Section of Electronic Supporting Information

for the paper:

Shortwave infrared luminescent Pt-nanowires: mechanistic study of emis-sion in solution and solid state.

by

Carl Cheadle,¹ Jessica Ratcliiff,¹ Mikhail Berezin,^{2*} Vadim Pal'shin,³ Victor Nemykin,⁴ and Nikolay Gerasimchuk^{1*}

Introduction to Pt-based 1D electric conductors.



Major characteristics and disadvantages of MX and KCP systems:

MX solids:

- 1) --Pt²⁺---X---Pt⁴⁺---X--- chains can be linear or form zigzag motif;
- 2) there is extensive H-bonding between one-dimensional chains which leads to "charge leakage", and chains not isolated from phononic interactions ("breathing");
- 3) significant Pierls distortion (non-equal, alternating Ptⁿ⁺---X distances) that leads to the charge-density-waves (CDW) instead of the spin-density-waves (SDW);
- 4) exhibit a very large metal-metal separation, typically more than 5.6 Å (!);
- 5) non-rigid, flexible neutral amine ligands such as ethylendiamine or cyclohexyldiamine allow significant conformational motion (boat/chair) that produces phononic "noise"

KCP solids:

- 1) there are short and direct Pt-Pt contacts by means of overlapping $5d_z^2$ orbitals;
- 2) equatorial CN-groups are strong electron acceptors, so the electron density on $5d_z^2$ orbitals is depleted which affects orbital overlap and one-dimensional conductivity;
- 3) there is substantial Pierl's distortion as well that leads to loss of metallic conductivity below 150 K.

A limited success in development of molecular electric conductor based on the *KCP* and *MX* systems is attributed to poor ligands design for one-dimensional metal-organic networks, insufficient control of the crystal architecture, and limited electronic tunability of the obtained systems. The most important disadvantage of these systems is their low solubility which precluded their deposition as thin films on dielectric surface for intended practical applications. Crystals of both types of compounds have metallic shine:







partially Br₂ oxidized

Initial K₂[Pt(CN)₄]

Syntheses of dark-green 1D polymeric Ptcyanoximates.

Actual photographic monitoring of the polymeric $Pt(PiPCO)_2$ formation. Top – initial K(PiPCO) solution in water.



A drop-wise addition of K_2PtCI_4 (left beaker) with a pipette started.





Actual photographic monitoring of the polymeric Pt(PiPCO)₂ formation (continued).

Actual photographic monitoring of the polymeric $[Pt(MCO)_2]_n$ formation.

A photographic monitoring of the $Pt(MCO)_2$ preparation at ambient conditions.







		Maxima in spectra and solvents parameters.			
Solvent	Solution color	PtPt stacks λ _{max} (nm)	Dielectric Constant, ε	Refractive Index, n	Dipole Moment, D
DMSO	Yellow		47.20	1.478	3.96
DMF	Green	787	36.70	1.430	3.86
Pyridine	Yellow		12.50	1.509	2.26
Chloroform	Green	796	4.70	1.446	1.87
Ethanol	Green	765	24.30	1.361	1.69
2-picoline	Yellow		9.80	1.500	
Acetone	Green	782	20.70	1.359	2.88
Acetonitrile	Green	782	36.20	1.344	3.92
THF	Green	771	7.32	1.405	1.63
DMAA	Green	787	37.80	1.438	3.81
DCM	Yellow		8.90	1.424	1.60
ethylacetate	Green	779	6.02	1.372	1.78
1,4-dioxane	Green	788	2.21	1.422	0.00
2,4,6-collidine	Yellow			1.498	
Morpholine	Yellow			1.454	
HMPA	Yellow			1.459	
MEK	Green	780	18.50	1.379	2.50
dichloroethane	Green	796	10.40	1.445	1.44
Methanol	Green	761	32.60	1.329	1.70
2-Propanol	Green	771	18.30	1.378	1.66
T-butanol	Green	774	10.90	1.525	
Formamide	Green	810	110.00	1.448	3.70
Water	Green	753	87.74	1.333	1.85
DEAA	Green	809		1.471	

Solution solubility data for $[Pt(MCO)_2]_n$ at room temperature, all solutions were made at ~0.001 M concentration.

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Pyridine	Yellow		12.50	1.509	2.26
Chloroform	Green	807	4.70	1.446	1.87
Ethanol	Green	820	24.30	1.361	1.69
2-picoline	Yellow		9.80	1.500	
Acetone	Green	817	20.70	1.359	2.88
Acetonitrile	Green	837	36.20	1.344	3.92
THF	Green	819	7.32	1.405	1.63
DMAA	Green	769	37.80	1.438	3.81
DCM	Green	821	8.90	1.424	1.60
ethyl acetate	Green	843	6.02	1.372	1.78
1,4-dioxane	Green	834	2.21	1.422	0.00
2,4,6-collidine	Yellow			1.498	
Morphaline	Yellow			1.454	
HMPA	Yellow			1.459	
MEK	Green	811	18.50	1.379	2.50
dichloroethane	Green	805	10.40	1.445	1.44
Methanol	Green		32.60	1.329	1.70
Propanol	Green	806	18.30	1.378	1.66
T-butanol	Green	803	10.90	1.525	
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Water	Green		87.74	1.333	1.85
DEAA	Yellow			1.471	

Solution solubility data for $[Pt(PiPCO)_2]_n$ at room temperature all solutions were made at a approximate concentrations of 0.001M

TG/SDC plots for polymeric Pt-cyanoximates.

DSC/TG data for dark-green polymeric $[Pt(PiPCO)_2]_n$; **A** – panoramic view; **B** – weight loss.



100

80

60

40

20+

Exo Up

200

400

600

Temperature (°C)

Weight (%)



DSC/TG data for dark-green polymeric $[Pt(MCO)_2]_n$; **A** – panoramic view; **B** – weight loss.



800

1000

Α

5

0

-5

-10

-15

+ -20 1200

Universal V4.5A TA Instruments

Heat Flow (W/g)

Detailed mass-spectrometric studies of 1D polymeric Pt-cyanoximates: case of green $[Pt(PiPCO)_2]_n$ in CH₃CN.

Panoramic view of all studied in this particular experiment range of masses from 200 to 3000 amu. Clearly seen clusters of peaks corresponding to monomeric, dimeric, trimeric and tetrameric species indicated by arrows.



The next several pages contain detailed analysis (including isotopic pattern) of masses and intensities of all the above species.

It should be noted that:

- Na⁺ and K⁺ cations are ubiquitous and present all the time in solutions (from glass vials) during sample preparation as well as in buffers, etc. Therefore, in modern mass-spectra there always signals that correspond to the mass of the volatile, ionized molecule(s) plus 23 or 39 amu respectively. Frequently water is the part of the cluster as well.
- The mass resolution is up to 4 digits after decimal point, which amounts to high-res spectra required for accurate identification of ions in chemical analysis conducted by mass-spectrometry.



Cluster of peaks for the monomeric species: **top** – overall cluster profile; **bottom** – $Pt(PiPCO)_2 \cdot Na^+$ and its isotopic profile/intensity fit.



Cluster of peaks for the monomeric species: **top** – overall cluster profile; **bottom** – $Pt(PiPCO)_2 \cdot K^+$ and its isotopic profile/intensity fit.



Cluster of peaks for the monomeric species: **top** – overall cluster profile, and below - $Pt(PiPCO)_2 \cdot K(H_2O)^+$ and its isotopic profile/intensity fit.

Intens. x10⁴ NG1 Pt(pipco)2 in AN-d3_RE1_01_459.d: +MS, 0.2-0.4min #13-23 1150.2252 1133.2373 1167.2272 1185.2317 m/z PtC16H20N6O4PtC16H20N6O4Na, M, 1133.2280 Intens 1+ 1133.2273 2000-1500-m/z Intens. x10⁴ NG1 Pt(pipco)2 in AN-d3_RE1_01_459.d: +MS, 0.2-0.4min #13-23 1150.2252 1133.2373 1167.2272 1185.2317 m/z PtC16H20N6O4PtC16H20N6O4KH, M, 1150.2098 Intens 1+ 1150.2090 500-m/z

Cluster of peaks for the dimeric species: **top** – overall cluster profile with fit for the $[Pt(PiPCO)_2]_2 Na^+$ and its isotopic profile/intensity below it; **bottom** - overall cluster profile with fit for the $[Pt(PiPCO)_2]_2 K^+$ and its isotopic profile/intensity below it.

Cluster of peaks for the dimeric species: **top** – overall cluster profile with fit for the $[Pt(PiPCO)_2]_2 K(H_2O)^+$ and its isotopic profile/intensity below it; **bottom** - overall cluster profile with fit for the $[Pt(PiPCO)_2]_2 K(H_2O)_2^+$ and its isotopic profile/intensity below it.







Cluster of peaks for the trimeric species: **top** – overall cluster profile with fit for the $[Pt(PiPCO)_2]_3 K(H_2O)^+$ and its isotopic profile/intensity below it; **bottom** - overall cluster profile with fit for the $[Pt(PiPCO)_2]_3 K^+(H_2O)_2$ and its isotopic profile/intensity below it. A group of peaks centered at 1759 amu represents $[Pt(PiPCO)_2]_3 K^+(H_2O)_2$ ion.



Hardware used in studies of emission of solid samples of polymeric Pt-cyanoximates, optical standard (Nd-doped glass) and solid matrix KBr.

The liquid N₂ filled cryostat assembly during variable temperature studies.



JKem-thermocouple

Opening for liquid N₂, ~ 180 mL

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Cold finger of the liquid N₂-filled cryostat and solid samples mounting: **A** – sample of KBr pellet with green polymeric [Pt(MCO)₂]_n, **B** – sample of pure dark-green powder of [Pt(PiPCO)₂]_n. Both samples are fixed at the cryostat tip with the help of a double-sided $\frac{1}{2}$ " transparent adhesive tape (Scotch Tape,®).



Top photograph shows 13 mm die/anvil hardened steel set used for pressing KBr pellets containing 5% (by weight) of studied compounds.



To assure reproducibility of the data a special insert was designed to keep the KBr pellet with embedded Pt-cyanoximates in the same position each time. Anodized aluminum insert with the slit 1 mm width was made, and the pellet securely sits at 45° angle inside the quartz cuvette allowing reproducible multiple measurements of the emission from the same pellet each time it is needed.



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Samples preparation for room temperature measurements of pure powders of synthesized darkgreen polymeric Pt-cyanoximates.

A – black cardboard with $\frac{1}{2}$ " wide double-sided Scotch tape and spread dark-green powder of [Pt(PiPCO)₂]_n, which then placed into 1 cm quartz cuvette for fluorescence measurements.

B – similar piece of cardboard with spread over the tape sample of KBr which was used for control purposes.





The emission spectra of the Scotch tape, solid KBr, the cryostat internal assembly and the Nddoped laser-glass for the spectrofluorimeter calibration. The integration time was 1s or 5s on used CCD camera. All these were thoroughly recorded each time prior to measurements of samples of Pt-cyanoximates and control compounds. Top – combined 3 spectra; bottom – 3D and 2D projections of excitation spectra of the laser-glass.





21 (continued)

The emission spectra (in scale!) of the Scotch tape, solid KBr, the cryostat internal assembly including quartz cuvette – top figure. Bottom – 3D and 2D projections of the excitation spectra of pure KBr pellet showing complete absence of signals at studied wavelength.





Investigations of dark-green polymeric Ptcyanoximates in solid state:

Structural studies – EXAFS, X-ray analysis
Scanning electron microscopy
EPR spectra
Electrical conductivity

EPR spectra of solid powders of 1D polymeric [Pt(MCO)₂]_n and [Pt(PiPCO)₂]_n

EPR spectroscopy of polymeric Pt-cyanoximates did not show presence of Pt(III) species [lowspin d⁷ configuration] as evident from stacked spectra of the instrument empty cavity, darkgreen polymeric complexes and standard Cr^{3+} ions in solid matrix.

All spectra were recorded on Bruker EMXplus X-band EPR spectrometer with dual-mode cavity and an Oxford cryostat system at +20 and -193 °C using a field sweep from 200 to 4600 G. The field was calibrated using DFPG, while the sensitivity of instrument was checked using a solid standard containing 1% of Cr³⁺ in isomorphous Al₂(SO₄)₃·6H₂O). Spectra were recorded as a sum of five repetitions with the time constant for each set at 160 ms.

Therefore, formation of mixed valence Pt(II)-Pt(III) species is excluded.



Formation of dimeric $[PtL_2]_2$ and 1D polymeric complexes and explanation of difficulty of crystallization of the latter.



these flexible units prone to multiple orientations in the chain...





Fragment of packing in the structure of monomeric yellow $Pt(MCO)_2$: view along *a* direction showing individual molecules overlay.



Dihedral angle between [PtN1O2N4O5] plane and morpholyl-group formed by N6-C13-C11 atoms to show the "basket shape" formation of the monomeric unit Pt(MCO)₂ unit.

Structure of yellow Pt(MCO)₂ viewed along *b*. Zig-zagged column of slipped monomeric units with platinum atoms separated by distances of 5.243 Å and 4.440 Å. H-atoms are omitted for clarity.



Fragment of crystal packing and details of structure of a yellow monomeric Pt(PiPCO)₂.

A. Dihedral angle between planes in the PtL₂ core.



B. The 60.17° tilt of individual Pt(PiPCO)₂ units relative to each other.



Crystal packing of yellow monomeric $Pt(PiPCO)_2$: prospective view of several molecules and a unit cell. **A** – view along [110] direction showing a zigzag chain of "slipped" monomeric units; **B** – view along *c*-direction.





В

The unit cell content in the structure of red-dimer $[Pt(MCO)_2xDMSO]_2$. **A** – view along *a* direction; **B** – view along *b* direction. The dimers are formed only with Pt2 centers, while Pt1 centers form zigzag columns without short metallophilic interactions.





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Two orthogonal views of one crystallographically distinct portion in the structure of the red dimer Pt(MCO)2 ·DMSO at Pt2 center. A – side view showing "up-only" configuration of the two morpholyl groups (indicated with arrows), B – top view. Nearby solvent molecule of DMSO is omitted for clarity.



Details of structure of columnar red-dimeric form of $[Pt(MCO)_2xDMSO]_2$. Only Pt2 – based units are shown, and solvent is omitted for clarity. **A** – view of one column along *a*; **B** – view along *c* packed 4 dimers; **C** – capped-stick view along *b*-direction showing two inter-platinum distances and Pt-Pt-Pt angle. H-atoms are omitted for clarity.



Details of structure of columnar red-dimeric form of [Pt(MCO)₂xDMSO]₂. Only Pt1 – based units that are not forming dimer are shown. Views along a and b-directions. The DMSO trapped between aligned units of the complex is shown to illustrate Pt---Pt stacks disruption by donor solvents as indicated by arrows.



Perspective view of three aligned $Pt(MCO)_2$ units in the structure of "red dimer" showing a large intermetallic separation (due to the solvent interference) and 180° angle in the chain of Pt1 atoms.



Bonds		Valence Angle	
Pt(1)-O(2)	2.029	O(2)-C(3)-C(1)	115.46
Pt(1)-O(5)	2.029	C(3)-C(1)-N(1)	114.62
Pt(1)-N(1)	1.951	O(5)-C(10)-C(8)	115.55
Pt(1)-N(4)	1.961	C(10)-C(8)-N(4)	113.63
N(1)-O(1)	1.248	O(2)-Pt(1)-N(1)	80.66
N(4)-O(4)	1.277	O(2)-Pt(1)-O(5)	96.51
N(1)-C(1)	1.361	N(1)-Pt(1)-N(4)	102.73
N(4)-C(8)	1.339		
O(2)-C(3)	1.285		
O(5)-C(3)	1.291		
C(1)-C(3)	1.455		
C(8)-C(10)	1.471		
C(1)-C(2)	1.430		
C(8)-C(9)	1.434		

Selected bond distances (Å) and angles (°) in the structure of the slipped zigzag-chain part of red [Pt(MCO)₂ x DMSO]₂. These are around Pt1 atom (see *SM 28,29* for its environment and structural arrangements in the chain).
Scanning electron microscopy (SEM) images of powders of studied Pt-cyanoximates.

The SEM images of dark-green powder of **Pt(MCO)**₂. All three photographs below were taken from the same area of the sample viewing field using different magnification power.



50 µm 10 µm

The SEM images of dark-green powder of Pt(MCO)₂. All three photographs below were taken from the same area of the sample viewing field using different magnification power.



A yellow arrow helps in navigating through images showing the same viewing area.

The SEM images of dark-green powder of **Pt(PiPCO)**₂. All three photographs below were taken from the same area of the sample viewing field using different magnification power.



50 µm



A yellow arrow helps in navigating through images showing the same viewing area.

The SEM images of dark-green powder of **Pt(PiPCO)**₂. All three photographs below were taken from the same area of the sample viewing field using different magnification power.







A yellow arrow helps in navigating through images showing the same viewing area.

The EXAFS studies.

The FEFF8.4 software code did a good job reproducing our Pt L3 edge data for dark-green polymer of [Pt(PiPCO)₂]_n. In the near edge region (XANES ~ less than 100 eV above the edge) peaks arise due to transitions of the core electron to unoccupied states, and also due to the multiple scattering of the low-energy photo electron. This is very different from the extended (EXAFS ~ 100-1000 eV) spectrum which is dominated by single scattering of the photoelectrons. Therefore, it is a good test of the model. If the model is correct, then not only it should produce a good EXAFS fit, but also a decent XANES simulation. The EXAFS by its nature is one-dimensional: it gives the information about distances, but not so much about angles and symmetry. The XANES, to the contrary, is very sensitive to symmetry, bond angles, etc. For this simulation the most important distances (Pt—O, Pt—N, Pt—Pt) were fixed to their best fit EXAFS values, and allowed some (~3%) compression of other distances in order to get a better fit for some features (mostly in the 11580-11620 eV region, it was not really critical).

These are the main results:

Even a single molecule (monomer) model produces a nice simulated spectrum. The peak at 11570 is not reproduced, and the white line region is not that great; however, the general shape of the spectrum is controlled by the monomer's structure and "stacking" only adds some details. Adding only Pt neighbors does not help much.



In fact, having at least two coordination shells in the two adjacent layers is required to produce the 11570 eV shoulder.

The model with 3 complete layers/monomers results in a very good fit in the 11550-11595 eV region. The "shape resonance" around 11610 eV is slightly shifted in the simulated spectrum

(continued)

because this is already the multiple scattering part of XANES. It could be corrected by a very careful adjustment of the distance between the layers relative to the bond lengths in the monomer. There is no good tool for varying those distances, it had to be manually change as X,Y,Z coordinates in the atoms list. Adding two more layers (for a total of 5) did not make a significant difference.



Photon Energy (eV)

One important comment: in order to carry out these simulations the cluster size had to be reduced the cluster size in the Full Multiple Scattering (FMS) calculation to about 4.25 Å. Beyond that, only the single scattering contribution is accounted for. If the cluster size will significantly increase, the simulated spectrum does not resemble the experimental data anymore.

It could be interpreted that as roughly the size of the cluster around the Pt atom for which we know the atomic positions, and not only the distances. Beyond that limit, the distances are more or less reliable but the bond angles are distorted compared to the model. There could be multiple reasons for this – twisting of the organic core, interaction between the monomers at multiple points leading to the distortion of the "flat" monomer molecule, or incorrect modeling of the ligands.Twisting is very likely, because with this FMS cluster size the simulated spectrum does not change much if I rotate the neighboring layers 90° around the Pt-Pt axis. However, knowing that most of the spectrum comes from the monomer contribution, it is a good estimate that there is significant disorder beyond the five-membered rings in studied coordination polymer. Hence, the molecule of a monomer has to be distorted out of nearly flat shape. That was proved by the X-ray analysis (see below).

B

N^{∭(}

The EXAFS studies (continued): structural results.



calculated:	found (in dimer):
1st shell:	
Pt—N1: r = 1.89 Å	~1.97 Å (~4.1%)
Pt—O1: r = 1.87 Å	~2.02 Å (~7.5%)
2nd shell:	
Pt—C1N: r = 2.71 Å	~2.81 Å (~3.6%)
Pt—C1O: r = 2.67 Å	~2.82 Å (~5.4%)
Pt—O2: r = 2.78 Å	~2.88 Å (~3.5%)



2_C³

c³

This is mostly the Pt neighbors and their 1st coordination shells (N1,O1). Higher shells in adjacent layers contribute very little, which means a relatively high degree of disorder.

Pt—Pt: r = 3.15 Å 3.133 Å (~0.5%)



Ρt

Ρ

Ó

 O^{i}

Solid state electrical conductivity measurements for neat powders of Ptcyanoximates using the AFM method.

Setup of the atomic force microscope (AFM) used for the measurements of electrical conductivity of fine dark-green powders of 1D polymeric Pt-cyanoximates.



Dimension 3100 SPM + C-AFM

- platinum-iridium (Ptlr) coated cantilever with a spring constant of 0.25 N/m (SCM-PIC: Veeco)
- Scanning rate: typically 1Hz
- Sample bias voltage: 50 mV

R; vertical resistance obtained for the film between the substrate and the tip via current measurement

A (contact area) = 19.5 nm²

I; film thickness (MCO; 264 nm, PiPCO; 216 nm)

Experimental data and recorded images from powdery $Pt(MCO)_2$ thinly spread on the base pad of the AFM. Electrical conductivity data were obtained from the area 2.5 x 2.5 nm. White lines on top two photographs indicate places where the needle was dragged across the surface of the complex.



Applied sample bias: 50 mV Average current=12.3 nA σ_{ave} = 33.3 [S/cm]

Experimental data and recorded images from powdery $Pt(PiPCO)_2$ thinly spread on the base pad of the AFM. Electrical conductivity data were obtained from the area 2.5 x 2.5 nm. White lines on top two photographs indicate places where the needle was dragged across the surface of the complex.

Scan size: 2 × 2 μ m



Applied sample bias: 50 mV Average current=10.0 nA

 σ_{ave} = 22.2 [S/cm]

Studies of cyanoximes and their 1D polymeric Pt-complexes in solutions:

- 1) UV-visible spectra of ligands
- 2) UV-visible spectra of Pt-complexes
- Formation of colloid systems (aggregation) and their disaggregation by dynamic light scattering method
- Mass-spectrometric investigations of Ptcyanoximates

UV-visible absorption spectroscopy of cyanoxime ligands.

UV-visible spectra of 0.5 mM solutions of HMCO (blue) and Na⁺MCO⁻ (red) in 1 mm cell in EtOH. An inset (dotted line) corresponds to 5mM solution of Na⁺MCO⁻ in EtOH in 1cm cuvette to show $n \rightarrow \pi^*$ transition in the same system.



UV-visible spectra of MCO⁻ anion (as triethylammonium salt) in several solvents showing its pronounced negative solvatochromism.

The color of MCO- solutions in polar protic solvents ROH is yellow, while in polar aprotic donor solvents such as DMSO and DMF is orange-pink. The energy difference between two limiting cases of H_2O and DMSO is 58.1 kJ/mol (or 7.20 eV).



UV-visible spectra of 0.5 mM solutions of HPiPCO (blue) and Na⁺PiPCO⁻ (red) in 1 mm cell in EtOH. An inset (dotted line) corresponds to 5mM solution of Na⁺PiPCO⁻ in EtOH in 1cm cuvette to show $n \rightarrow \pi^*$ transition in the same system.



UV-visible spectra of PiPCO⁻ anion (as triethylammonium salt) in several solvents showing its pronounced negative solvatochromism.

The color of PiPCO⁻ solutions in polar protic solvents ROH is yellow, while in polar aprotic donor solvents such as DMSO and DMF is orange-pink. The energy difference between two limiting cases of H₂O and DMSO is 39.9 kJ/mol (or 0.413 eV = 413 meV).



Dynamic light scattering experiments and disaggregation of 1D polymers in solutions.

Actual photographs of $[Pt(MCO)_2]_n$ in solutions in 1 cm quartz cuvette upon illumination with the red laser beam (λ_{max} =625 nm).

A: the Tyndall effect in aggregated opalescent solutions of dark-green $[Pt(MCO)_2]_n$ in DMF showing a significant light scattering due to the formation of particles of 1D polymeric complex.

B: the yellow monomeric species of Pt(MCO)₂ in the same solution after addition of 2 drops of DMSO; clearly seen absence of light scattering in the cuvette which evidences a complete breakdown of colloidal 1D polymer to a monomer.



day light conditions

in dark

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Studies of formation of colloidal solution of green $[Pt(PiPCO)_2]_n$ in an anhydrous DMFA (left part of the graph) followed by addition of quenching solvent which disrupts weak Pt---Pt bonds in aggregated 1D polymeric stacks (right part of the graph). A monotonic decline of intensity of scattered red laser light after addition of DMSO evidences larger particles random breakdown in progressively getting more yellow-colored system. Yet a small quantity of large size particles abruptly drops practically to zero in agreement with a steep decrease of the light scattering power.



Custom made specialty quartz cuvette (1 cm) used for monitoring of formation of dark-green 1D Pt-cyanoximates under anaerobic conditions. A – general view and description after mixing of reagents; B – cycle when the ligand solution in frozen under vacuum, and solid K₂PtCl₄ is in the optical part; C – thaw cycle when both chambers are under argon and ready for mixing.







Another option for the formation of Pt(IV) species could be the disproportionation of Pt(II) complexes into Pt(0) and Pt(IV):

The effect of addition of polar donor solvent to green $[Pt(MCO)_2]_n$ in DMF: the absorbance at 790 nm decreased over time while ligands' bands increase intensities as shown by arrows. One drop of pure pyridine was added and spectra were recorded every 15 seconds for 1400 seconds time period; room temperature, 1 cm quartz cuvette.

No constant isosbestic points were observed.



The UV-visible spectroscopic response of green $[Pt(PiPCO)_2]_n$ in DMF solution treated with 2 drops of DMSO. Arrows indicate intensity decrease of the Pt - - - Pt band observed at 806nm over time. At the same time lidand's bands in UV-visible region of spectrum increase intensities. Spectra were recorded every 20 seconds for 3600 seconds; room temperature, 1 cm quartz cuvette.

No constant isobestic points were observed.



A – Changes in the UV-visible spectra of Na-decanoate (detergent) upon addition of dark-green complex $[Pt(PiPCO)_2]_n$; **B** – time profile of micelles stability with an inset showing their actual appearance;



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Solubilization of dark-green polymeric $[Pt(MCO)_2]_n$ (left 2 vials) and $[Pt(PiPCO)_2]_n$ (right 2 vials) into colloidal solutions upon addition of sodium decanoate (labeled as C10) and sodium dodecylsulfate (labeled as SDS). The amount of water used was 5 mL and the amount of detergent used was ~20 mg.

 ${\bf A}$ – immediately after mixing of complexes with detergents and an ultrasound bath for 5 minutes; ${\bf B}$ – one month later.



В



Data of particles size measurements for micelles of dark-green polymeric $[Pt(MCO)_2]_n$ in D₂O solution of sodium dodecylsulfate, SDS.

Size Distribution: uniformed, single size.

Mean Diam. By Intensity:	320.2 nm	
Mean Diam. By Volume:	326.1 nm	
Mean Diam. By Number:	321.3 nm	
Average size: 322.5 nm = 3225 Å		
At PtPt bond = 3.15 Å (according t	to EXAFS data) there are ~ 920 units in the stack.	



Data of particles size measurements for micelles of dark-green polymeric $[Pt(PiPCO)_2]_n$ in D₂O solution of sodium decanoate, C₁₀.

Size Distribution: uniformed, single size.

Mean Diam. By Intensity:	219.5 nm	
Mean Diam. By Volume:	216.6 nm	
Mean Diam. By Number:	206.3 nm	
Average size: 214.1 nm = 2141 Å		
At PtPt bond = 3.15 Å (according	to EXAFS data) there are ~ 680 units in the stack.	





CV (black traces) and DPV curve (red traces) for yellow monomeric Pt(MCO)₂ in DMSO.

CV (black trace) and DPV curve for pure cyanoxime, HMCO in DMSO.





CV (black trace) and DPV curve (red trace) for yellow monomeric Pt(PiPCO)₂ in DMSO.

CV (black trace) and DPV curve (red trace) for pure cyanoxime, HPiPCO in DMSO.



Tabulated values of redox potentials (relatively to FcH/FcH⁺ couple) of the target compounds determined by CV and DPV experiments in DMSO / 0.1M TBAP system.

Compound	Peaks potential, mV
HMCO	+535, -1265, -1505
HPipco	+630, -1475, -1900
Pt(MCO) ₂	+230, -1275, -1510
Pt(Pipco) ₂	+165, -1425, -1705

All potentials are ±5 mV. All observed processes are irreversible.

UV-visible absorption spectroscopy of Ptcyanoximates.

Change in λ_{max} for dark-green [Pt(MCO)₂]_n, showing the maximum and minimum absorbance dependent on the solvent. The DEAA stands for the N,N'-diethylacetamide. The energy difference is 8.68 kJ/mol



Change in λ_{max} for dark-green [Pt(PiPCO)₂]_n, showing the maximum and minimum absorbance dependent on the solvent. The energy difference is 13.66 kJ/mol.





The 1D polymeric dark-green $[Pt(MCO)_2]_n$ complex (**A**) and $[Pt(PiPCO)_2]_n$ (**B**) in different solvents: certain correlation with solvent parameters can be envisioned.

Solvents: DMAA – dimethylacetamide, FA – formamide, DMF – dimethylformamide, DEAA – diethylacetamide, THF – tetrahydrofurane.

UV-visible spectra of Pt-cyanoximates in the process of their chemical oxidation in solutions. $A - Pt(MCO)_2$ solution in DMF upon addition of AgPF₆. B - Suspensions in mineral oil for polymeric [Pt(PiPCO)₂]_n and product of its oxidation by Br₂; dashed line marks position of the CT band in the initial complex and shows its partial presence in the oxidation product.



Investigations of dark-green polymeric Ptcyanoximates in solid state:

Photoluminescence

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Chemical oxidation experiments on solid complexes: **top** – initial pellet; **bottom** - an addition of elemental bromine to KBr pellet with 5% of dark-green 1D polymeric Pt-cyanoximate. Clearly seen Cu-shine characteristic of mixed valence Pt-based extended solids.





Actual microscope photographs of fine powders of studied 1D polymeric complexes at x20 magnification.

 $Pt(MCO)_2$







Background information regarding application of the NIR emission for biomedical purposes.

Within the NIR range, two optical windows suitable for imaging are generally recognized: a traditional NIR window I (650-950 nm) and window II (950-1600 nm) (1,2) also known as extended NIR (exNIR) (3,4). Absorption bands seen in exNIR of biological tissue components relate to overtones and combination bands of their corresponding fundamental vibrations (tones). The overtone and combination bands appear significantly blue-shifted with respect to tones. The latter are typically observed at mid-infrared (400–4000 cm⁻¹ or 2500–25000 nm) by IR or Raman spectroscopy. Overtone and combination bands are due to the anharmonicity of the vibration that is the deviation from an ideal harmonic oscillator, such as that seen in a bond with two identical atoms. The anharmonicity increases when the bond connects atoms with dramatically different masses, such as in cases of C-H as compared to C-C bonds. Because of the anharmonicity of tissue forming molecules, the exNIR range is dominated by signals from bonds involving hydrogen atoms such as O-H (water, carbohydrates), C-H (lipids), and N-H (proteins). Being forbidden transitions by vibrational selection rules (5), the intensity of the overtone and combinations by vibrational selection rules (5), the intensity of the overtone and combination bands are generally 10–100 times weaker when compared to fundamental vibrations (6).

Tissue has a set of exNIR-active endogenous chromophores, such as water and lipids, but with relatively low absorption coefficients (see our previous publication (4) for measurement of absorption coefficients of tissue components in this spectral range). This leaves the exNIR optical absorption band transparent enabling exNIR photons to penetrate deep into the tissue. Scattering in exNIR is quite low, especially compared to the NIR range. Rayleigh scattering of photons in tissue is inversely proportional to the 4th power of the photon's wavelength ($\sim \lambda^{-4}$), the scattering coefficient decreases with the wavelength in accordance with a power law (7). The Mie scattering also decreases with longer wavelengths, but is less wavelength-dependent and depends on tissue morphology. Attenuation of scattering leads to the increase in transparency of the biological tissue and to the improvement in the depth penetration.

The potential of exNIR for deep tissue with Pt-cyanoximates imaging can be illustrated using a simple experiment. A finger of the co-author (MB) is placed on the source of a white halogen light with a broad and relatively uniform output from 300 to 2000 nm. The transmitted light is detected using an InGaAs detector. Several well-separated sharp transmission peaks in the exNIR window are observed that reflect the transparency of the tissue. One of the transmission peaks of 1050-1150 nm directly corresponds to the emission of Pt-cyanoximates.

One of the transmission peaks of 1050-1150 nm coincides with the emission of one of the Pt-cyanoximates which is shown by the green arrow below in Figure 1.

Very recently, studying contrast in thick water phantoms from 650 to 1625 nm, we demonstrated that the high contrast can be achieved at *ca*. 1075-1375 nm (Figure 2) (8).



Figure 1. The exNIR spectrum of tissue demonstrated the transmission bands at 950, 1050-1150 and 1250-1350 nm



Figure 2. Optical window (colored in light blue) based on the measured Michelson contrast of an Intralipid-India Ink phantom is from 1050 to 1375 nm. Adapted from reference [14] (*J. Biomed. Optics.*).
Overall, much higher tissue penetration (>2X, depending on the wavelength and type of tissue) can be achieved at >1000 nm as predicted and utilized by several groups (9-11) including optoacoustic (12) and two photon excitation fluorescence at 1550 nm (13,14). This, along with a lack of auto-fluorescence and attenuated scattering, makes the exNIR spectral range attractive for deep imaging. In response to the opportunity, the field of exogenous emitters in exNIR emerged and currently includes single wall carbon nanotubes (15), quantum dots (16-18), neodymium doped nanoparticles (19) and cyanine dyes (20). Herein we report a new class of the emitters based on Pt complexes that can potentially be utilized as a contrast agent.

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Variable temperature photoluminescence studies of solid samples of both Pt-cyanoximates.

Details of VT experiment for 1D polymeric $[Pt(PiPCO)_2]_n$ freshly pressed pellet (5% in KBr). Linear fit for the upward part of the curve of the PL change with temperature for studied dark-green complex's sample.



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Details of VT experiment for 1D polymeric $[Pt(MCO)_2]_n$ freshly pressed pellet (5% in KBr). Full range of studied temperature dependence has s-shape, but a "linear" portion can be approximated between -108 and +10°C. Linear fit for that upward part of the curve of the PL change with temperature for this studied dark-green complex is shown.



Full line shape analysis of the spectroscopic emission envelope for 1D polymeric dark-green $[Pt(MCO)_2]_n$ at two extreme temperatures. A sufficient fit was obtained using two Gaussian lines. Black – experimental data; blue – individual fit; red – sum of fits.





green 1D Pt(MCO), at -194°C; 5% in KBr



Full line shape analysis of the spectroscopic emission envelope for 1D polymeric dark-green $[Pt(PiPCO)_2]_n$ at two extreme temperatures. A good fit was obtained using two Gaussian lines. Black – experimental data; blue – individual fit; red – sum of fits.





1D green Pt(PiPCO), 5% in KBrat-192°C



Variable temperature photoluminescence of the dark-green 1D polymeric $[P(MCO)_2]_n$ complex: **A** – profile of overall intensity/wavelength of the spectroscopic envelope; **B** – energies of individual deconvoluted main and major peaks. Clearly observed synchronous hypsochromic shift of both peaks with the temperature increase (indicated by the arrow).



Variable temperature photoluminescence of the dark-green 1D polymeric $[P(MCO)_2]_n$ complex: **A** – areas of individual components (main and minor peaks), showing pronounced temperature dependence; **B** – line width of two peaks at ½ height showing slight temperature dependence for the main component and significant dependence for the minor component of observed photoluminescence.



Variable temperature photoluminescence of the dark-green 1D polymeric $[P(PiPCO)_2]_n$ complex: **A** – profile of overall intensity/wavelength of the spectroscopic envelope; **B** – energies of individual deconvoluted main and major peaks. Clearly observed synchronous hypsochromic shift of both peaks with the temperature increase (indicated by the arrow).



Variable temperature photoluminescence of the dark-green 1D polymeric $[P(PiPCO)_2]_n$ complex: **A** – areas of individual components (main and minor peaks), showing very weak temperature dependence; **B** – line width of two peaks at ½ height showing lack of temperature dependence for both deconvoluted peaks of observed photoluminescence.



Details of the quantum yield determination for solid samples of both Pt-cyanoximates.

An example of actual data set is shown here.

Freshly made 1D dark-green $[Pt(MCO)_2]_n$, 5% in KBr pellet; excitation at 770 nm via fiber optical guide; the wavelength range was 700 – 1450 nm; integration times were used 0.5 sec for excitation and 5 sec for the emission. White integrating sphere, detector – CCD; slits were set to 10 nm. For excitation and 15 nm for the emission. Signal treatment: T1c/R1 (lamp) with the dark offset.



Similar data were collected for all samples of both 1D polymeric $[Pt(MCO)_2]_n$ and $[Pt(PiPCO)_2]_n$ complexes in KBr pellets at 0.1, 0.5, 1 weigh % concentrations. These are tabulated in the next page.

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Complex concentration (%)	Quantum yield, QY (%)		
	[Pt(PiPCO) ₂] _n	[Pt(MCO) ₂] _n	
5	0.91	0.21	
1	1.25	0.99	
0.5	1.65	1.24	
0.1	1.98	1.59	

Tabulated values of QY for studied 1D polymeric Pt-cyanoximates in KBr pellets.

Observed concentration dependence of the QY could be satisfactory fitted by the exponential function:



Photoluminescence properties of solid samples of 1D polymeric Pt-cyanoximates: pure complexes and their solid solutions in KBr matrix at variable concentrations.

Data of the NIR emission wavelength at different weigh concentrations of **Pt(PiPCO)**₂ in KBr pellets: 0.1%, 0.5%, 1%, 5% as well 100% - pure powdery complex.



The increase of concentration of the 1D polymer in the matrix leads to the bathochromic shift of the emission line as a result of interaction of photons (re-absorption and then re-emission) in multiple coupled oscillators.

A thousand-fold change in concentration of the NIR emitter – from pure sample to its 0.1% solid solution – leads to the shift of 908 cm⁻¹, which is equivalent to 10.86 kJ/mol, or 112 meV.

Intensity data obtained with the help of Ninox image camera using medium size reading area (~1/2 diameter spot) and Nikkor lens 1:28, long pass 800 nm filter. The excitation was provided with 735 nm bright LED from Thorlabs. The exposition time was set in all experiments at 0.5 s and -15°C sensor temperature.

Data of the NIR emission intensity at different weigh concentrations of **Pt(PiPCO)**₂ in KBr pellets: 0.1%, 0.5%, 1%, 5% concentrations. Values correspond to normalized on concentration of the complex in the pellet intensities.



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Data of the NIR emission intensities at different weigh concentrations of $Pt(MCO)_2$ in KBr pellets: 0.1%, 0.5%, 1%, 5% concentrations. **A** – experimental values of PL with error bars obtained after 4 different pellets were prepared and studied to investigate consistency and reproducibility of pelets, **B** – normalized on complex' concentration. Intensity data obtained with the help of Ninox image camera as above. Both intensity change profiles are well fit with single exponent curves.



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Photoluminescence life-times measurements from solid samples of Pt-cyanoximates at 5% weight concentrations in KBr matrix.

Emission profiles for dark-green polymeric **Pt(PiPCO)**₂ complex recorded prior to their life-times measurements using Fluorolog 3-21NIR spectrophotometer. Emission of complex at 1030 nm.



For lifetime measurements DeltaDiode 727 nm was used for excitation; detector: H1033-45; Emission monochromator slit: 5 nm. Below: top curve – signal decay; bottom curve – standard deviation.



T1 = 3.37×10^{-9} sec (st. dev. = 5.01×10^{-11} sec); T2 = 1.26×10^{-8} sec (st. dev. = 1.74×10^{-10} sec). Average Time = 4.79×10^{-9} sec.

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Emission profiles for dark-green polymeric **Pt(MCO)**₂ complex recorded prior to their life-times measurements using Fluorolog 3-21NIR spectrophotometer. Emission of complex at 1038 nm.



For lifetime measurements DeltaDiode 727 nm was used for excitation; detector: H1033-45; Emission monochromator slit: 5 nm. Below: top curve – signal decay; bottom curve – standard deviation.



T1 = 2.73×10^{-9} sec (st.dev. = 5.37×10^{-11} sec); T2 = 6.21×10^{-9} sec (st. dev. = 1.21×10^{-10} sec). Average Time = 3.45×10^{-9} sec.

Images of KBr pellets containing different concentrations of $[Pt(MCO)_2]_n$

Ninox image camera and Nikkor lens 1:28, long pass 800 nm filter.

A – no illumination photograph of all 4 pellets; **B** – same pellets illumined (excited) with 735 nm bright LED from Thorlabs. The exposition time was set in all experiments at 0.5 s and -15°C sensor temperature; **C** – same pellets, but two of the highest concentration of mixed valence Ptpolymer covered with Petri dish filled with 6 mm layer of water [to inspect the effect of "absorbing in this reagion of spectra" water] showing the emission coming through the dish.





85 (continued)



The excitation spectra of dark-green 1D polymeric [Pt(PiPCO)₂]_n at 5% in KBr pellet

Top panel – 3D view; bottom – 2D map showing continuous emission at any excitation wavelength from 300 to 800 nm.

