

Electronic Supplementary Information (ESI)

Gold nanocomposites with rigid fully conjugated heteroditopic ligands shell as nanobuilding blocks for coordination chemistry

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Experimental

All reagents and solvents were purchased from Aldrich and used as received. (4'-pyridine)-2,2',6',2''-terpyridine (*TerPy*),^{1,2} 2,9-dimethyl-1,10-phenanthroline-5,6-dione,³ 4'-(4-tolyl)-2,2',6',2''-terpyridine (*TolylTerpy*) and *TolylTerpyRuCl₃*,⁴ 2-Chloroisonicotinaldehyde⁵ were synthesized following the procedures previously reported, without modifications and with similar yields. – ESI-MS measurements were carried out with a HP 5989B single quadrupole mass spectrometer equipped with an electrospray source from Analytica of Branford. Measurements were realized in positive ion mode. – ¹H (300 MHz) NMR spectra were obtained at room temperature in 5 mm o.d. tubes on a Bruker Avance 300 spectrometer equipped with a QNP probe head. – Visualization of gold nanocomposites was performed with a transmission electron microscope (TEM), microscope JEOL 2010 UHR, in the "Centre Régional de Mesures Physiques", Paris 6: a drop of diluted solution was deposited and dried on a grid. – Elemental analyses were performed by the "Service Central d'Analyse du CNRS", Vernaison (France). – UV/Vis spectra were recorded in DMF or in EtOH/H₂O (1/1) using a Perkin Elmer UV/Vis/NIR lambda 19 PC scanning spectrophotometer.

(4-(2-chloropyridine)imidazo[4,5-f])-2,9-dimethyl-1,10-phenanthroline (*NeoCl*).

A glacial acetic acid (40 mL) solution of 2,9-dimethyl-1,10-phenanthroline-5,6-dione (238 mg, 1.0 mmol), NH₄OAc (1.54 g, 20 mmol) and 2-chloroisonicotinaldehyde (170 mg, 1.2 mmol) was stirred at 120°C for 4 h. *NeoCl* was precipitated by addition of concentrated ammonia (28%), filtrated, washed with ethanol and dried with diethyl ether (306 mg, 92%); δ_{H} (CDCl₃) 13.8 (1H, s, broad, NH); 8.72 (2H, d, H_{phen}); 8.53 (1H, d, H_{pyr}); 8.21 (1H, s, H_{pyr}); 8.17 (1H, d, H_{pyr}); 7.63 (2H, d, H_{phen}); 2.78 (6H, s, -CH₃). ESI-MS (positive ion mode): [C₂₀H₁₄N₅Cl + H⁺] m/z exp. (theo.) 360.5 (360.8).

4'-(2-chloropyridine)-2,2',6',2''-terpyridine (*TerCl*).

2-chloroisonicotinaldehyde (593.6 mg, 4.2 mmol), 2-acetylpyridine (970 μ L, 8.8 mmol) and KOH_(aq) (3 mL, 2.5 M) were stirred in methanol. After addition of concentrated ammonia (32 mL, 28%) the resulting mixture was stirred at room temperature for 2 days. The yellow precipitate was filtered and washed with cold methanol (10 mL). The crude product was dissolved in CH₂Cl₂, washed with water and dried over MgSO₄. The pure product *TerCl* was obtained as a cream-coloured solid after evaporation of the solvent (435 mg, 30%); δ_{H} (CDCl₃) see Table S1. ESI-MS (positive ion mode): [C₂₀H₁₃N₄Cl + H⁺] m/z exp. (theo.) 345.2 (345.8).

(4-(2-mercaptopyridine)imidazo[4,5-f])-2,9-dimethyl-1,10-phenanthroline (*NeoSH*).

NaSH (100 mg, 1.8 mmol) and *NeoCl* (200 mg, 0.6 mmol) were dissolved in ethylene glycol and the mixture was stirred at 140°C overnight. (Caution: H₂S released during the synthesis was neutralized using a concentrated solution of NaOH and bleach). A precipitate was formed when the solution was cooled to room temperature. Acetone (60 mL) was then added and the solution stirred 15 min. The crude product was filtered, washed with acetone, and dissolved in HCl (20 mL, 0.5 M). The acidic solution was concentrated to ca. 7 mL leading to the precipitation of *NeoSH*. *NeoSH* was recovered by filtration, washed with cold ethanol, dried with diethyl ether and isolated as chloride salt of the protonated form (160 mg, 62%); δ_{H} (DMSO-*d*₆) 13.8 (1H, s, broad, NH); 13.68 (1H, s, -SH); 8.79 (2H, d, H_{phen}); 7.75 (2H, d, H_{phen}); 7.6 (1H, d, H_{pyr}); 7.15 (1H, s, H_{pyr}); 7.05 (2H, d, H_{phen}); 2.79 (6H, s, -CH₃) ppm. ESI-MS (positive ion mode), see Figure S1: [C₂₀H₁₅N₅S + H⁺] m/z exp. (theo.) 358.3 (358.4). Anal. Found (Calc.) for C₂₀H₁₅N₅S₂HCl: C, 55.63 (55.81); H, 4.02 (3.98); N, 16.14 (16.27); S 7.37 (7.45); Cl 16.64 (16.47).

4'-(2-mercaptopyridine)-2,2',6',2''-terpyridine (*TerSH*).

NaSH (100 mg, 1.8 mmol) and *TerCl* (207 mg, 0.6 mmol) were dissolved in ethylene glycol and the mixture was stirred at 140°C overnight. Contrary to what was observed during the similar synthesis of *NeoSH*, no precipitate was generated when the solution was cooled to room temperature. The crude

solid was precipitated after addition of acetone and HCl (5 mL, 4 M). (Caution: H₂S released during the synthesis was neutralized using a concentrated solution of NaOH and bleach). The precipitate was then filtrated, washed with acetone and dissolved in HCl (20 mL, 0.5 M). The acidic solution was concentrated to ca. 7 mL leading to the precipitation of *Ter*SH. *Ter*SH was finally recovered by filtration, washed with cold ethanol and dried with diethyl ether and isolated as chloride salt of the protonated form (212 mg, 75 %); δ_{H} (DMSO-*d*₆) see Table 1. ESI-MS (positive ion mode): [C₂₀H₁₄N₄S + H⁺] *m/z* exp. (theo.) 343.2 (343.4), see Figure S1. Anal. Found (Calc.) for C₂₀H₁₄N₄S₂HCl₃·3H₂O: C, 51.08 (51.17); H, 4.06 (4.72); N 11.71 (11.93); S 6.88 (6.83); Cl 15.26 (15.10).

Au-*Ter*SH-NCs in DMF and purification by anionic exchange and solvent transfer.

An aqueous solution of NaBH₄ (1.44 mL, 0.35 M) was added to a DMF solution (119 mL) of *Ter*SH (30 mg, 6.4 10⁻² mmol) and the mixture was stirred for 2 minutes. A DMF solution (1 mL) of HAuCl₄·3H₂O (69.6 mg, 0.18 mmol) was then added at once and the reaction mixture was stirred for 3 h. Acetone (240 mL) was added; the resulting mixture was stirred for 30 min and then maintained at -30°C overnight. The black precipitate formed was recovered by centrifugation while the yellow filtrate was analyzed by UV-vis to quantify the amount of non-grafted *Ter*SH. The precipitate was dissolved in water (30 mL) and a saturated aqueous solution of KPF₆ was then added until a flocculation was observed. The new precipitate was recovered by centrifugation and dispersed in acetone (30 mL). The Au-*Ter*SH-NCs were precipitated by addition of NBu₄Cl (100 mg) and recovered by centrifugation. The above treatments could then be reiterated in order to remove traces of free *Ter*SH. The purified Au-*Ter*SH-NCs can be isolated as chloride or hexafluorophosphate salt and can be dispersed in a variety of solvents (water, ethanol, water/ethanol, DMF, DMSO).

Au-*Ter*SH-NCs in H₂O/EtOH (1/1) and purification by anionic exchange and solvent transfer.

*Ter*SH was dissolved in mixed solvent H₂O/EtOH (10/10 mL). HAuCl₄·3H₂O (5.8 mg, 1.46 10⁻² mmol) and NaBH₄ (90 μ L, 0.35 M) were added successively and the resulting mixture was stirred for 2 h. An aqueous solution (10 mL) of KPF₆ (12 mg, 6.5 10⁻² mmol) was added; the precipitate of the hexafluorophosphate salt of Au-*Ter*SH-NCs thus formed was recovered by centrifugation and dissolved in acetone (10 mL). NBu₄Cl was added to the acetone mixture leading to the flocculation of the chloride salt of Au-*Ter*SH-NCs. The precipitate was recovered by centrifugation and was dispersed in water (10 mL). The anionic exchange could be reiterated and the Au-*Ter*SH-NCs isolated as chloride or hexafluorophosphate salt.

Au-*Neo*SH-NCs in DMF and purification by anionic exchange and solvent transfer.

Au-*Neo*SH-NCs were synthesized in DMF and purified according to the above described procedure using *Neo*SH-NCs (32 mg, 7.4 10⁻² mmol) instead of *Ter*SH.

Formation of [TolylTerpyRu*Ter*Cl]²⁺, UV-vis study.

TolylTerpyRuCl₃ (5.3 mg, 10⁻² mmol) was added to a solution of *Ter*Cl (3.5 mg, 10⁻² mmol) in H₂O/EtOH (20/100 mL) and the resulting mixture was stirred at 80°C for 16 h. The reaction was followed by UV-vis spectrometry (see Figure S8). The final solution was analyzed by ESI-MS: [C₄₂H₃₀ClN₇Ru]²⁺ exp. (theo.) 384.5 (384.6).

Reaction of TolylTerpyRuCl₃ with Au-*Ter*SH-NCs in H₂O/EtOH.

Au-*Ter*SH-NCs were synthesized in DMF and purified according to the above described procedure, using 69.6 mg of HAuCl₄·3H₂O (0.18 mmol) and 30 mg of *Ter*SH (6.4 10⁻² mmol). The final precipitate of the chloride salt of Au-*Ter*SH-NCs was dissolved in H₂O/EtOH (20/100 mL). TolylTerpyRuCl₃ (3.7 mg, 7 10⁻³ mmol) was then added and the resulting mixture was stirred at 80°C for 16 h. The reaction of complexation was followed by UV-vis spectrometry. The amount of

TolylTerpyRuCl₃ used in this reaction of complexation was determined so as to induce a coating of 70% of the surface of the Au-NPs by the ruthenium complex [*TolylTerpyRuTerSH*]²⁺ (see calculations below).

Calculations of the number of Au atoms per particle and of the surface of the Au-NPs

The mean diameter of the Au-NPs stabilized by *TerSH* in DMF was determined by TEM to be 3.8 ± 0.6 nm. The number of Au atoms per particle was determined to be 1667 using a tight-packed spherical model, with an atom density of bulk gold of $58.01 \text{ atoms.nm}^{-3}$.⁶ The surface of the Au-NPs was calculated to be 45.4 nm^2 .

Calculations of the coverage of *TerSH* and [*TolylTerpyRuTerSH*]²⁺ to Au-NPs

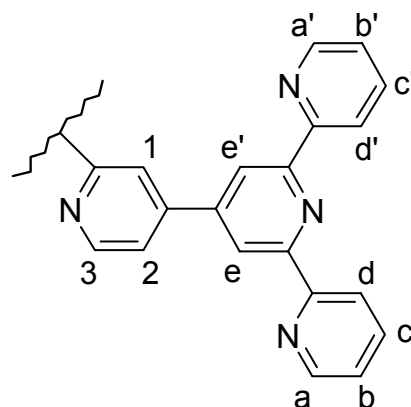
Coverage ratio of TerSH to Au-NPs: The footprint area of *TerSH* was determined to be 0.33 nm^2 using the software ChemDraw. The maximum number of *TerSH* grafted on the surface of the 3.8 nm Au-NPs was therefore calculated to be 138. The average number of *TerSH* on the Au-NPs was estimated by measuring the concentration of free *TerSH* remaining in solution after removal and purification of the Au-*TerSH*-NCs. The number of *TerSH* per particle was 90, leading to a formula $\text{Au}_{1667}\text{TerSH}_{90}$ and a corresponding coverage ratio of 65%.

Coverage ratio of [TolylTerpyRuTerSH]²⁺ to Au-NPs: Similar calculation was performed with [*TolylTerpyRuTerSH*]²⁺. The footprint area of the ruthenium complex was determined to be 0.47 nm^2 and the maximum number of [*TolylTerpyRuTerSH*]²⁺ grafted on the surface of the Au-NPs was calculated to be 97. Due to this theoretical maximum value, we inserted an amount of *TolylTerpyRuCl₃* corresponding to a ~ 70% coverage ratio. This coverage ratio corresponds to a value of 67 ruthenium complex per particle, which means that ~ 75 % of the 90 *TerSH* ligands grafted per particle during the synthesis of the Au-*TerSH*-NCs were expected to react with *TolylTerpyRuCl₃*.

References

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¹H NMR data for *TerCl* and *TerSH*



Ligand	H ^a , H ^{a'}	H ^b , H ^{b'}	H ^c , H ^{c'}	H ^d , H ^{d'}	H ^e , H ^{e'}	H ¹	H ²	H ³	-SH
<i>TerCl</i>	8.76 d	7.42 dd	7.94 dd	8.7 d	8.77 s	7.86 s	7.76 d	8.56 d	/
<i>TerSH</i>	9 d	7.84 dd	8.39 dd	8.92 d	8.88 s	7.83 s	7.35 d	7.87 d	13.68 s

Figure S1: ESI-MS spectrum of *NeoSH*

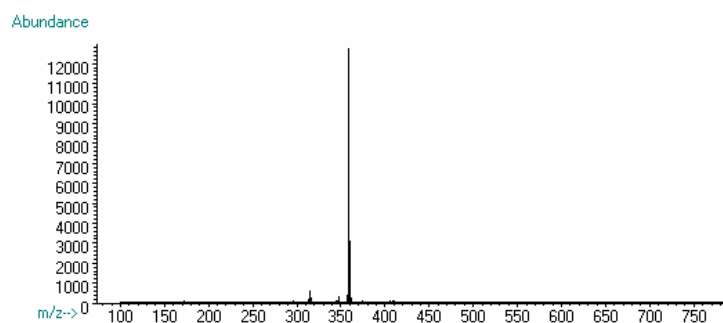


Figure S2: ESI-MS spectrum of *TerSH*

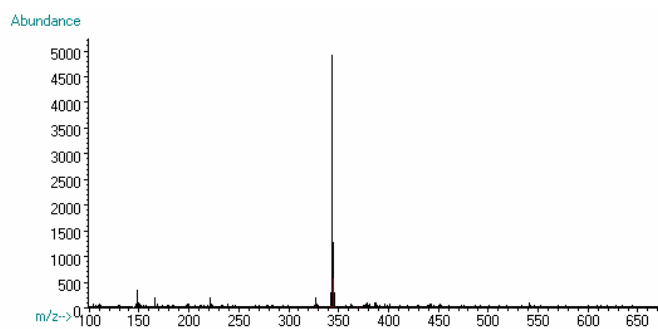


Figure S3: TEM image of Au-*Ter*SH synthesized in H₂O/EtOH (v/v, 5/1), [Au³⁺]/[*Ter*SH] = 0.7.
Scale: 50 nm.

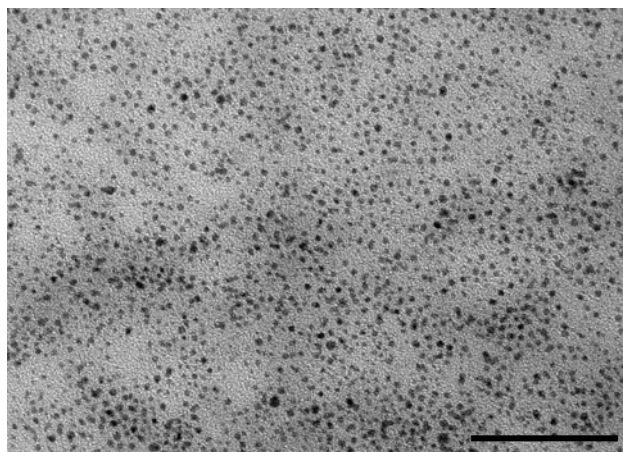


Figure S4: TEM image of Au-*Neo*SH synthesized in DMF [Au³⁺]/[*Neo*SH] = 2.8.
Scale: 50 nm. Corresponding histogram.

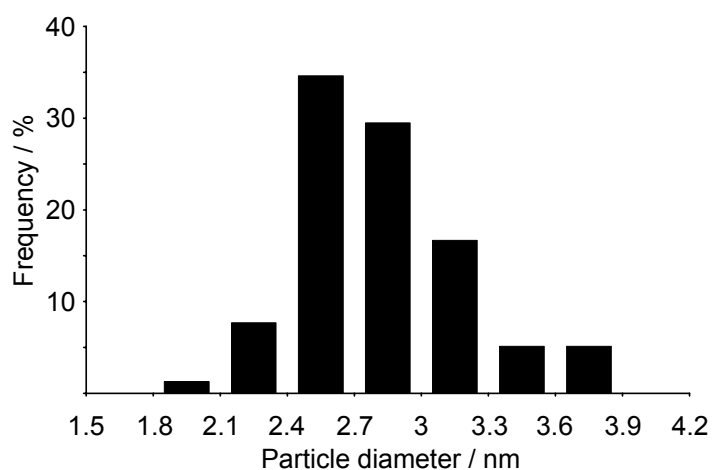
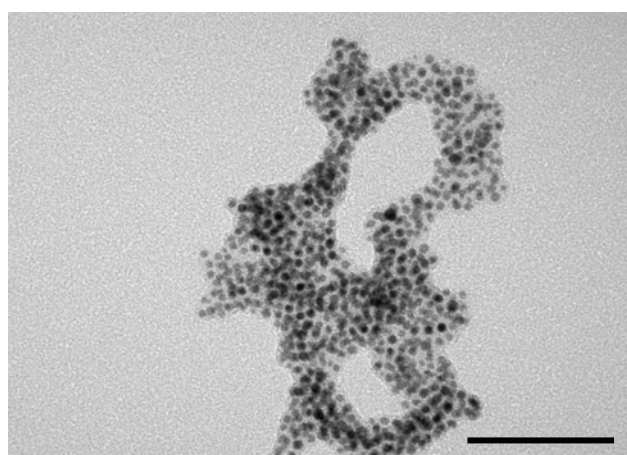


Figure S5: TEM image of Au-*Ter*SH synthesized in DMF, $[\text{Au}^{3+}]/[\text{TerSH}] = 2.7$, before purification. Scale: 50 nm. Corresponding histogram.

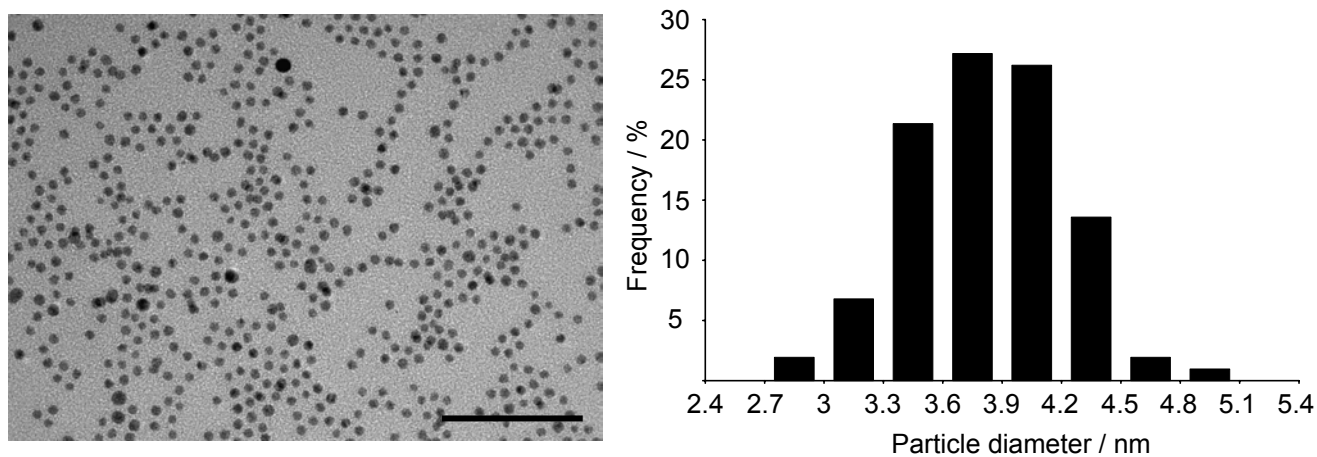


Figure S6: TEM image of Au-*Ter*SH synthesized in DMF, $[\text{Au}^{3+}]/[\text{TerSH}] = 2.7$, after purification. Scale: 50 nm. Corresponding histogram.

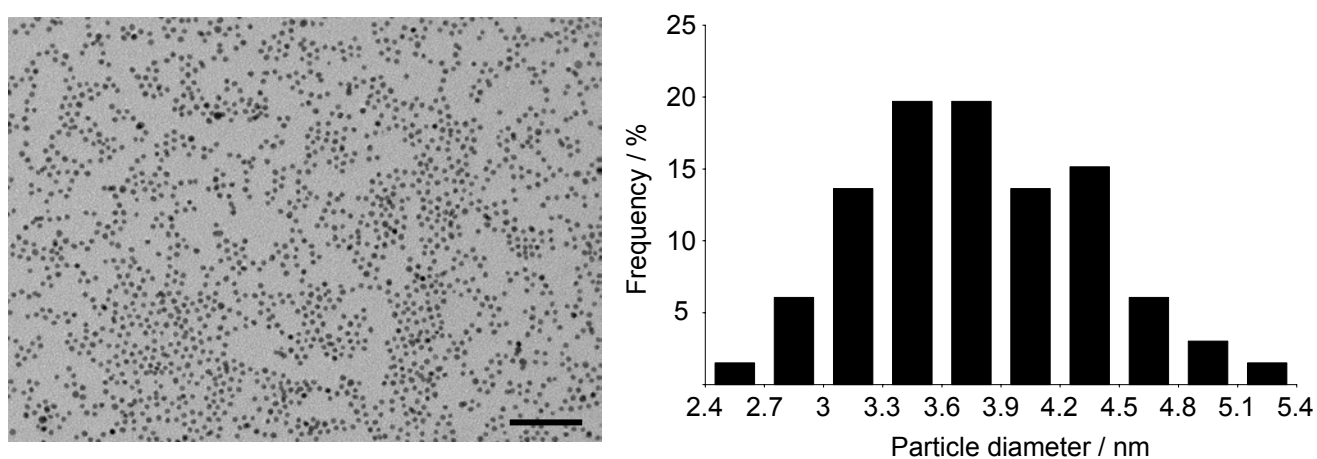


Figure S7: Solubilization of *Toly*/TerpyRuCl₃ in H₂O/EtOH at 80°C (v/v, 1/5) followed by optical absorption measurements.

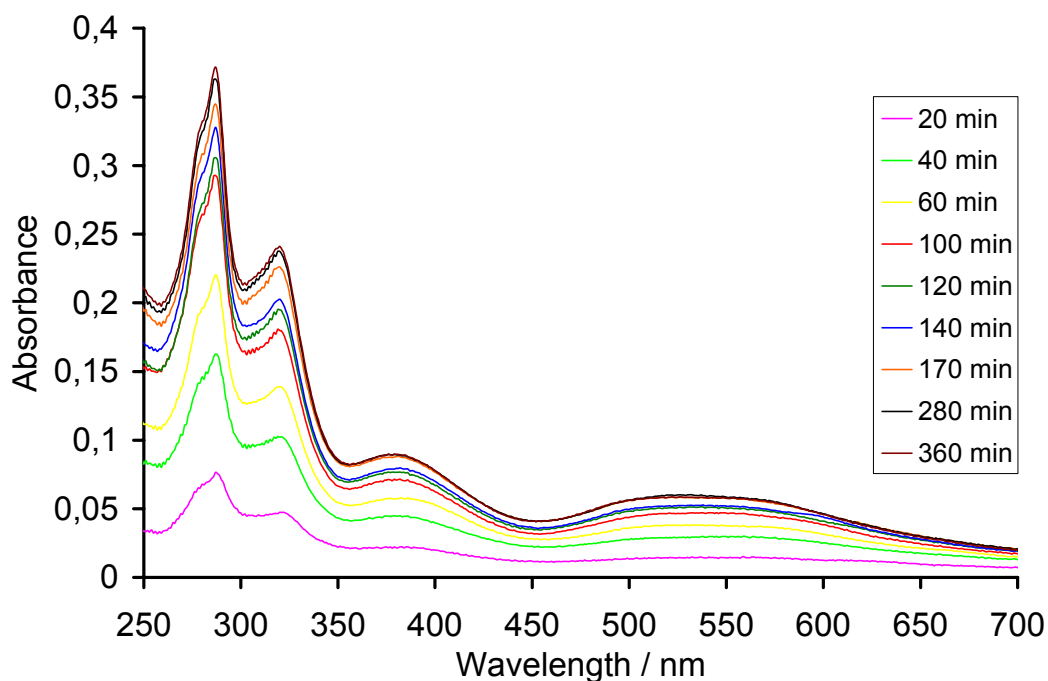


Figure S8: Study of the reactivity of *Toly*/TerpyRuCl₃ toward *Ter*Cl in H₂O/EtOH at 80°C (v/v, 1/5) followed by optical absorption measurements.

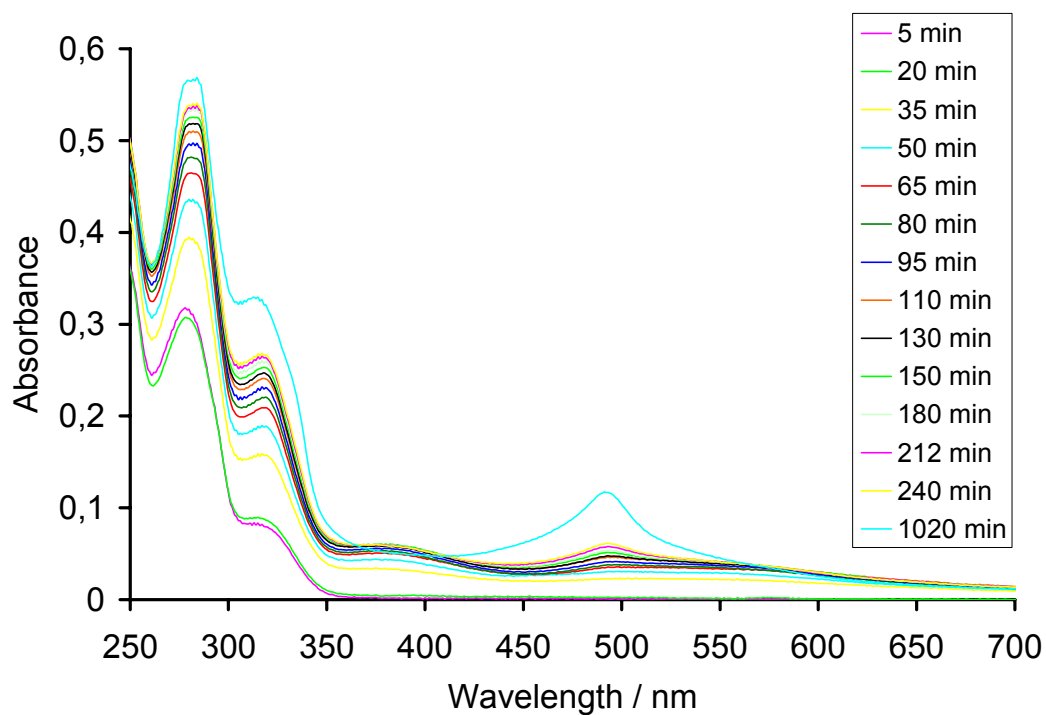


Figure S9: Study of the reactivity of *Toly*/TerpyRuCl₃ toward Au-*Ter*SH-NCs in H₂O/EtOH at 80°C (v/v, 1/5) followed by optical absorption measurements.

