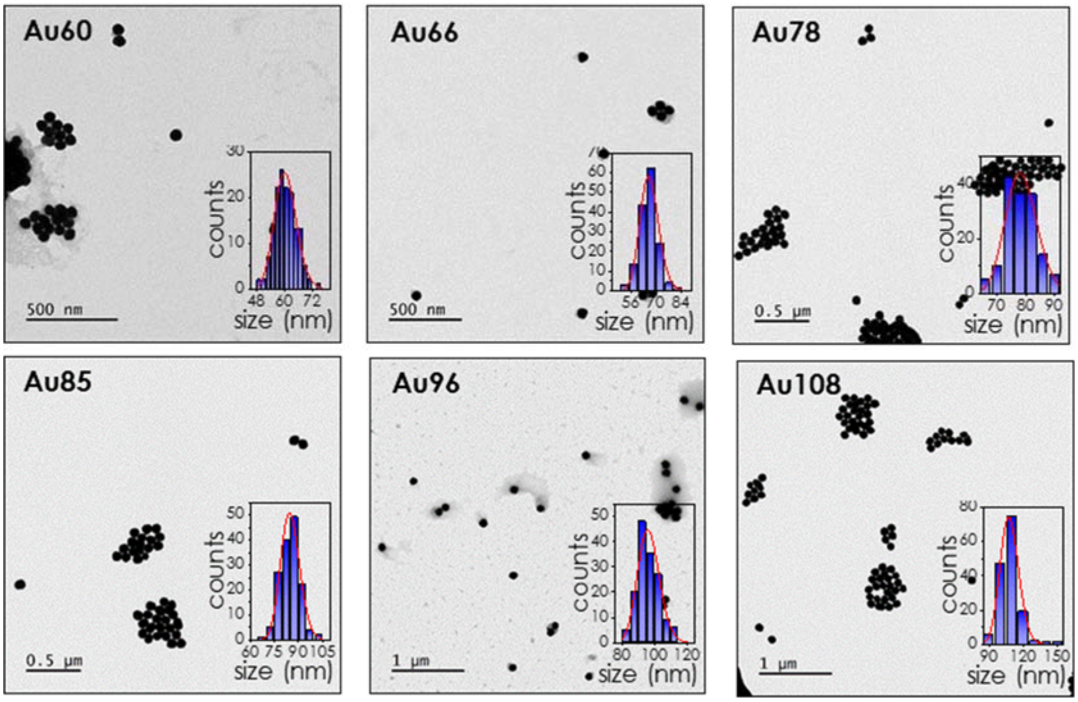


Figure S 1. TEM images of the twelve AuNP suspensions prepared in this study.

2. Determination of the AuNP concentration in our samples based on the methods established by Haiss (2007)

The group of Haiss has published a method in 2007 where they showed that by measuring the extinction spectra of a suspension of gold nanoparticles, they can precisely determine the nanoparticle diameter and their concentration.[1] From the wavelength of the localized surface plasmon resonance (LSPR), they determine the nanoparticle diameter. Using this data, they have access to the molar extinction ε of the nanoparticles Then, by using the value of the absorbance of a wavelength of 450 nm, they deduce the nanoparticle concentration. In the table below, we report our experimental values for the twelve gold suspensions of our study and the corresponding concentrations computed according to Haiss' method.

Sample	**Au16**	**Au24**	**Au36**	**Au44**	**Au47**	**Au52**	**Au60**	**Au66**	**Au78**	**Au85**	**Au96**	**Au108**
A_{450}	0,39198	0,34667	0,4559	0,53065	0,58371	0,62875	0,64155	0,65893	0,65027	0,63395	0,58	0,53
ε /M-1.cm-1	2,79E+08	1,03E+09	3,52E+09	6,48E+09	8,31E+09	1,16E+10	1,75E+10	2,31E+10	3,67E+10	4,50E+10	5,95E+10	7,45E+10
C_{calc} /mol.l^{-1}	1,40E-09	3,37E-10	1,30E-10	8,19E-11	7,02E-11	5,43E-11	3,66E-11	2,86E-11	1,77E-11	1,41E-11	9,73E-12	7,16E-12
[AuNPs] / x10^{18} NPs.m^{-3}	0,8461	0,2027	0,078	0,0493	0,0423	0,0327	0,0220	0,0172	0,0107	0,0085	0,0059	0,0043

Table S1. Experimental values needed for computing the nanoparticle concentration using the method established by Haiss and co-workers.

3. Calculation of the three cross sections for the twelve samples

The absorption, extinction and scattering cross sections of spherical gold nanoparticles are calculated with the Mie theory,[2-4] using the online calculator setup for this study.[5] These calculations are carried out considering water as surrounding medium (*n* = 1.33).

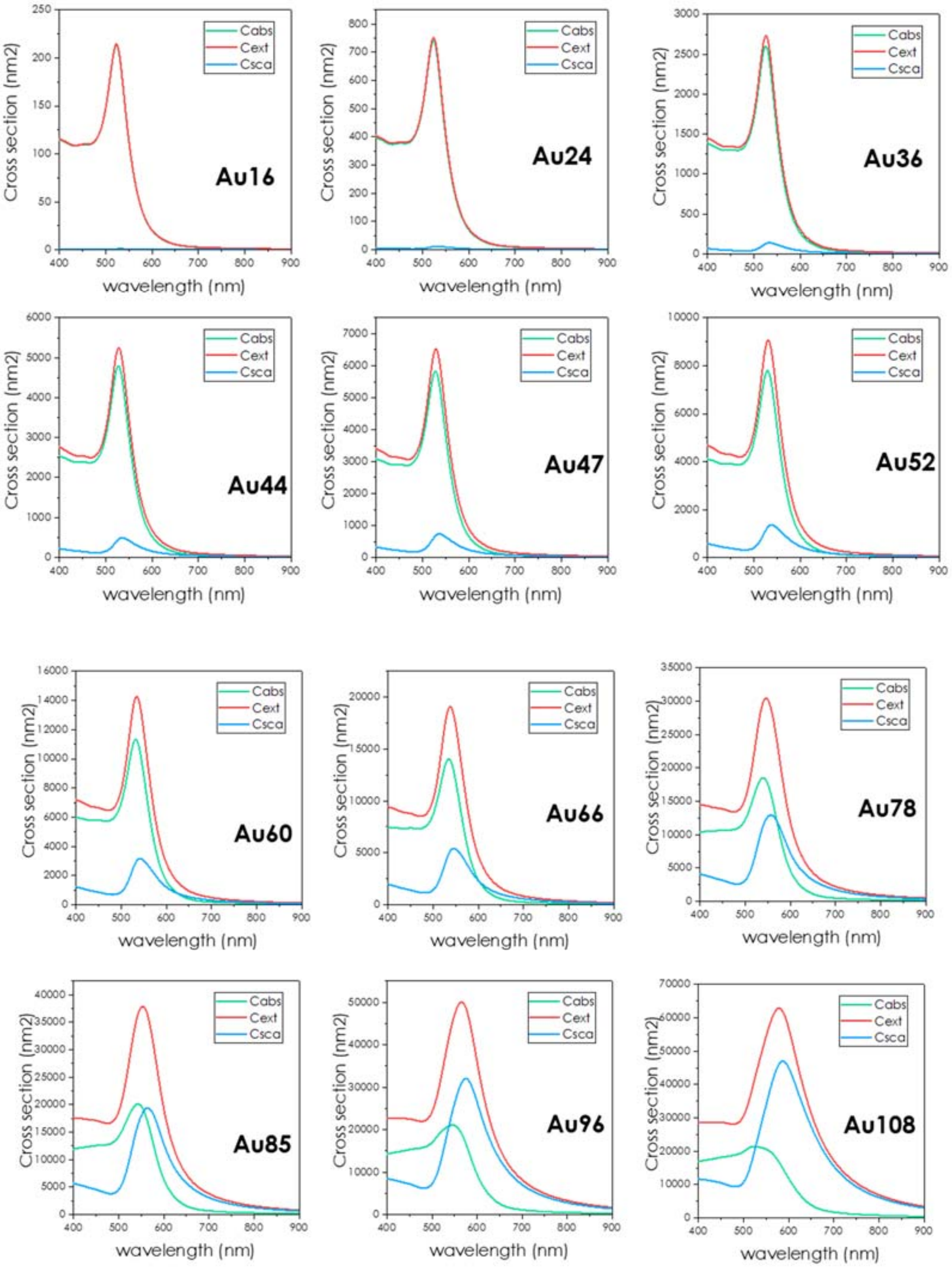


Figure S 2. Absorption, extinction, and scattering cross sections calculated with the Mie theory for the twelve spherical gold nanoparticles suspension considered in this study from 16 nm diameter until 108 nm.

4. Mathematical derivation of the transmission and scattering equations

Here we derive equations (2) and (3) of the main text, that are used to calculate the transmission and diffusion spectra across an assembly of gold spherical nanoparticles.

Case of the transmission.

Suppose that the material under consideration has a thickness d and is situated at position 0 the x axis, as shown in Figure S 3-a. The luminous power impinging on the surface S writes: $I_0 S$. Inside the material, we consider a very thin layer of thickness dx between the positions x and $x + dx$. The intensity at $x + dx$ is $I(x + dx)$ and results from the intensity $I(x)$, minus the portion that has been absorbed by the material. This removed portion of energy is proportional to the extinction cross section times the impinging intensity, times the number of nanoparticles $n \cdot S \cdot dx$ in the thin section dx. Therefore, we can write:

$$S \cdot I(x + dx) = S \cdot I(x) - n \cdot S \cdot dx \cdot \sigma_{ext} \cdot I(x) \tag{S1}$$

Since $I(x + dx) - I(x) = (dI/dx) \cdot dx$, the equation simplifies into:

$$\frac{dI}{dx} = -n \cdot \sigma_{ext} \cdot I(x) \tag{S2}$$

This last equation can be solved easily into $I(x) = B\ \exp(-\ n\sigma_{ext}x)$ where B is an integration constant. Since $I(x) = I_0$, we can determine the constant B and write:

$$I(x) = I_0\ \exp(-\ n\sigma_{ext}x) \tag{S3}$$

Moreover, after crossing the full materials, the light intensity is given by:

$$I_T = I_0\ \exp(-\ n\sigma_{ext}d), \tag{S4}$$

which is equivalent to the Beer-Lambert law, that writes

$$I_T = I_0 \times 10^{\varepsilon_{AuNP} \cdot C \cdot d} \tag{S5}$$

By equating the last two equations, we can write: $n \cdot \sigma_{ext} \cdot d = \ln 10 \cdot \varepsilon_{AuNP} \cdot C \cdot d$, which corresponds to the relation given in the main text.

Equation (S4) is used to predict the transmitted spectrum of a material which contains nanoparticles whose extinction cross section is known for all the wavelengths of interest.

Case of the diffuse reflectance spectra

The derivation of equation (3) of the main text is similar and follows the processes depicted in Figure S 3-b.

We consider a thin section of the material situated between the positions x and $x + dx$ over a beam section S. This portion of material contains $n \cdot S \cdot dx$ nanoparticles. These nanoparticles are irradiated with an intensity $I(x)$ given by equation (S3). Therefore, the luminous power backscattered by the portion dx of material writes at position x :

$$S \times dI_{diff}(x) = I_0\ \exp(-\ n\sigma_{ext}x) \times n \cdot S \cdot dx \times \sigma_{sca} \tag{S6}$$

The luminous intensity that finally exits the material at $x = 0$ after the backscattering events at x, is absorbed through the material one more time and writes:

$$dI_{diff}(x) = I_0\ \exp(-\ 2n\sigma_{ext}x) \times n \cdot dx \times \sigma_{sca} \tag{S7}$$

The integration of equation (S7) over the full width of the material from $x = 0$ to $x = d$, finally yields:

$$I_{Diff} = \frac{1}{2} I_0 \frac{\sigma_{sca}}{\sigma_{ext}} [1 - \exp(-2\sigma_{ext} \cdot n \cdot d)] \tag{S8}$$

As explained in the main text, Equation (S8) consider only the exact back-scattering at 180° whereas the measure with an integrating sphere integrates over all the solid angles of a half space. Therefore Equation (S8) underestimates the total energy back reflected. In order to correct this simplification without producing a heavy mathematical formulation, the equation is adapted by adding a coefficient β in the following way:

$$I_{Diff} = \frac{1}{2} \beta I_0 \frac{\sigma_{sca}}{\sigma_{ext}} [1 - \exp(-2\sigma_{ext} \cdot n \cdot d)] \tag{S9}$$

The value $\beta = 0.2$ yields a correct agreement between measures and calculations. This equation (S9) is the one used in the main text and provides an excellent match between the diffuse reflectance spectra and the simulated spectra.

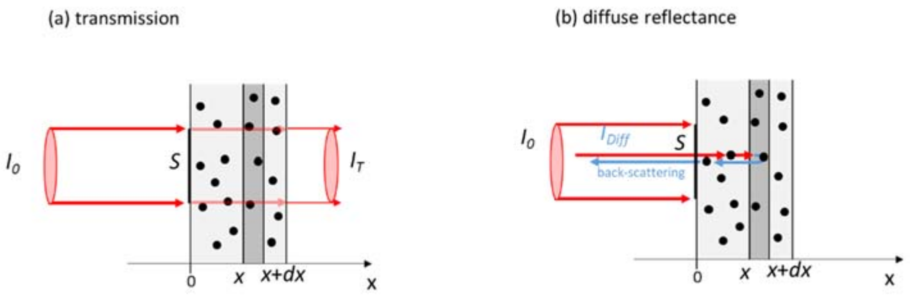
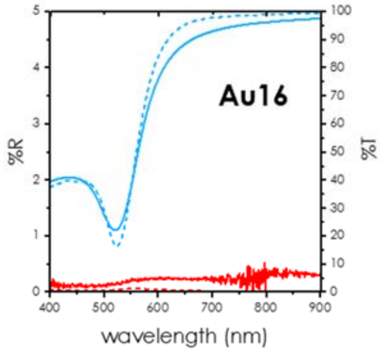
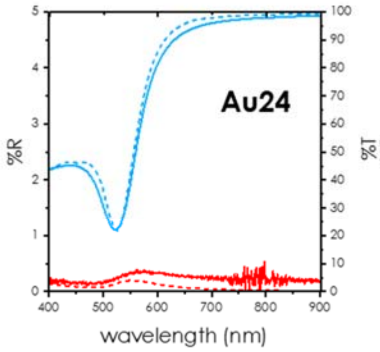


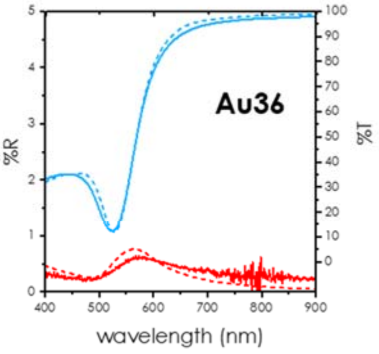
Figure S 3. Schemes for calculating the transmitted (a) and the diffused (b) light intensities by an assembly of spherical nanoparticles. In the case of the diffuse reflectance we consider only the 180° back scattered light beam.

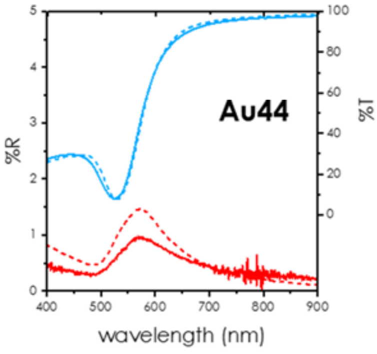
5. Results of the calculation for all the transmitted and diffused spectra

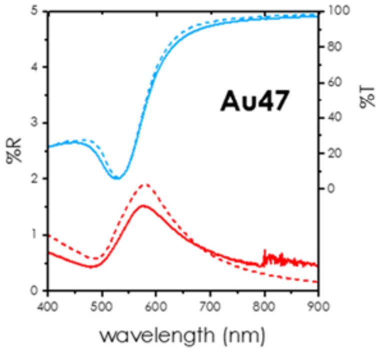
The twelve figures below display the full results for our twelve samples. Each graph displays the transmitted spectra (blue lines) and the diffused spectra (red lines). The simulations are plotted according to equations (2) and (3) of the main text or equations S4 and S9 of this ESI. For the spectra in diffusion the value $\beta = 0.2$ was used. The comparison between these simulated spectra and the experiments show an excellent agreement.

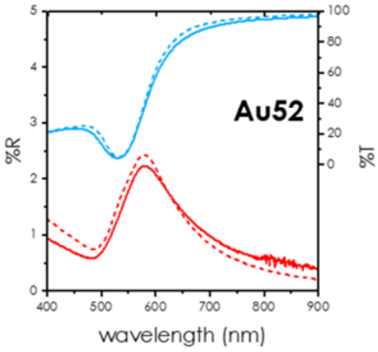












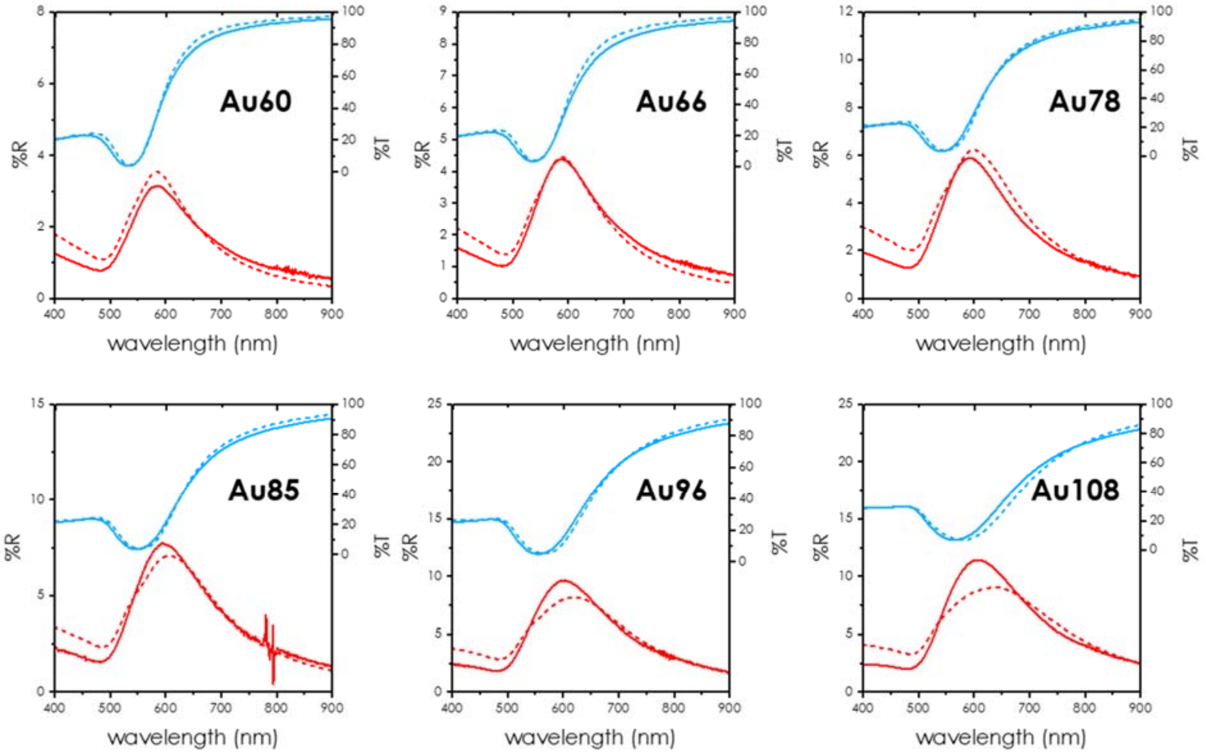
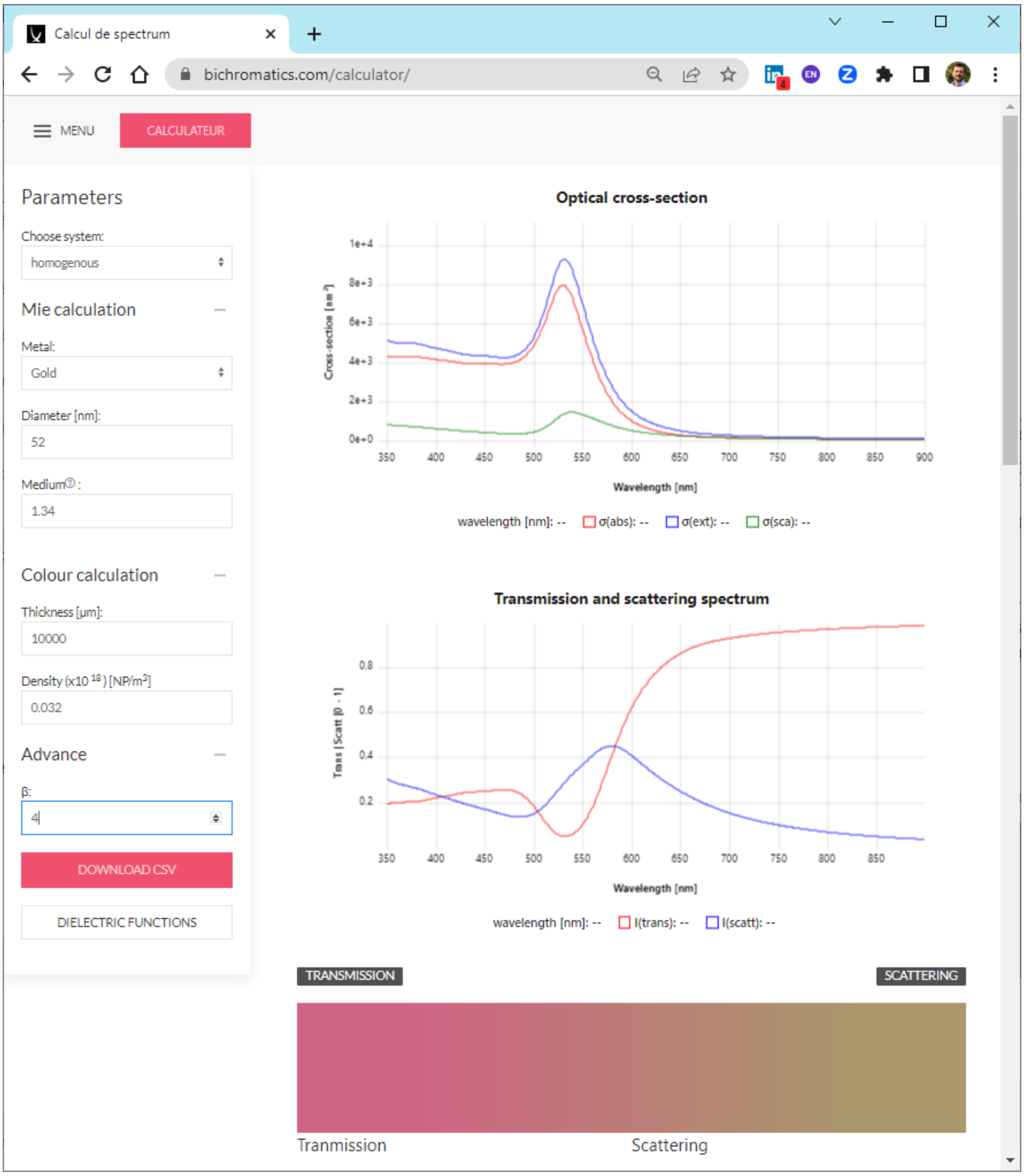


Figure S 4. Transmitted spectra (red lines and right scale) and diffuse reflectance spectra (blue lines and left scale) for the twelve spherical AuNPs considered in this study. On each graph the spectra calculated from Equations (2) and (3) are represented with the dotted lines, whereas the experimental curves are plotted in solid lines.

6. Web interface developed for Bichromatics

The full calculations of the spectra presented in Figure S4 were implemented into an online calculator.[5] Its interface is presented below and it allows an immediate calculation of three main data:

1- The three optical cross sections (extinction, absorption and scattering) according to the Mie theory.
2- The two spectra (transmission and diffusion reflection) for a given material containing a class of nanoparticles. These calculations are carried out according to equations (2) and (3) of the main text or equations S4 and S9 of this ESI.
3- The colours perceived in transmission and in diffusion if the light source is a D65 illuminant. These two colours are expressed in the various colorimetric coordinates: XYZ, *L*a*b**, L*C*h* and RGB.



Parameters

Choose system: homogenous

Mie calculation

Metal: Gold

Diameter [nm]: 52

Medium: 1.34

Colour calculation

Thickness [µm]: 10000

Density (x10 ^{18}) [NP/m ^{3}]: 0.032

Advance

β: 4

Figure S 5 Example of the web interface and the results in the case of spherical 54 nm AuNPs in water (*n* = 1.34). The resulting colour in case of a thickness of 10 mm and a NP density of 0.032x10 ^{18} NP/m ^{3} is represented in the bottom coloured rectangle. This AuNPs suspension is pink in transmission and green-brown in scattering.

7. Values of the colours for the twelve samples

Using the web interface developed for this work, we present in the table below the colour values within the L*a*b coordinates for our 12 samples. These values are the calculated values.

Sample	Au16	Au24	Au36	Au44	Au47	Au52	Au60	Au66	Au78	Au85	Au96	Au108
L*a*b*	75.58	78.15	71.09	65.67	63.55	60.39	55.76	51.68	45.43	42.45	41.88	43.41
	41.65	37.77	47.08	52.60	54.31	56.19	57.14	56.68	49.36	41.48	24.67	8.02
	13.46	9.65	11.44	11.12	10.46	8.22	2.34	-2.95	-15.47	-21.96	-28.50	-30.08
L*C*h	75.58	78.15	71.09	65.67	63.55	60.39	55.76	51.68	45.43	42.45	41.88	43.41
	43.77	38.98	48.44	53.76	55.31	56.79	57.19	56.76	51.73	46.94	37.70	31.13
	17.91	14.33	13.66	11.93	10.90	8.32	2.34	357.02	342.60	332.11	310.88	284.93
sRGB	264.51	264.57	257.93	249.06	244.68	236.69	221.59	206.51	172.33	148.96	115.62	84.37
	155.01	165.74	137.82	117.30	109.63	98.86	85.37	75.16	69.45	71.72	86.03	100.73
	163.43	177.06	155.40	142.04	137.81	133.60	131.78	130.14	134.45	137.10	145.94	152.24
aRGB	239.44	241.33	231.20	220.83	216.14	208.05	193.70	179.84	150.47	131.51	107.81	89.84
	153.55	164.22	136.59	116.57	109.15	98.81	86.00	76.40	71.08	73.20	86.65	100.63
	161.60	175.11	153.30	139.87	135.60	131.29	129.21	127.43	131.43	134.00	142.76	149.16

Table S2. Colour coordinates for the transmission

Sample	Au16	Au24	Au36	Au44	Au47	Au52	Au60	Au66	Au78	Au85	Au96	Au108
L*a*b*	8.44	19.57	39.49	52.56	57.26	64.61	75.16	81.42	81.19	81.86	80.91	80.89
	-3.62	-6.76	-5.51	-2.53	-1.07	1.28	4.97	8.17	11.44	12.55	12.45	11.99
	6.19	10.26	17.63	23.01	24.98	27.98	32.01	34.20	33.32	32.80	31.50	30.54
L*C*h	8.44	19.57	39.49	52.56	57.26	64.61	75.16	81.42	81.19	81.86	80.91	80.89
	7.17	12.29	18.47	23.15	25.01	28.01	32.40	35.16	35.23	35.12	33.87	32.81
	120.31	123.39	107.36	96.26	92.45	87.38	81.17	76.56	71.06	69.06	68.44	68.56
sRGB	23.10	43.04	94.77	135.39	151.16	176.42	214.11	238.63	242.94	246.51	242.96	241.70
	25.52	49.78	94.83	125.49	136.64	154.34	180.17	195.15	192.42	193.54	191.08	191.36
	14.84	32.21	64.11	85.81	93.81	106.74	126.31	138.64	139.90	142.72	142.70	144.42
aRGB	29.98	48.77	94.96	131.55	145.85	168.99	203.93	226.53	229.27	232.35	228.98	228.05
	31.46	53.03	95.00	124.55	135.44	152.90	178.66	193.75	191.00	192.13	189.65	189.92
	22.79	38.12	67.64	88.41	96.17	108.80	128.08	140.28	141.28	143.95	143.79	145.40

Table S3. Colour coordinates for the diffusion

References

1. W. Haiss, N. T. K. Thanh, J. Aveyard and D. G. Fernig, *Analytical Chemistry*, 2007, **79**, 4215-4221.
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3. K. L. Kelly, E. Coronado, L. L. Zhao and G. C. Schatz, *J. Phys. Chem. B*, 2003, **107**, 668-677.
4. D. Tzarouchis and A. Sihvola, *Appl. Sci*, 2018, **8**, 184.
5. W. L. Watkins and O. Pluchery, Bichromatics, spectrum calculator, www.bichromatics.com/calculator/, 2020).