Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Spatial Organization and Optical Properties of Layer-by-Layer Assembled Upconversion and Gold Nanoparticles in Thin Films

Jun Xiang, Xia Tong, Feng Shi, Paul-Ludovic Karsenti and Yue Zhao*

Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, J1K 2R1, Canada.
Corresponding Author to Prof. Yue Zhao. E-mail: yue.zhao@usherbrooke.ca;

Table S1. Size and Zeta Potential of Nanoparticles

Sample	Physical size [nm][a]	Zeta potential [mV][b]
UCNP-PAA[c]	—	-33.2
AuNP[d]	58.1	-41.5

[a]The values are obtained from TEM statistics over 100 particles. [b]Measured by a Malvern Zetasizer Nano ZS ZEN3600 system. Results are given in number mean. [c]pH 6.0 in ultrapure H_2O. [d]pH 8.0 in 20 mM Tris buffer solution.

Table S2. Linear Regression (y = a + b·x) of the Plots of Luminescence Intensity (y) vs. Number of Bilayer (x) for Different Emission Peaks.

Wavelength [nm]	Intercept		Slope		R-square
	a	Std. Error	b	Std. Error	
451	35.74739	9.8602	1438.887722	19.08683	0.99873
346	34.12757	4.3579	1259.55466	23.15576	0.99786
475	45.46109	7.19823	576.35443	8.15784	0.99893
362	42.39889	4.57817	561.50592	8.94388	0.99355
579	41.28572	3.74999	136.94878	2.25938	0.99783
511	47.33908	4.56176	52.29483	1.51735	0.99540

1. TEM

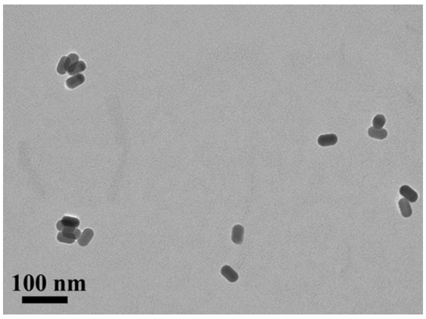

Figure S1. TEM image of UCNP functionalized with poly(acrylic acid) (PAA).

2. FTIR

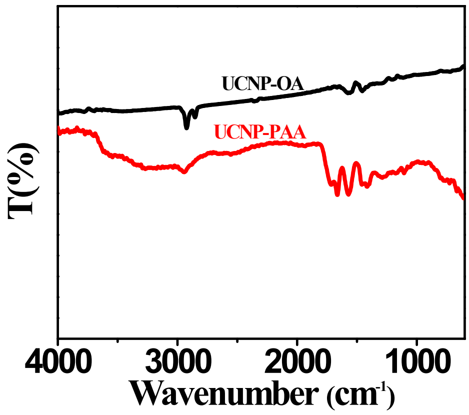

Figure S2. FT-IR spectra of UCNP-OA (oleic acid) and UCNP-PAA.

3. UV-vis-NIR

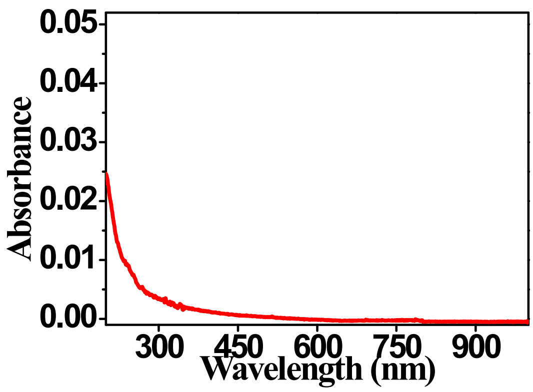

Figure S3. UV-vis-NIR extinction spectrum of $(UCNP\text{-}PAA/PAH)_{11}$.

4. Upconversion Luminescence

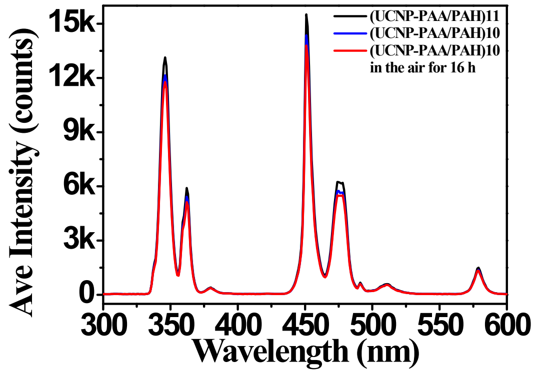

Figure S4. UCL emission spectra of $(UCNP\text{-}PAA/PAH)_{10\ or\ 11}$ LBL films (λ_{ex}=980 nm, 2.55 kW cm^{-2}): $(UCNP\text{-}PAA/PAH)_{10}$ (blue); $(UCNP\text{-}PAA/PAH)_{10}$ kept in the air for 16 h (red); $(UCNP\text{-}PAA/PAH)_{11}$ (black).

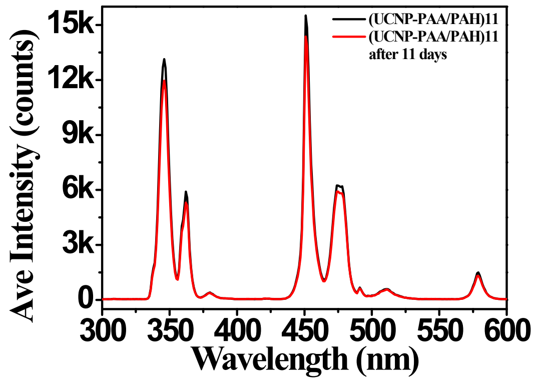

Figure S5. UCL emission spectra of $(UCNP\text{-}PAA/PAH)_{11}$ film (λ_{ex}=980 nm, 2.55 kW cm^{-2}): 0 h (black); after keeping in the air for 11 d (red).

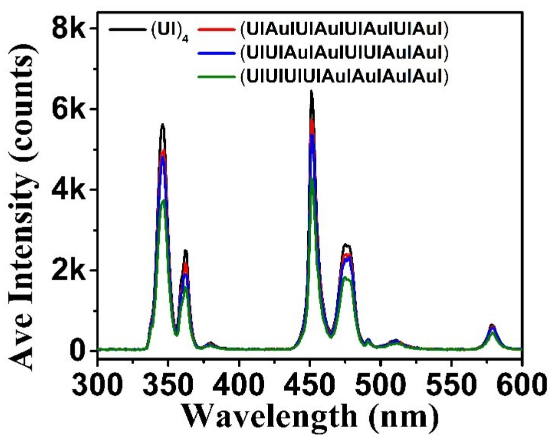

Figure S6. UCL emission spectra for a 4-bilayer UCNP and three UCNP/AuNP multilayers containing the same number of UCNP bilayers and prepared using different LBL deposition sequences. The spectra were recorded under the same 980 nm excitation intensity of 2.55 kW/cm^2.

5. LBL Assembly of AuNP Bilayers

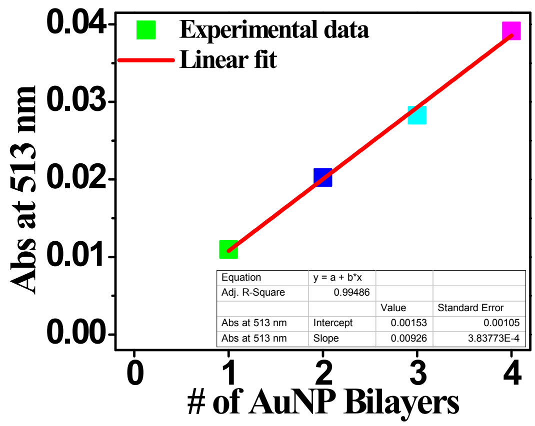

Figure S7. Linear fit of the plot of absorbance at 513 nm vs. number of AuNP bilayers.

6. NIR Laser Power Density Calibration

The real power and the beam diameter (*d*) are two key parameters used to calculate the real excitation power density. At first, the real irradiation power at the LbL site was accurately measured and the data were summarized in **Table S3**. Then, the beam diameter was measured by a Knife-edge method. Briefly, the razor blade was mounted on a wide metal sheet on the motorized stage, and moved in a direction (z-axis) perpendicular to the propagation direction of the 980 nm light. Each power was recorded while varying the z-axis position over a range from 3.00 mm to 5.00 mm (in steps of 0.05 mm). Measured power profile of Gaussian beam can be fitted with an error function, where we got a standard deviation of 0.06373, see **Figure S6**. To get the FWHM, it has to multiply by $2\sqrt{2ln2}$. So the valid beam diameter was ~150 μm and an irradiation area of 0.01767 mm^2 ($S_{laser\ beam} = (\frac{d}{2})^2\pi$) was used to calculate the average exciting power density.

Table S3. The Relationship between the Output Power of 980 nm Laser and its Real Power when the Light Beam Reached Sample

Output power/mW	1000	2000	3500
Real power/mW	450.5	1113.3	2080.0
Power density/Kw cm^{-2}	2.55	6.30	11.77

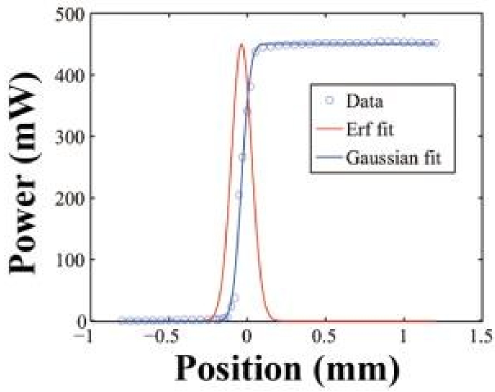

Figure S7. The power distribution of 980 nm laser across the calibrated beam. The plot was fitted by Gauss curve (red line).

References

1. G. Ok, S.-W. Choi, K. Park and H. Chun, *Sensors*, 2013, **13**, 71-85.