Supporting Information

MATERIALS AND METHODS

The starting compounds, ruthenium chloride ($RuCl_3 \cdot xH_2O$), 2,2´-bipyridine-4,4-dicarboxylic acid (dcbpy), 2,4,6-trimercapto-1,3,5-triazine ($C_3S_3N_3H_3$ – tmt), trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$ – cit) and tetrachloroauric acid ($HAuCl_4$) were purchased from Sigma-Aldrich. All the reagents employed were of analytical grade and used as supplied. Citrate-stabilized gold nanoparticles (*cit*-AuNP) were obtained according to the method introduced by Turkevich[45] and modified by Frens[46] They were always freshly prepared and monitored by UV-visible spectroscopy, dynamic light scattering (DLS) and hyperspectral microscopy. The UV-vis absorption spectra were recorded on a Hewlett Packard 8453A diode-ray spectrophotometer, in the 190 to 1100 nm range.

Analysis for $[Ru(dcbpy)_2(tmt)]Cl \cdot 4H_2O$ (MW = 801.4 g): C: 37.49; H: 3.07; N: 10.65; Calc. (%): C: 37.14; H: 3,00; N: 11.23. ^{1}H-NMR(ppm): H(α)=9.77, H(α')=8.70, H(β)=7.96, H(β')=7.96, H(δ)=8.80, H(δ')=8.76, H(6)=7.79, H(6')=7.64, H(5)=7.34, H(5')=7.34, H(3)=8.63 and H(3')=8.61. ESI-MS: $[Ru(dcbpy)_2(tmt)]^+$=765.9 m/z.

Theoretical Calculations: Geometry optimization was performed at the MM+ level using a conjugated gradient method implemented in the HyperChem Professional 8.05 program, adopting 1×10^{-7} kcal Å^{-1} mol^{-1} as the convergence criterion. SCF molecular orbital calculations were performed at RHF level using ZINDO/S method and the default parameters $k_{p\sigma}$ = 1.267 and $k_{p\pi}$ = 0.585. The electronic spectra were calculated considering single configuration interactions

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(CI) in an active space of 20 frontier molecular orbitals (MO), 10 highest occupied and 10 lowest unoccupied MOs.

Table S1: Percent contribution of Ru(II), dcbpy and tmt wave functions on the MOs of complex (1), calculated by ZINDO/S.

Molecular Orbital	Contribution per species		(%)
	Ru	dcbpy	tmt
109	0.04	99.83	0.02
110	0.06	99.81	0.02
111	0.08	99.91	0.01
112	0.05	99.92	0.02
113	0.04	99.84	0.01
114	0.07	99.81	0.01
115	77.77	16.94	5.06
116	71.8	19.43	9.25
117 HOMO	60.15	36.11	3.52
118 LUMO	0.43	30.73	68.83
119	6.58	65.64	27.78
120	11.20	86.46	2.7
121	0.59	1.90	97.51
122	1.43	98.00	0.54
123	1.96	97.58	0.42

124	0.58	98.81	0.54
125	2.06	97.67	0.25
126	0.39	0.31	81.25

Table S2: Assignment of complex electronic spectra.

λ_{max} / nm	Assignment	Molecular Orbital	Oscillator Strength
248	n→π*	112 → 123	0.0351
300		116 → 124	0.0390
305	π→π*	117 → 123	0.0481
369	MLCT-1: Ru→ dcbH$_2$	117 → 124	0.1907
		117 → 125	
465	MLCT-3: Ru→ TMT	115 → 118	0.1364
505-528	MLCT-2: Ru→ dcbH$_2$	117 → 119	0.1132
		117 → 118	0.0002

The pK_a values were determined by spectrophotometric titration of 3×10^{-5} mol L^{-1} complex solution in H$_2$O/ethanol mixture (3:1 v/v) containing 0.5 molL^{-1} NaCl as electrolyte, using a quartz cuvette. Three acid-base equilibria were registered in the pH 1 to 13 range.
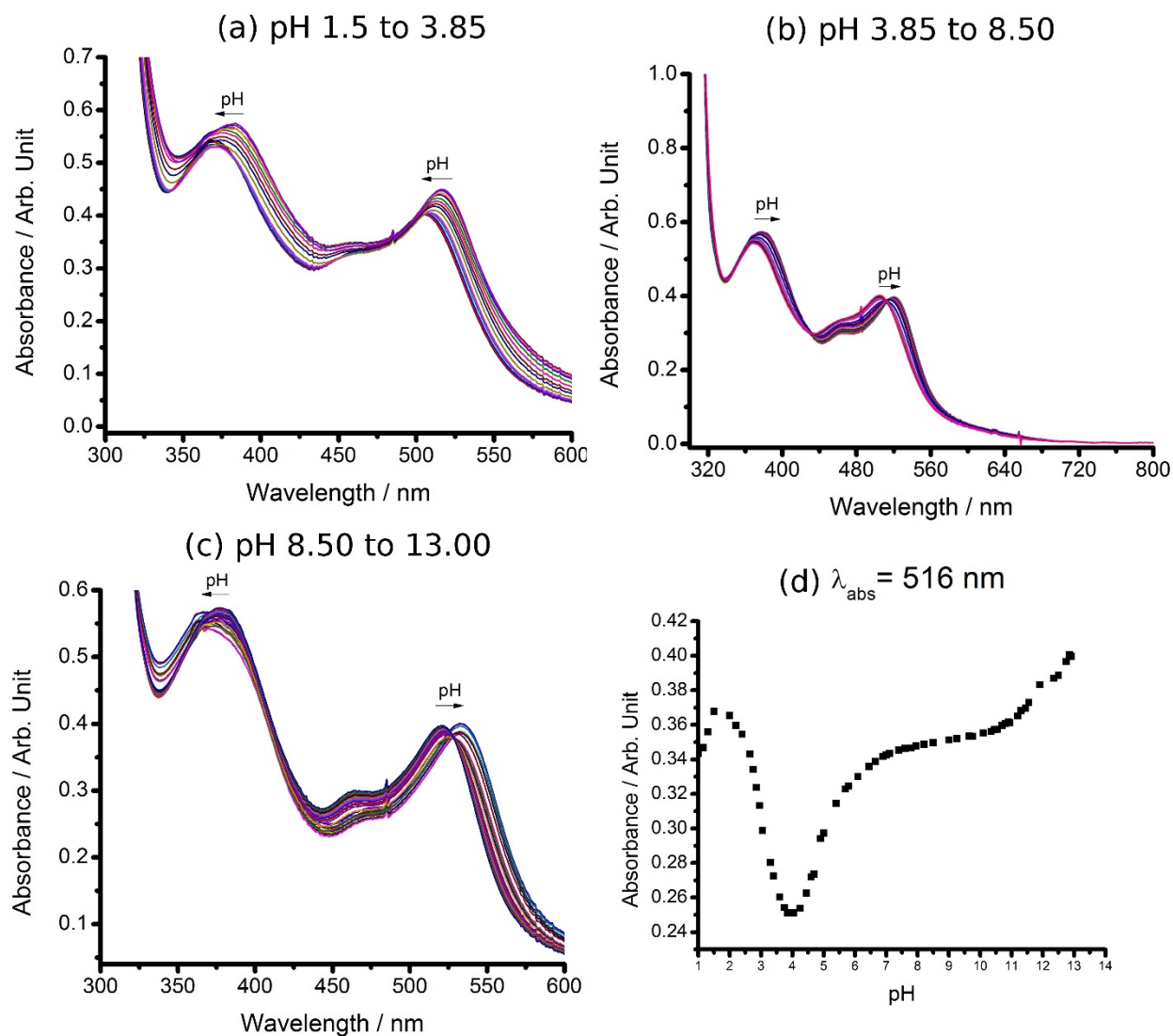
Figure S 1: Electronic spectra for the spectrophotometric titration in the range of pH 1.5 to 3.85 (a), 3.85 to 8.50 (b) and 8.50 to 13.0 (d). Plot of the absorbance at 516 nm as function of pH
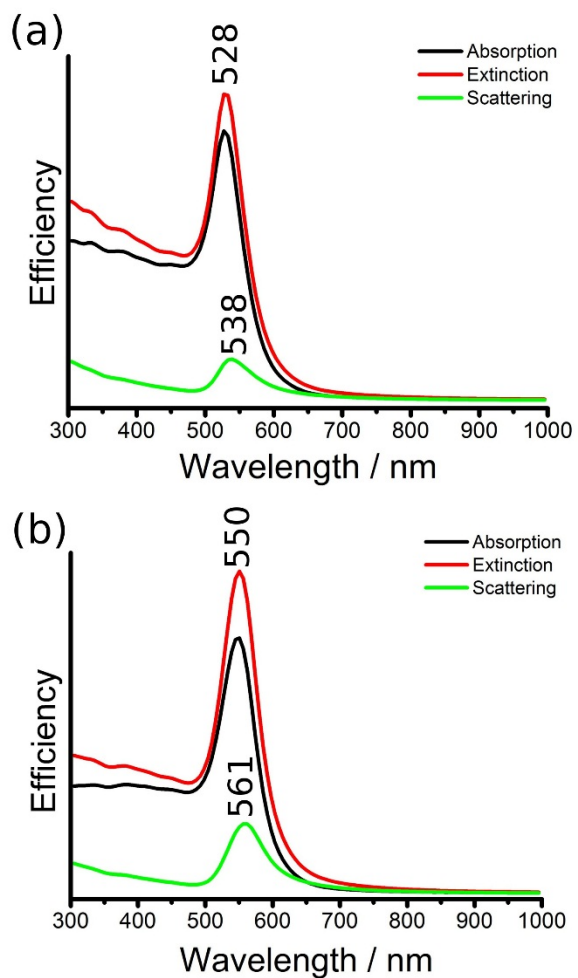
(a)

(b)

Figure S 2. Calculated absorption (black line), scattering (green line) an extinction (red line)

spectra for spherical gold nanoparticles with 45 nm in water (a) an in silica with refractive index
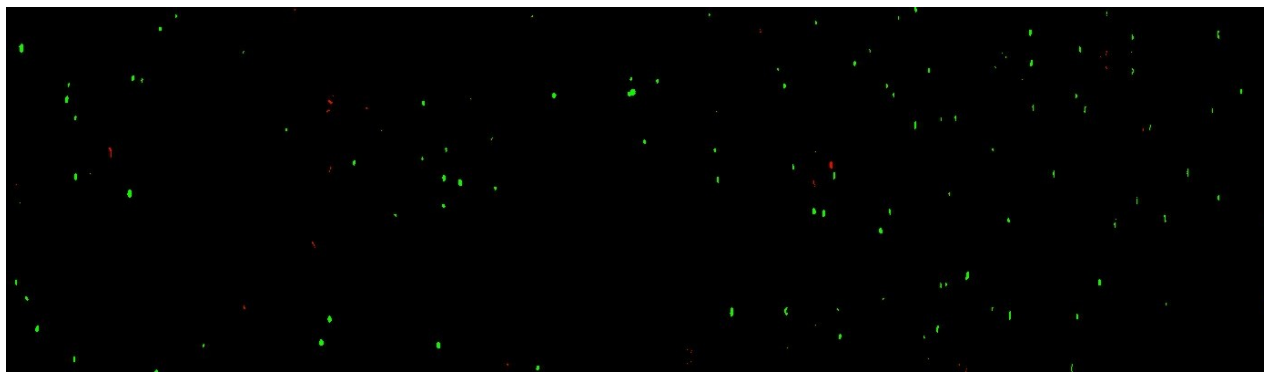
of 1.52 (b)

Figure S 3: Mapping image for AuNP-[Ru(dcbpy)$_2$(tmt)] immobilized on MPTS-coated glass. The green dots pixels reflect scattering spectra of the isolated gold nanoparticles, and the few red dot pixels arise from the distinct scattering spectra the nanoparticle dimers.
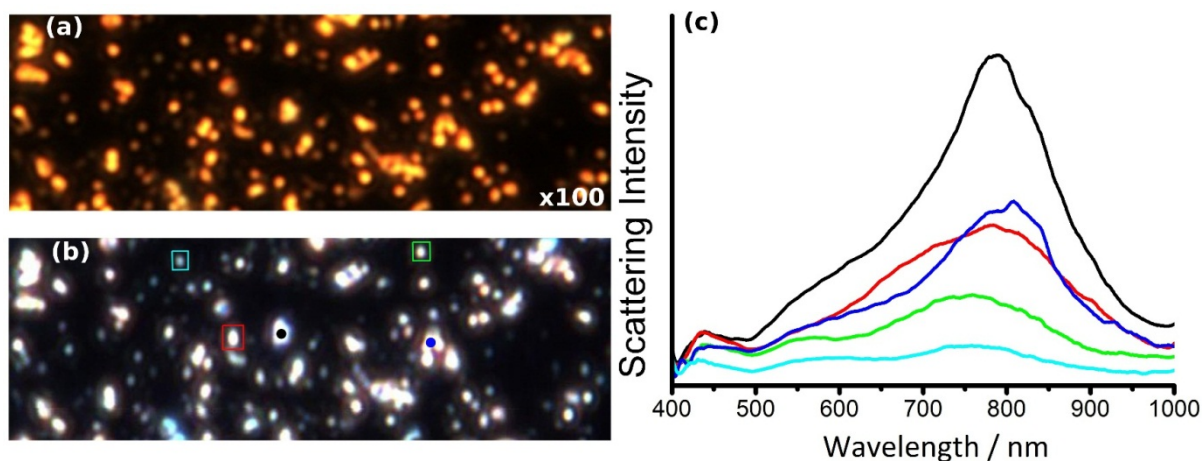

Figure S 4. Dark-field microscopy (a), hyperspectral image (b) and scattering spectra (c) of a sample prepared with Turkevich AuNP in the absence of the [Ru(dcbpy)$_2$(tmt)]$^{3-}$ complex, immobilized on a MPTS funcionalized glass. The spectral spots are indicated in Fig. S3b, with the corresponding colors of the scattering spectra.
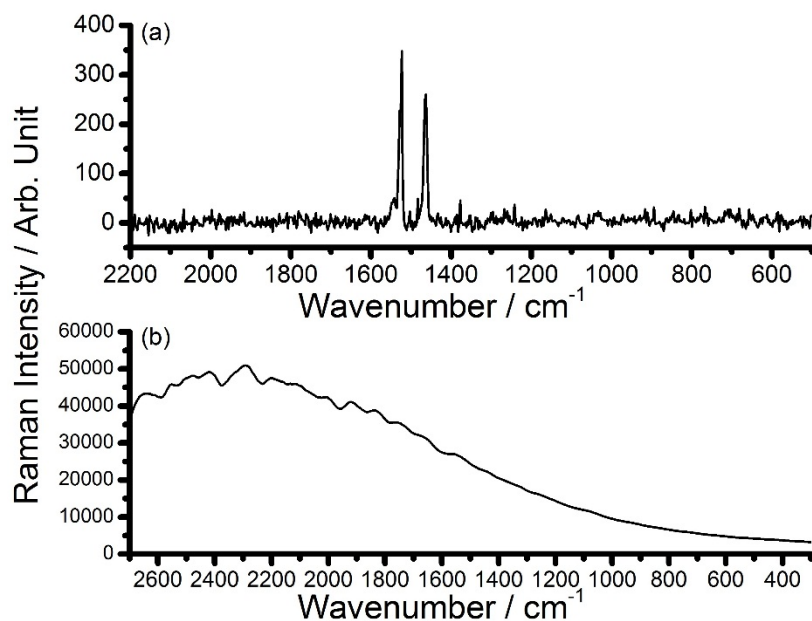
Figure S 5. Resonance Raman spectra of 2 x 10^{-5} molL^{-1} solution of $[Ru(dcbpy)_2(tmt)]^{-3}$ with excitation wavelength of 532 nm, laser power of 7.5mW and integration time of 120s (a). Raman spectra of 10 mmol L^{-1} solution of $[Ru(dcbpy)_2(tmt)]^{-3}$ recorded at 633 nm, laser power of 7.5 mW and integration time of 120s (b).
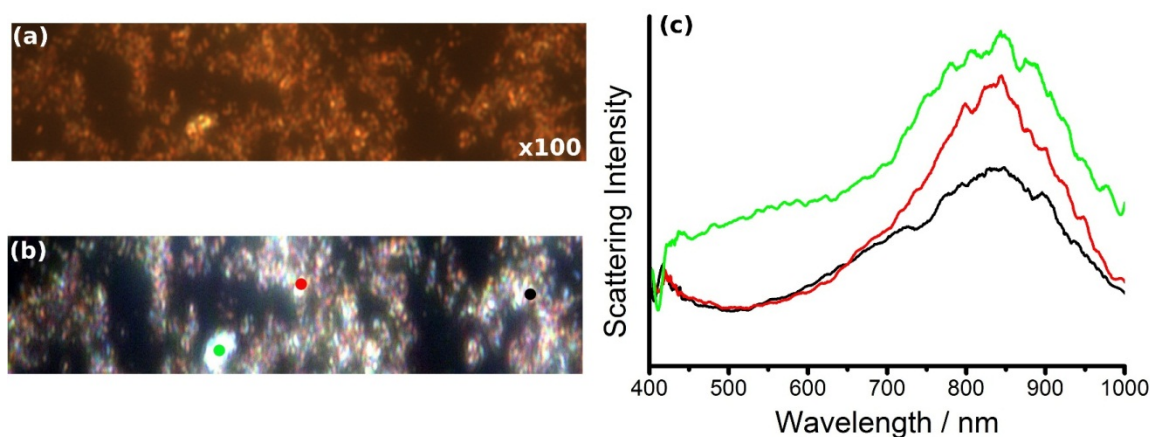
Figure S 6. Dark-field microscopy (a), hyperspectral image (b) and scattering spectra (c) of a sample prepared with agglomerated Turkevich AuNP (+ NaCl 3 mmol L^{-1}) on MPTS functionalized glass.