Arrays of Ag and Au Nanoparticles with Terpyridine- and Thiophene-based Ligands: Morphology and Optical Responses

Markéta Prusková[1], Veronika Sutrová[1], Miroslav Šlouf[2], Blanka Vlčková[1], Jiří Vohlídal[1*], Ivana Šloufová[1*]

[1]Charles University, Faculty of Science, Department of Physical and Macromolecular Chemistry, Hlavova 2030, 128 40 Prague 2, Czech Republic

[2]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

*E-mail for I.Š.: sloufovi@natur.cuni.cz, *E-mail for J.V.: vohlidal@natur.cuni.cz

Supporting Information

Terms used for TEM image analysis by NIS-Elements software:

The occupied area fraction: a ratio of segmented image area and the area of a square measurement frame. It has a strong stereological interpretation – in the case of isotropic uniform random sections it is equal to the volume fraction.
The zones of influence: Points that belong to one zone of influence have the nearest distance to the boundary of the same nanoparticle.

Table S1. Results of the TEM image analyses of the Ag/ligand and Au/ligand arrays with the NIS-Elements software; λ_E is the SPE band position; $\langle d \rangle_{NPs}$ average diameter of NPs; $\langle d_{ZI} \rangle$ average zone-of-influence diameter; $\langle x \rangle$ average inter-particle distance; $\langle x_{CSP} \rangle$ average inter-particle distance of CSPs (for cut-off value 4 nm); σ_{Oc} the occupied area fraction.

Array	λ_E [nm]	$\langle d \rangle_{NPs}$ [nm]		$\langle d_{ZI} \rangle$ [nm]		$\langle x \rangle$ [nm]		$\langle x_{CSP} \rangle$ [nm]		σ_{Oc}	
		value	std	value	std	value	std	value	std	value	std
Ag/tpy	730	25,3	6,8	29,1	7,3	4,4	1,3	2,4	1,1	0,67	0,04
/T-tpy	670	25,2	7,9	32,2	11,8	6,1	2,6	2,0	0,6	0,58	0,03
/tpy-2T-tpy	610	23,7	7,4	37,2	9,9	10,4	4,1	2,5	0,9	0,41	0,01
/tpy-3T-tpy	595	24,8	9,5	41,7	13,4	12,0	5,5	2,1	1,1	0,38	0,03
Au/tpy	790	30,5	4,9	34,9	7,8	-	-	-	-	0,73	0,05
/T-tpy	745	31,0	4,1	37,1	5,5	6,02	1,5	2,1	0,9	0,66	0,04
/tpy-2T-tpy	700	31,7	5,1	44,8	8,5	16,2	3,0	1,9	0,5	0,49	0,02
/tpy-3T-tpy	695	31,3	6,2	46,4	11,5	15,8	2,9	2,0	0,7	0,51	0,04

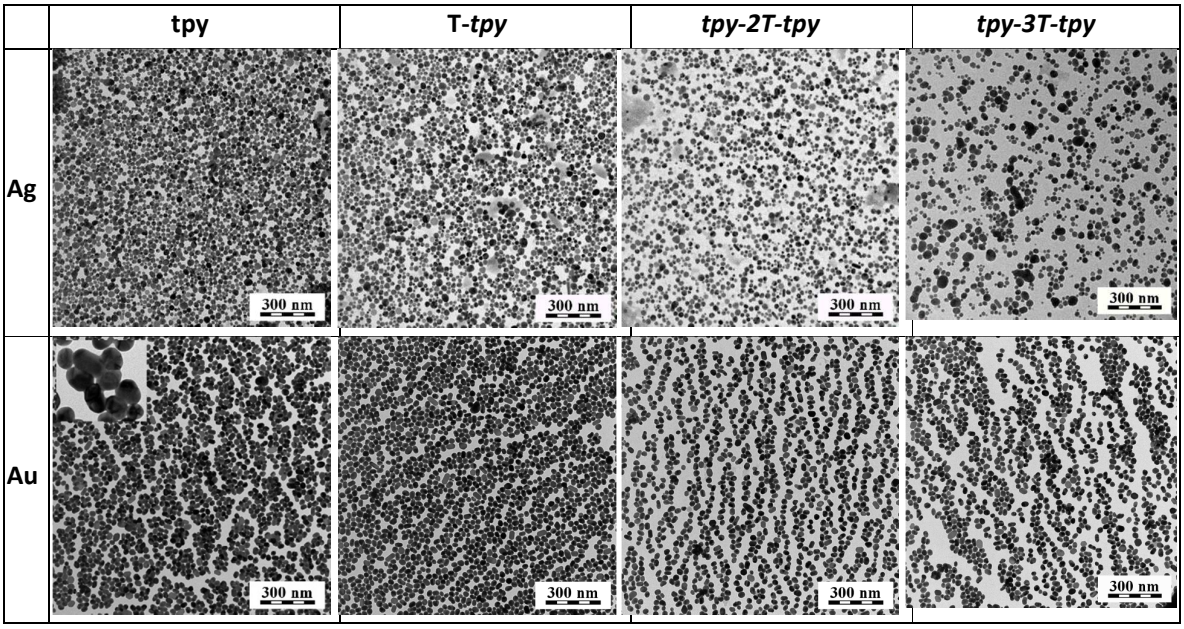


Figure S1 - TEM micrographs of the studied Ag/ligand and Au/ligand arrays deposited on carbon coated Cu grids.

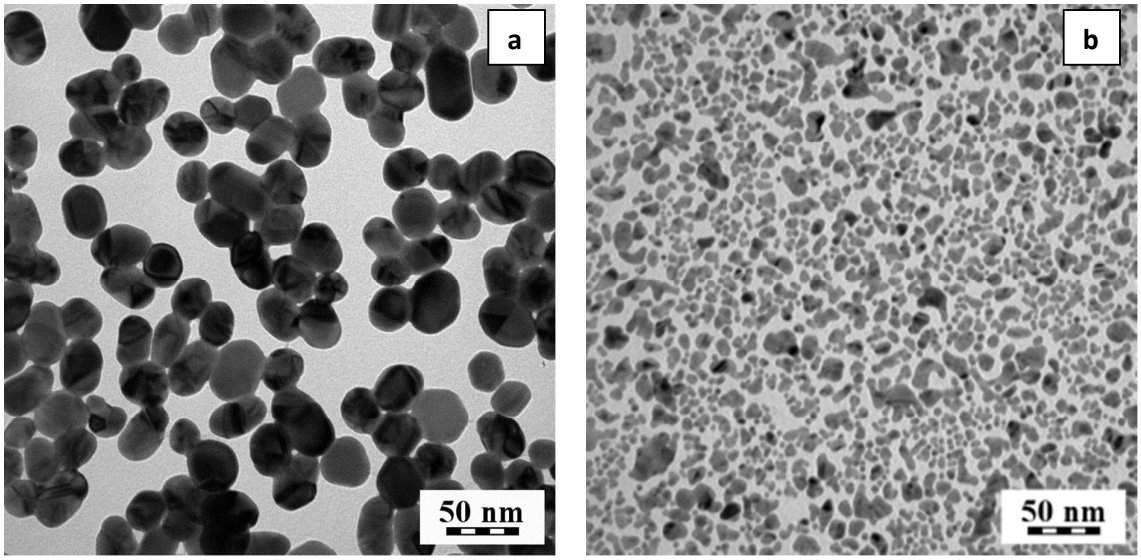


Figure S2 –Au/tpy array – sintered NPs, prepared from Au hydrosol reduced by a) $NH_2OH.HCl$ (ie. hydrosol used throughout this work), b) $NaBH_4$ (original size of NPs 5 nm – ref. 27).

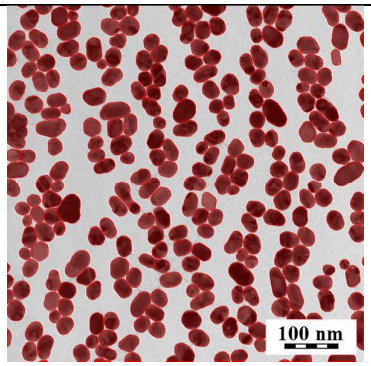
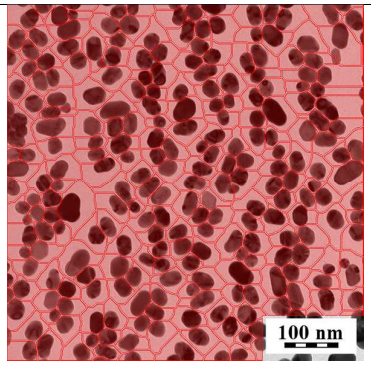
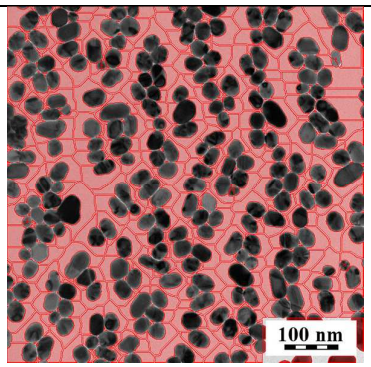
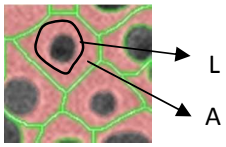
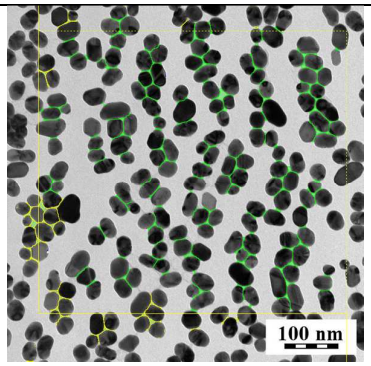
	Segmentation and conversion to the binary image, determination of $\langle d \rangle_{NPs}$
	Conversion of the binary image into "zone-of-influence" (points belonging to one zone of influence have the nearest distance to the boundary of the same object) $\langle d_{ZI} \rangle$
	The average interparticle distance $\langle x \rangle$ was determined as a double value of „width". $width = \frac{A}{L}$, A is the area of the „zone-of-influence" without the area of  particle, L is length:
	Determination of the isolated islands (the distance to the neighbour islands is more than 4 – 5 nm [7]. Determination of the average interparticle distance of closely space Particles $\langle x_{CSP} \rangle$, from single parameter „width".

Figure S3 – TEM image analysis using the NIS-ELEMENTS software.

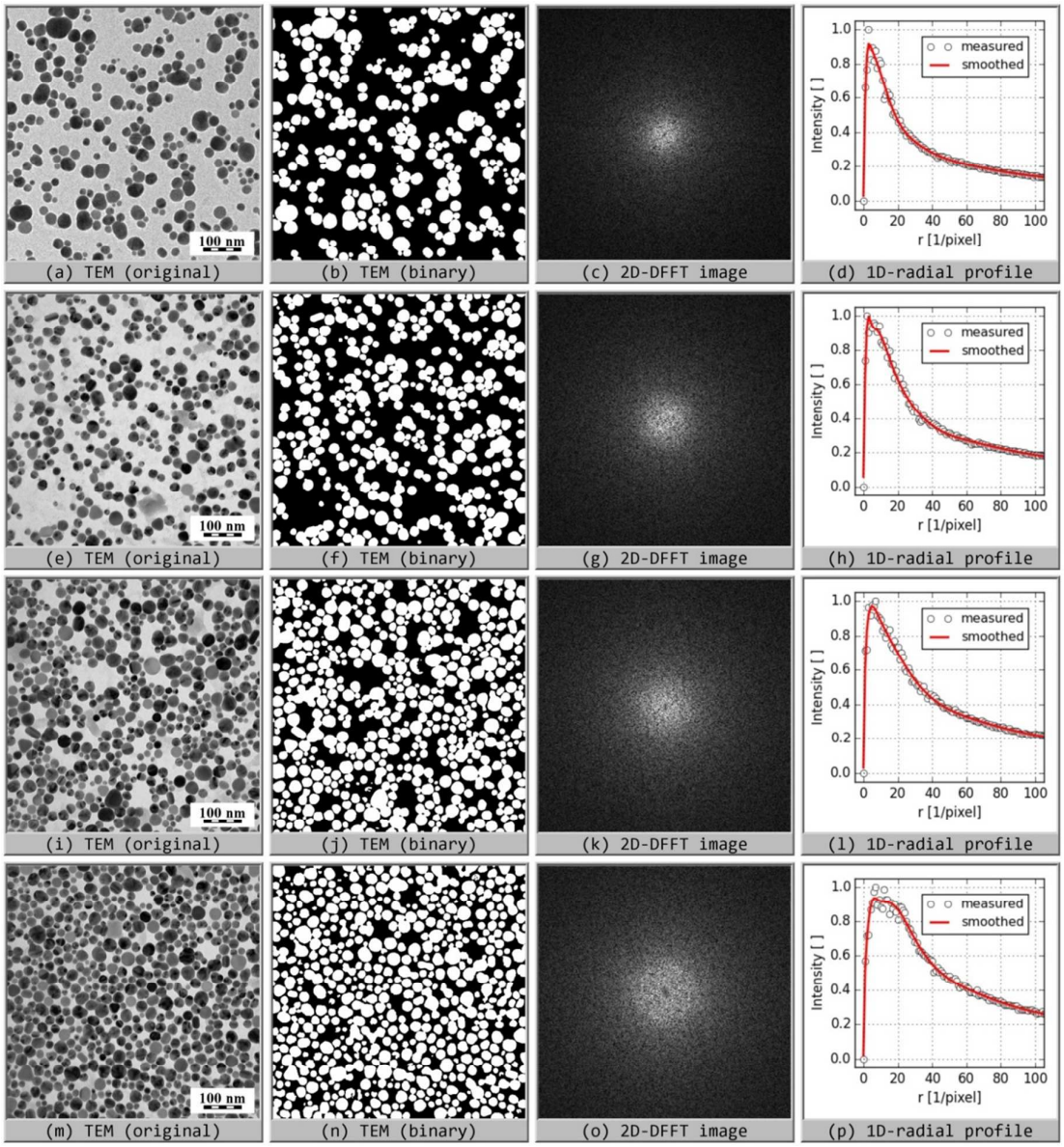


Figure S4 – Analysis of TEM micrographs by means of Fourier transform: TEM micrographs Ag/ligand arrays of and their processing by two-dimensional discrete fast Fourier transform (2D-DFFT): the first (a–d), second (e–h), third (i–l) and fourth row (m-p) show the results for sample X1, X2, X3 and X4, respectively. All TEM micrographs (the first column; Figs. a, e, I, m) were segmented and converted to binary (black-and-white) images using freeware program ImageJ [68] (the second column; Figs. b, f, j, n), then 2D-DFFT images were calculated using our own program MDFT [69] (the third column; Figs. c, g, k, o), and finally the 2D-DFFT images were converted to one-dimensional radial profiles (1D-profiles), still within the MDFT program (the fourth column; Figs. d, h, l, p). The 1D-profiles represent Fourier transform of the original images and, as a result, they are analogous to the curves from small-angle X-ray scattering (SAXS). Therefore, the peaks and/or shoulders on the radial profile indicate periodic distances within the investigated sample. The periodic distances are calculated from the 1D-profiles in the same way as those from SAXS curves. In our case, strong periodicity was confirmed only for the last sample (Fig. p, right bottom), where it was 30.4 nm. Note that 2D-DFFT images are 3 times enlarged in order to enhance the differences between the samples.

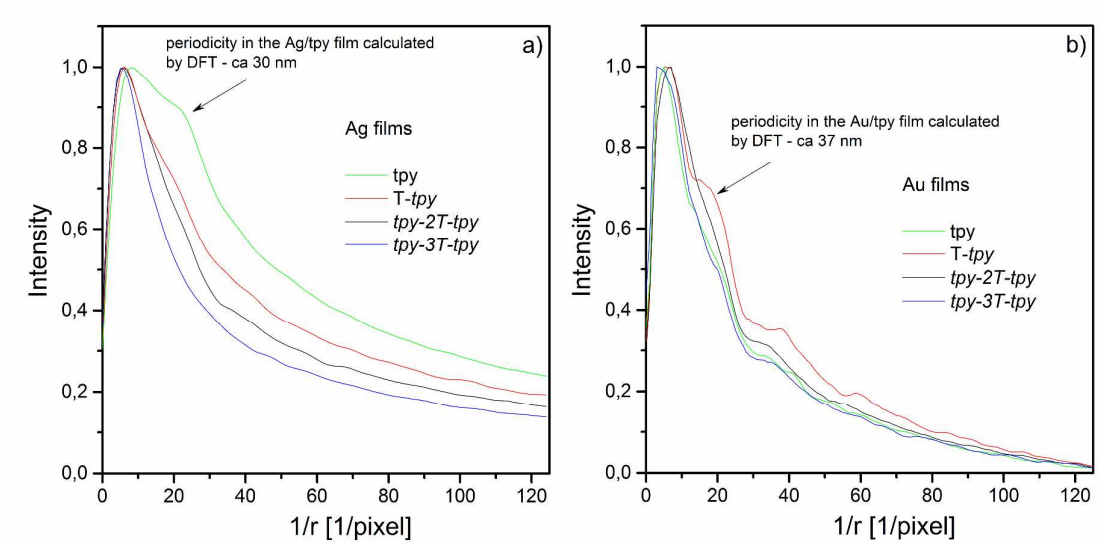


Figure S5 – 1D profiles obtained by 2D-DFFT of TEM images. The peaks and/or shoulders indicate periodic distances within the investigated sample.

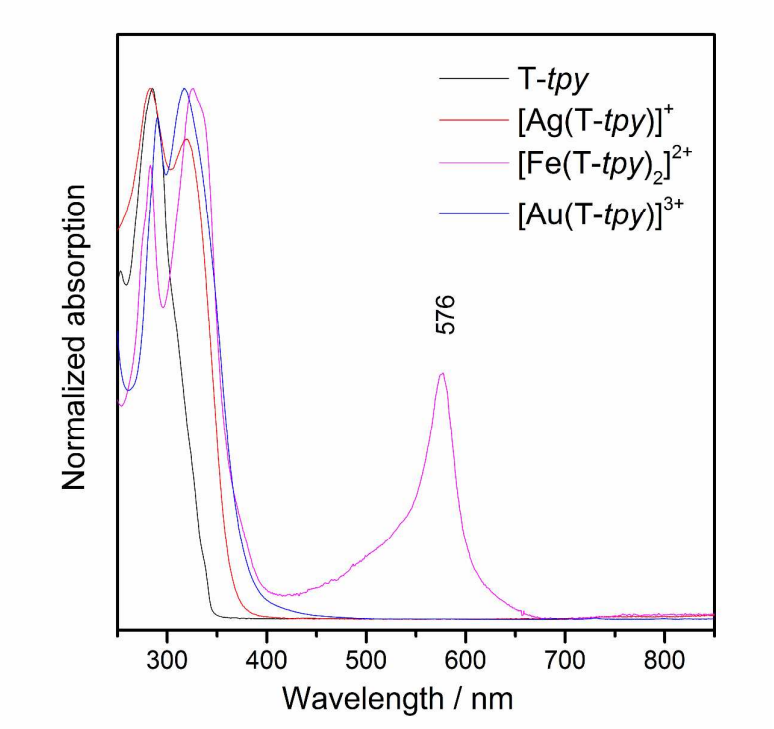


Figure S6 - UV/vis spectra of T-*tpy* and T-*tpy* complexes used as adsorbates. T-*tpy* was measured in acetone, [Ag(**T-*tpy***)]NO_3 in methanol, [Au(**T-*tpy***)]Cl_3 in acetonitrile and [Fe(**T-*tpy***)$_2$]SO_4 in water/methanol (1:1) solution. (Absorbance normalized to the maximal band).

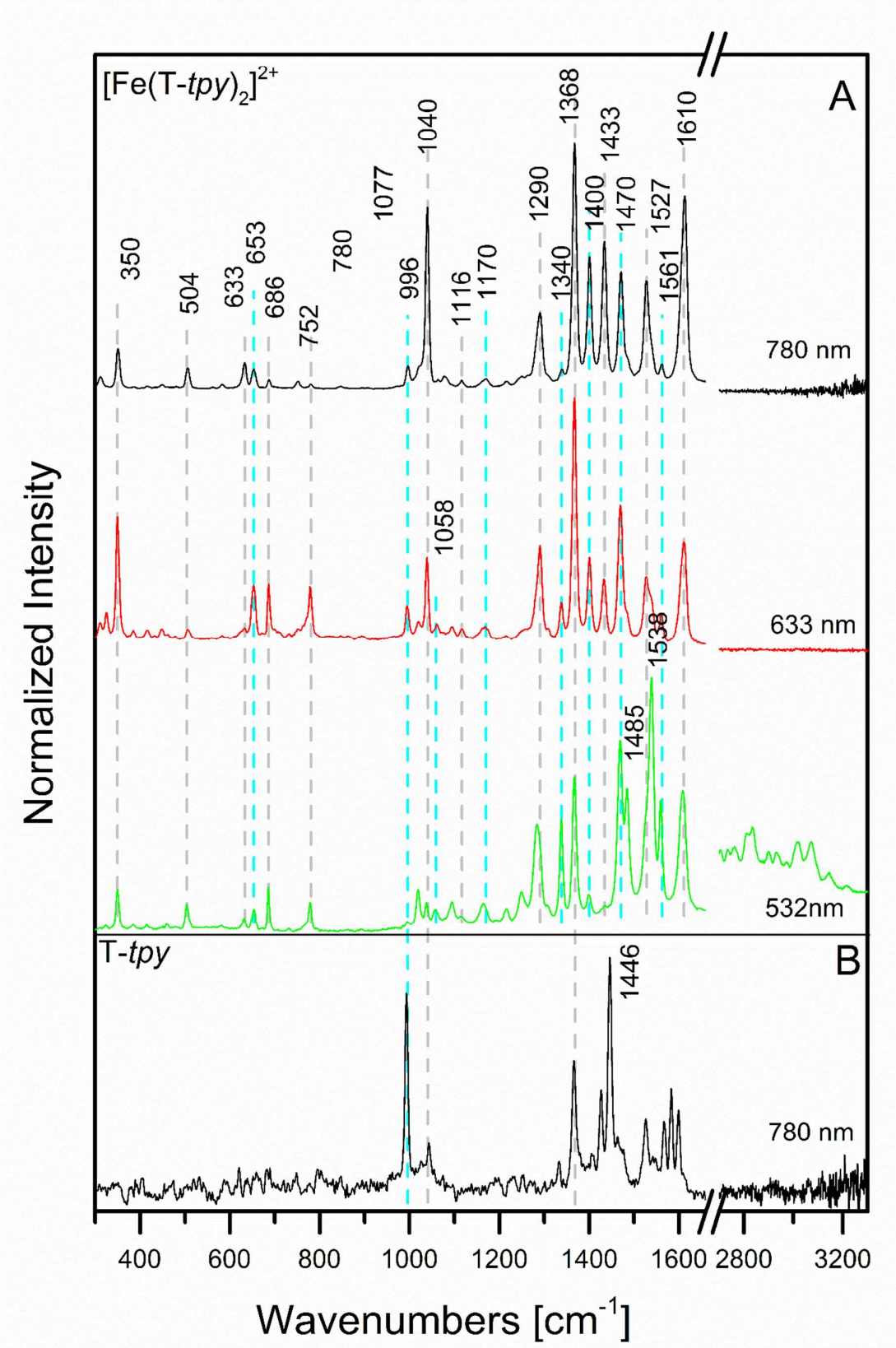


Figure S7 – (A) Raman and resonance Raman spectra of $[Fe(T\text{-}tpy)_2]SO_4$ complex, (B) Raman spectrum of T-*tpy*.

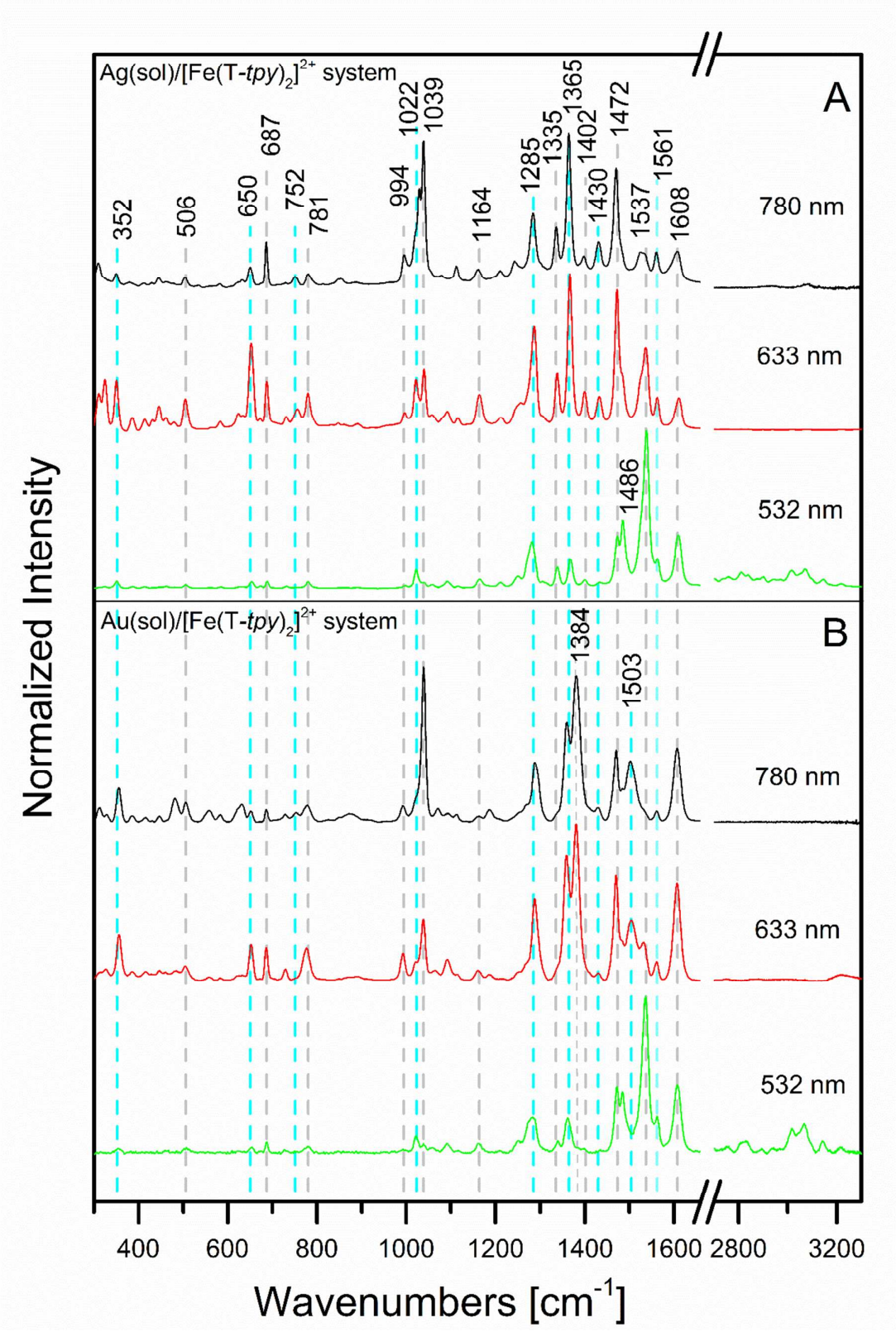


Figure S8 - SE(R)RS spectra of (A) Ag(sol)/[Fe(T-*tpy*)$_2$]$^{2+}$ system, (B) of Au(sol)/[Fe(T-*tpy*)$_2$]$^{2+}$ system

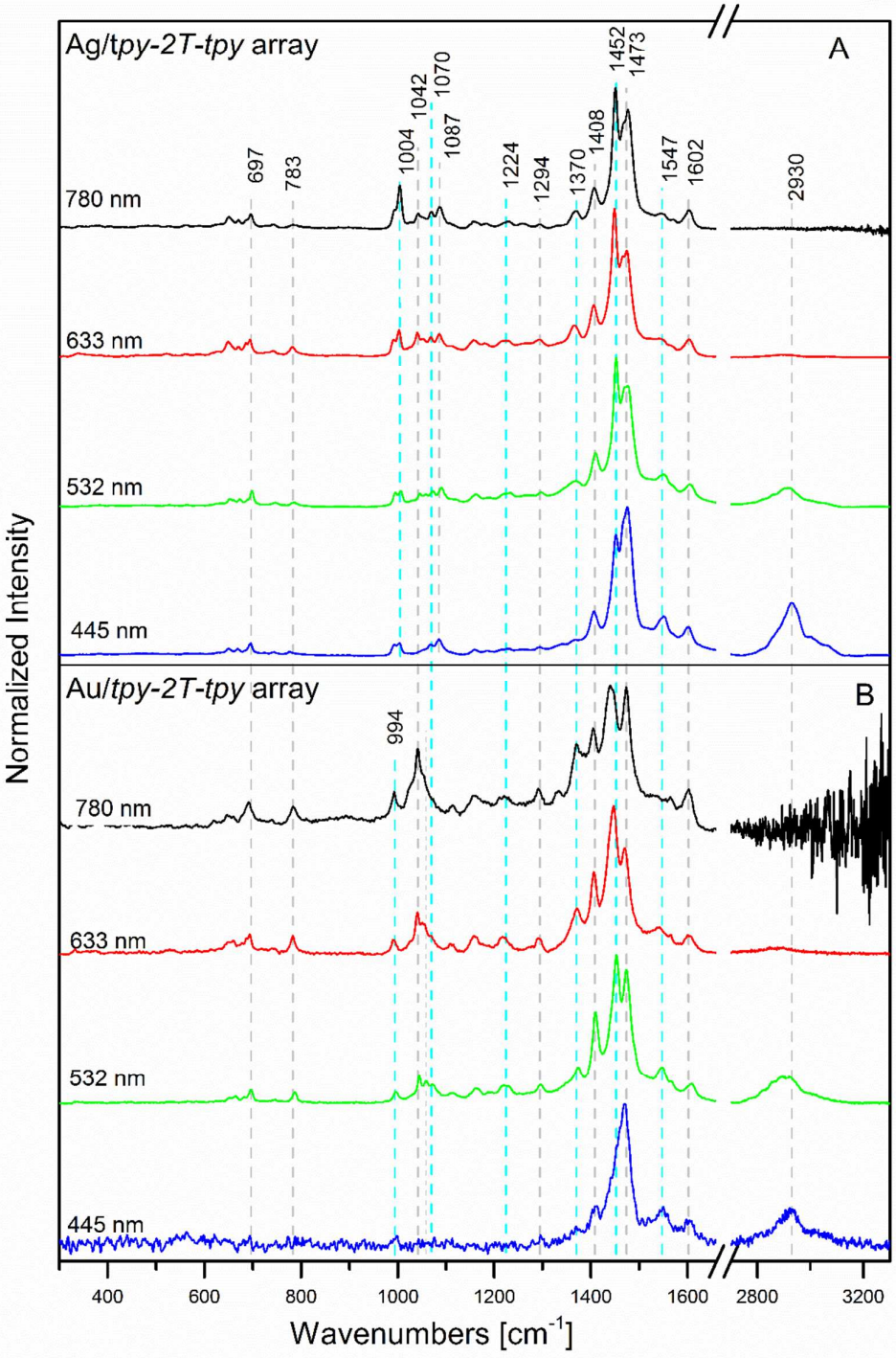


Figure S9 – (A) SERS spectra of Ag/*tpy-2T-tpy* NCs array and (B) RR (445 nm) and SERS (532-780 nm) spectra of Au/*tpy-2T-tpy* NCs array

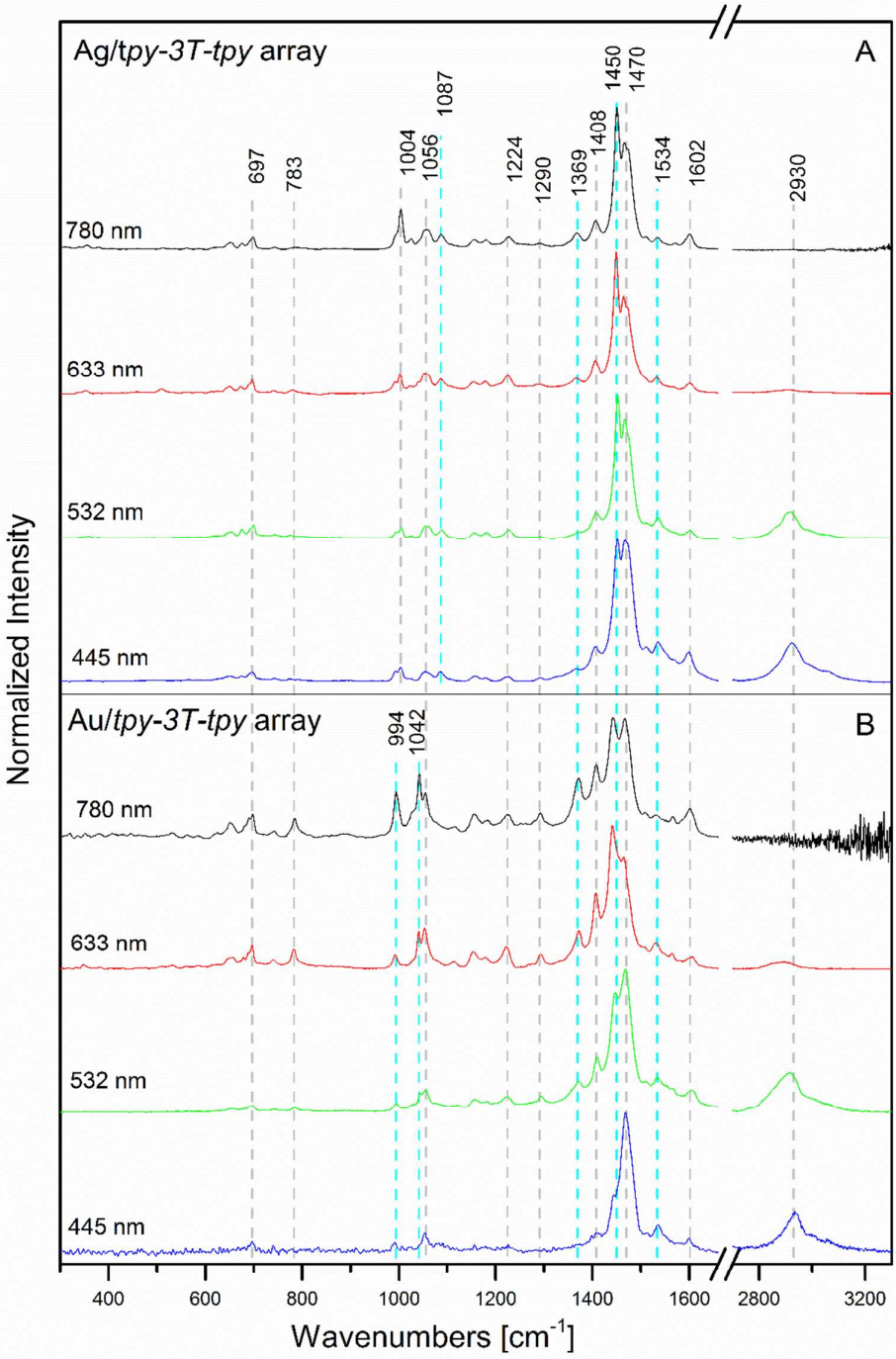


Figure S10 – (A) SERS spectra of Ag/*tpy-3T-tpy* NCs array and (B) RR (445 nm) and SERS (532-780 nm) spectra of Au/*tpy-3T-tpy* NCs array

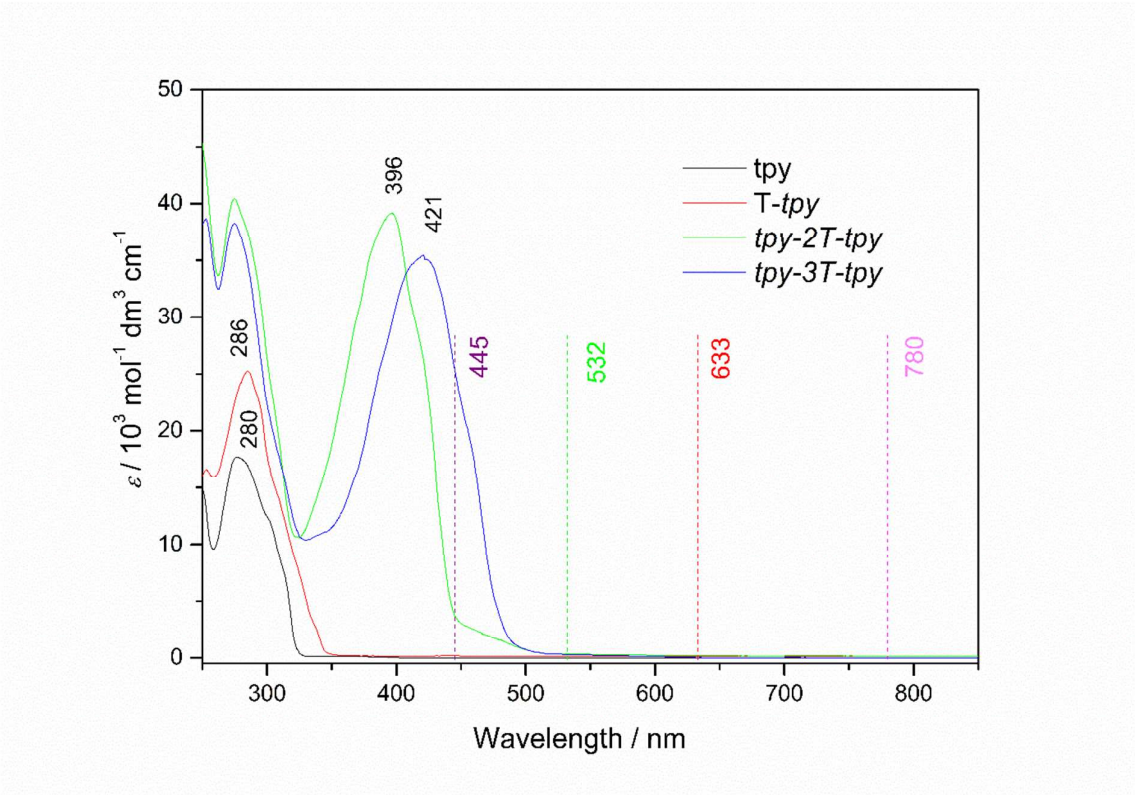


Figure S11. UV/vis spectra of *tpy* compounds used as adsorbates. tpy and T-*tpy* were measured in acetone, *tpy-2T-tpy* and *tpy-3T-tpy* were measured in tetrahydrofurane.

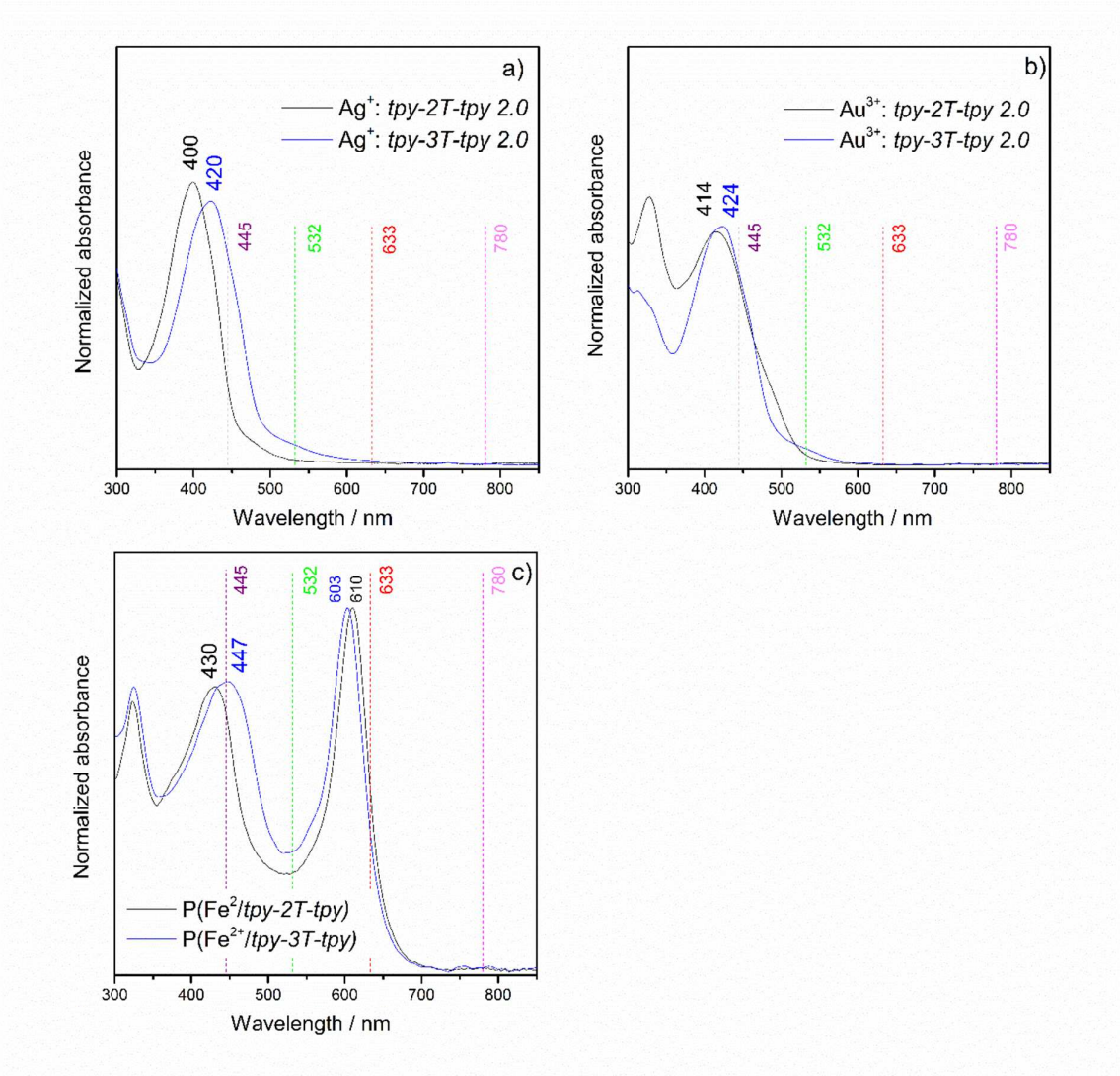


Figure S12 - Normalized UV/VIS spectra of (a) [Ag(*tpy-2T-tpy*)]$^{+}$ and [Ag(*tpy-3T-tpy*)]$^{+}$ complexes, (b) [Au(*tpy-2T-tpy*)]$^{3+}$ and [Au(*tpy-3T-tpy*)]$^{3+}$, (c) [Fe(*tpy-2T-tpy*)$_2$]$^{2+}$ and/or [Fe(*tpy-3T-tpy*)$_2$]$^{2+}$ complexes.

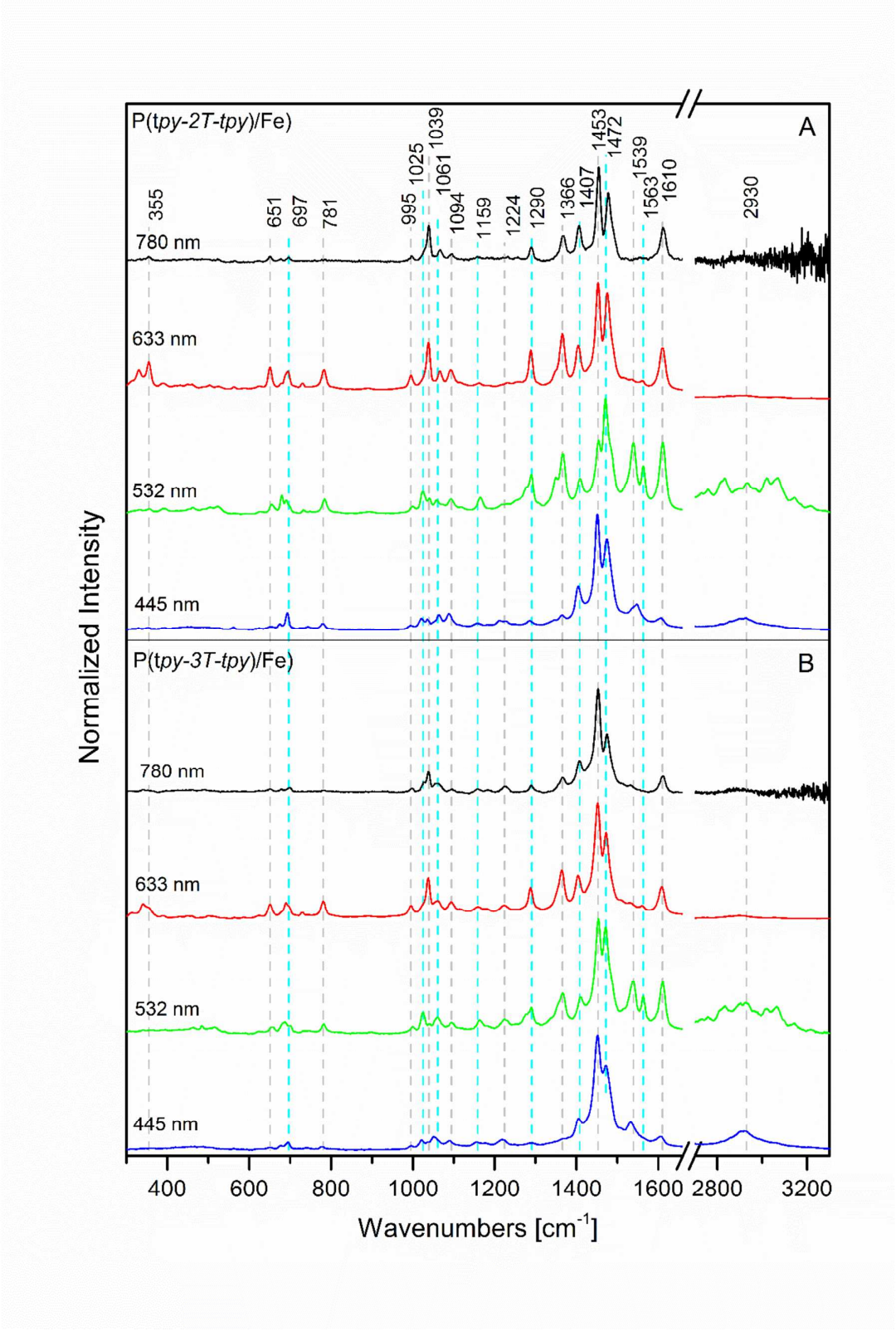


Figure S13 – Normal Raman and RR spectra (A) P(*tpy-2T-tpy*/Fe), (B) P(*tpy-3T-tpy*/Fe) polymer complexes