Electronic Supplementary Materials *Mendeleev Commun.*, 2020, **30**, 22–24

New antitumor hybrid materials based on Pt^{IV} organic complex and polymer nanoparticles consisting of *N*-vinylpyrrolidone and dimethacrylates

Svetlana V. Kurmaz, Natalya V. Fadeeva, Boris S. Fedorov, Galina I. Kozub, Nina S. Emel'yanova, Vladimir A. Kurmaz, Roman A. Manzhos, Anastasya A. Balakina and Alexei A. Terentyev

Table of Contents

Experimental

Materials and methods.

^{1}H NMR spectra of copolymers were recorded on an AVANCE III 500 MHz Bruker BioSpin NMR-spectrometer using deuterated chloroform as solvent in NMR tubes at 295K. The concentrations of copolymers were 6 mg ml^{-1}. DLS measurements for buffer (pH 6.8) solutions of Pt(IV)C1–Pt(IV)C3 were carried out at the detection angle of 90° using a Photocor Compact (Photocor Instruments Inc., USA) equipped with a diode laser operating at the wavelength of 654 nm. The experimental data were processed using DynaLS v. 2.8.3. TGA measurements were performed using an STA 409C LUXX NETZSCH synchronous thermal analyzer (Germany, 2006). FTIR spectra were recorded on a Bruker ALPHA FTIR spectrophotometer in the range of 4000−400 cm^{-1}, the number of scans was 16. The CHN content was analyzed on a Vario cube instrument (Elementar GmbH). The absolute molecular weights of copolymers were determined using a HPLC Waters GPCV 2000 (2 columns PS-gel, 5 microns, MIXED-C, 300×7.5 mm) equipped with a WYATT DAWN HELEOS II (658 nm) refractometric and light scattering detector in *N*-methyl pyrrolidone in the presence of LiCl (1%) in order to avoid the macromolecules aggregation.

Synthesis of Pt^{IV} complex.

A solution (14.6 mM) of *N*-(nitroxyethyl)isonocotinamide (3.1 g) in water (250 ml) was added to solution of $K_2[PtCl_6]$ (3.5 g, 7.19 mM) in H_2O (100 ml) at 40–60 °C. After stirring for 5 h, the reaction mixture was filtered out, and a yellow crystalline precipitate was washed out with ethanol and dried at a room temperature.

Isolation of copolymers 1–3.

Copolymers **1** and **3** were isolated from the toluene solution by precipitating the reaction mixture with a 10-fold excess of hexane. Copolymer **2** precipitated from the reaction mixture under the conditions of VP–TEGDM copolymerization. All the copolymers were dried from toluene and hexane in air and *in vacuo* until the constant weight.

Encapsulation of Pt^{IV} complex.

Solutions of copolymers **1**–**3** in Pr^{i}OH (Fluka) with their concentrations of 3.7, 1.5 and 3.5 mg ml^{-1} and of the complex in freezing-purified DMSO (12.8 mg ml^{-1}) were prepared. The solution of Pt(IV)C (0.12, 0.054 and 0.12 ml) was added dropwise to the solution (20 ml) of a copolymer in the alcohol under constant stirring with a magnetic stirrer. Pt(IV)C content per copolymers **1**–**3** was 2.1, 2.1 and 2.2%, respectively. Then, the organic solvents were evaporated in air and *in vacuo*. Their absence in the obtained polymer composites was controlled by IR spectroscopy. Phosphate buffer solution (PBS) similar by its composition to the physiological solution (137 mM NaCl, 2.68 mM KCl, 4.29 mM Na_2HPO_4, and 1.47 mM KH_2PO_4, pH 6.8–7.0) was added to the dry residues.

For chemical analysis, the polymer composites based on copolymer **1** were prepared. Solution of Pt (IV)C in DMSO (0.48 ml, 12.8 mg ml^{-1}) was added dropwise to a solution (15 ml) of copolymer **1** in Pr^{i}OH (3.7 mg ml^{-1}) and dried from the solvents in air and *in vacuo* until the constant weight.

For IR spectroscopic study, the polymer composites based on copolymer **3** containing 18% of Pt^{IV} complex were prepared. Solution of Pt (IV)C in DMSO (0.93 ml, 12.8 mg ml^{-1})

was added dropwise to a solution (16 mL) of copolymer **3** in Pr^{i}OH (3.5 mg ml^{-1}) and dried from the solvents in air and *in vacuo* until the constant weight.

Quantum-chemical calculations.

The calculations were carried out within the framework of density functional theory (DFT) with full optimization of the geometry of the initial molecules and their complexes (tpssh / lanl2dz) using the Gaussian 09 program.[S1] Using the polarized continuum model (PCM), an influence of the solvent (water) was taken into account. In results of calculations, there are no imaginary oscillation frequencies, all the optimized structures correspond to the minimum potential energy. Theoretical spectra of reagents and adduct were simulated using ChemCraft program (version 1.8).[S2]

The TEM study of polymer particles loaded by Pt^{IV} complex.

The aqueous solution of P(IV)C3 was applied to the substrate, water was quickly evaporated, and image was obtained by Leo 912 AB equipment.

The electrochemical study of encapsulation Pt^{IV} complex.

Electrochemical experiments were carried out in a three-electrode quartz cell *ca.* 10 cm^3 of volume *via* cyclic voltammetry with using an IPC-ProL potentiostat (IPCE of RAS, Russia). The working electrode was a glassy carbon (**GC**) disc of 1.6 mm diameter, polymerized into an inert PEEK polymer (AES, Japan), the auxiliary electrode was a Pt wire, and the reference electrode was a silver/silver chloride electrode (Ag/AgCl), relative to which all the potentials were measured and given in the paper. GC-electrode was polished immediately before an experiment by a diamond suspension (diameter of 1 μm) then rinsed with ultrasonic machining in a media where the investigation was performed (water or a respective non-aqueous solvent).

The estimation of the complex and polymer particles cytotoxicity.

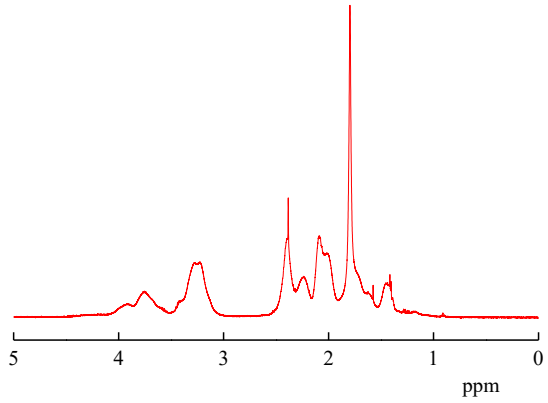
The study was carried out on the culture of mammalian cells. As a model of tumor cells, A-172 culture (human glioblastoma) was used. It was obtained from the collection of the Institute of Cytology, Russian Academy of Sciences. Cell cultivation was carried out according to the standard procedure in an atmosphere of 5% CO_2 and a temperature of 37 °C. Cells were cultured in DMEM medium (PanEco, Russia) with the addition of 10% fetal calf serum (BioWest, France).

The study of the cytotoxic properties of PC and polymer particles was performed using the MTT test. The cells were seeded into 96-well culture plates at a concentration of 7×10^4 cells / ml. The studied compounds were introduced into the culture medium 24 h after sieving. MTT dye (3-(4.5-dimethylthiazol-2-yl)-2.5-diphenyl-2*H*-tetrazolium bromide) was added to the incubation medium 48 h after the introduction of the compounds. The resulting formazan crystals were dissolved in 100% DMSO. The optical density was measured at a fundamental wavelength of 570 nm and a background wavelength of 620 nm using a Spark 10M multifunctional microplate reader (Tecan, USA). The cytotoxicity index (IC_{50}) was determined on the basis of dose-dependent curves using a median effect analysis. The results of three independent experiments are presented as mean ± SD. The evaluation of statistical significance was performed using the *t*-test. The criterion of statistical significance was $*p < 0.05$.

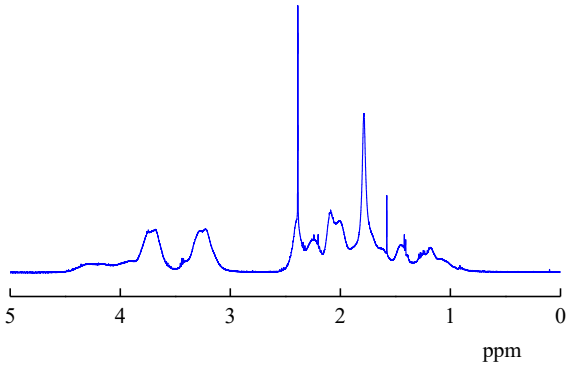
Details of Pt^{IV} complex synthesis, instrumentation, electrochemical, ^{1}H NMR, IR, TGA and cytotoxicity study could be found in refs. S7–S13.

^{1}H NMR spectra of the copolymers 1–3

(*a*)



(*b*)



(*c*)

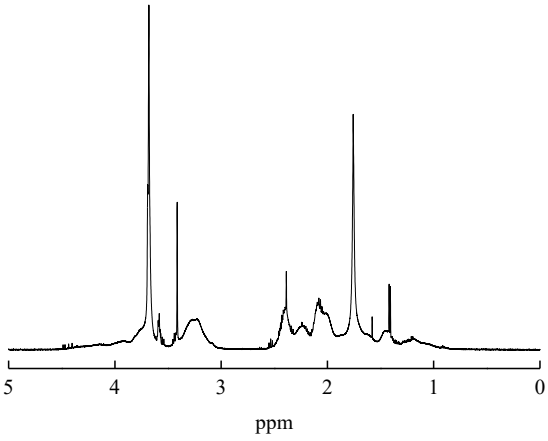


Figure S1 ^{1}H NMR spectra of the copolymers (*a*) **1**, (*b*) **2** and (*c*) **3** recorded in $CDCl_3$.

Molecular weight (MW)–eluent volume V_R dependences

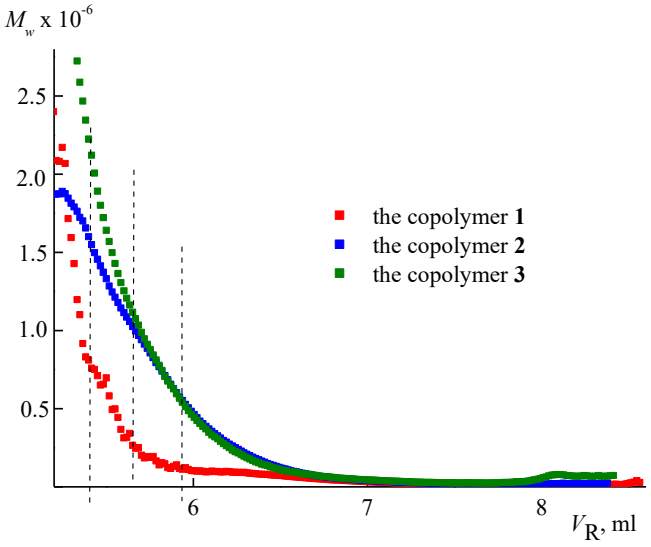


Figure S2 Dependences of average MW on eluent volume V_R for copolymers **1**–**3**.

The direct evidence of differences in topological structure of copolymers **1**–**3** was revealed by the analysis of dependences of MW on the eluent volume V_R (Figure S2). Macromolecules **2** and **3** with higher molecular weight were eluted by the same V_R within V_R range of 5.2–7 ml. This evidences on higher package density of their polymer chains with respect to copolymers **1**.

TEM image of Pt(IV)C3

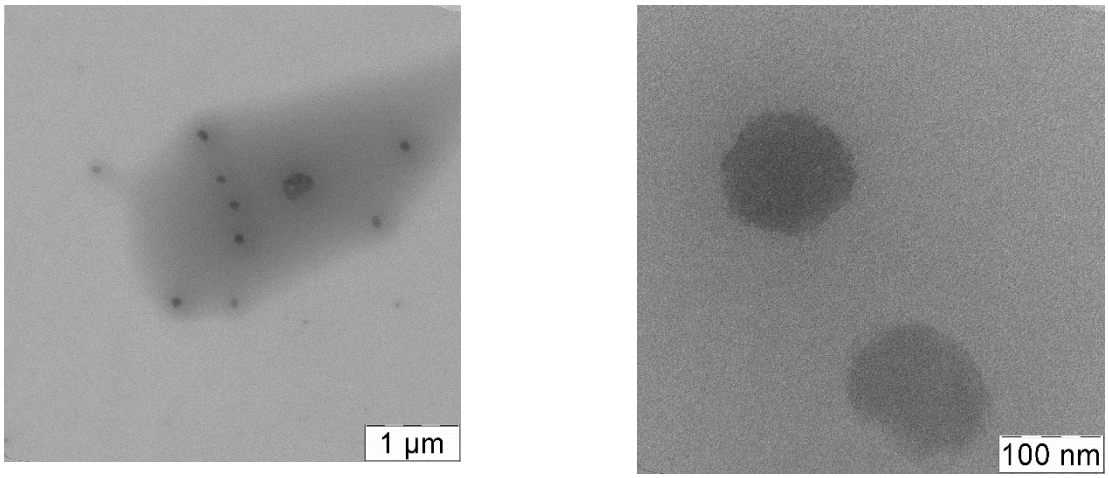
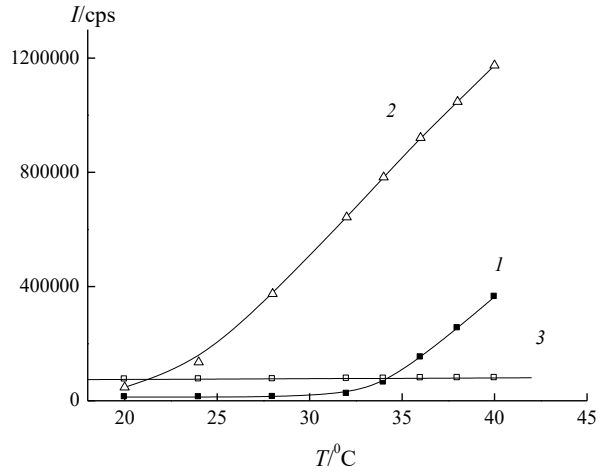


Figure S3 TEM image of polymer particles **3** loaded with Pt^{IV} complex.

Dependences of the light scattering intensity *I* and hydrodynamic radius R_h for aqueous buffer (pH 6.8) solutions of Pt(IV)C1–Pt(IV)C3 on temperature *T*

(*a*)



(*b*)

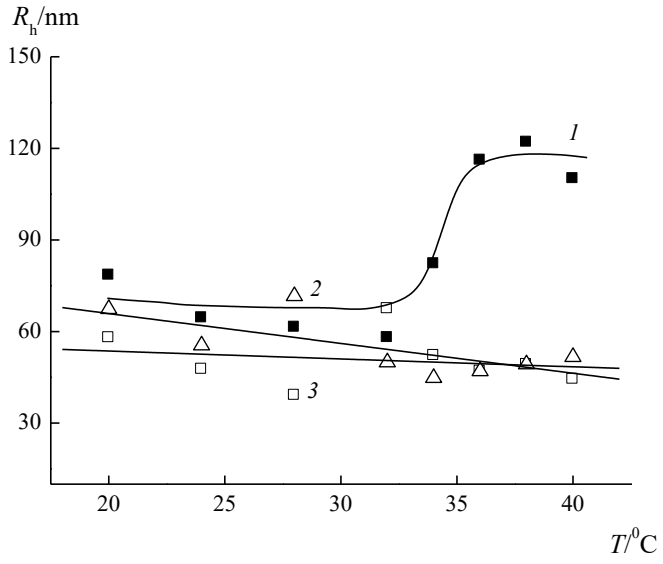


Figure S4 Dependences of the (*a*) light scattering intensity and (*b*) hydrodynamic radius for aqueous buffer (pH 6.8) solutions of Pt(IV)C1–Pt(IV)C3 (curves *1–3*, respectively) on the temperature. The concentrations of Pt(IV)C1–Pt(IV)C3 were 1.4, 1.8 and 1.4 mg ml^{-1}, respectively.

The TGA curve for the Pt^{IV} complex

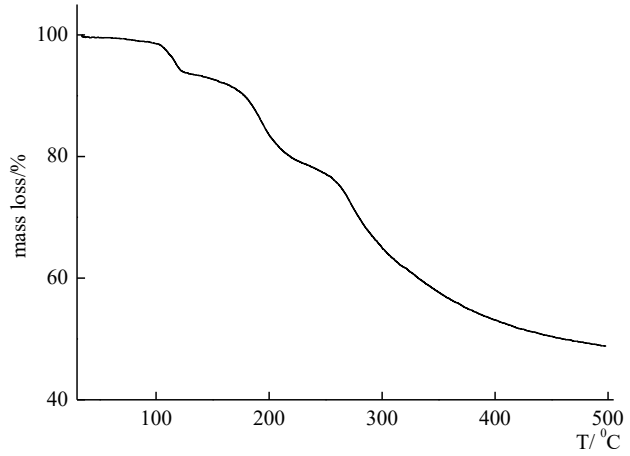


Figure S5 The TGA curve for the Pt^{IV} complex. The heating rate was 5 degrees min^{-1}. Ar atmosphere.

IR spectra of Pt(IV)C, copolymer 3,and Pt(IV)C3

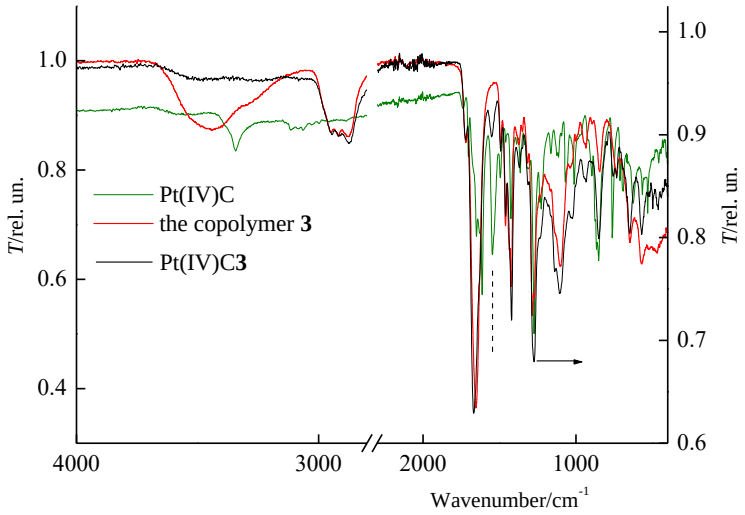


Figure S6 IR spectra of Pt(IV)C, copolymer **3**, and the Pt(IV)C3.

The tpssh / lanl2dz optimized structures

Pt(IV) complex

78	0.206318000	1.721874000	0.051887000
17	-0.263900000	2.351444000	2.344939000
17	-1.369688000	3.340076000	-0.738019000
17	1.966489000	3.339385000	-0.031953000
17	0.672091000	1.054438000	-2.233393000
6	3.625299000	-1.413630000	1.542898000
6	2.725387000	-1.772709000	0.517349000
6	1.726796000	-0.872113000	0.131761000
7	1.609283000	0.348363000	0.727240000
6	2.462015000	0.710115000	1.731184000
6	3.467417000	-0.160516000	2.165714000
1	2.775238000	-2.741304000	0.032225000
1	1.030216000	-1.089329000	-0.666797000
1	2.312634000	1.692780000	2.156851000
1	4.115392000	0.131028000	2.983920000
6	-3.586050000	-1.333949000	0.251690000
6	-2.678461000	-1.252320000	1.328206000
6	-1.583072000	-0.389342000	1.243604000
7	-1.354331000	0.352669000	0.120057000
6	-2.198148000	0.261321000	-0.947100000
6	-3.323591000	-0.571058000	-0.903689000
1	-2.829000000	-1.856486000	2.215164000
1	-0.890125000	-0.250927000	2.062575000
1	-1.951064000	0.867241000	-1.808222000
1	-3.961480000	-0.626307000	-1.778442000
6	-4.723622000	-2.322589000	0.354511000
8	-4.499570000	-3.470105000	0.833121000
6	4.666207000	-2.362218000	2.084026000
8	4.770937000	-2.530270000	3.329764000
7	-5.975158000	-1.949930000	-0.085298000
1	-6.681353000	-2.684061000	-0.044364000
7	5.461987000	-3.064576000	1.195462000
1	6.063795000	-3.748113000	1.651550000
6	5.740008000	-2.773047000	-0.222303000
1	4.992511000	-2.083131000	-0.614197000
1	5.693380000	-3.697831000	-0.806069000
6	7.142301000	-2.142739000	-0.366201000
1	7.200950000	-1.159095000	0.108463000
1	7.929577000	-2.792341000	0.030227000
6	-6.448655000	-0.596970000	-0.430018000
1	-6.472090000	-0.440408000	-1.517067000
1	-5.755393000	0.136440000	-0.006851000
6	-7.853606000	-0.295744000	0.125190000
1	-8.066635000	-0.836444000	1.051630000
1	-7.981373000	0.778974000	0.277850000
8	-8.943003000	-0.545713000	-0.867620000
8	7.304355000	-2.006800000	-1.835291000
7	8.638961000	-1.435820000	-2.215173000
8	9.424632000	-1.155778000	-1.264133000

8	8.783543000	-1.318956000	-3.449494000
7	-9.403987000	-1.959510000	-0.936254000
8	-8.780389000	-2.809795000	-0.226391000
8	-10.373191000	-2.121463000	-1.703154000

The copolymer consisting of three VP-units

6	2.735859000	-0.702769000	1.231304000
1	2.792813000	-1.467663000	0.448721000
6	1.338752000	-0.750179000	1.888471000
1	1.241533000	-1.728535000	2.378034000
1	1.276956000	-0.001607000	2.689918000
6	0.135924000	-0.527336000	0.933448000
1	0.216343000	0.463870000	0.473668000
6	-1.177153000	-0.619903000	1.755276000
1	-1.203867000	-1.579683000	2.289106000
1	-1.138481000	0.160682000	2.527522000
6	-2.504053000	-0.497127000	0.967020000
1	-2.573659000	-1.307553000	0.231889000
6	-3.709133000	-0.608842000	1.941287000
1	-3.590572000	-1.541835000	2.508939000
1	-3.663477000	0.210937000	2.672158000
7	-2.566348000	0.745677000	0.168473000
6	-2.838888000	0.758670000	-1.178248000
8	-3.095948000	-0.266362000	-1.885611000
1	-3.562119000	2.415820000	-2.383399000
1	-1.802580000	2.336981000	-2.187809000
1	-2.253498000	3.966105000	-0.428718000
1	-3.884032000	3.318780000	-0.170692000
6	-2.843391000	3.047939000	-0.375883000
6	-2.760983000	2.203820000	-1.671039000
6	-2.320670000	2.094976000	0.733638000
1	-1.249783000	2.242584000	0.924116000
1	-2.858192000	2.221379000	1.678193000
7	0.155817000	-1.466251000	-0.205635000
6	0.239205000	-1.051617000	-1.515524000
8	0.351159000	0.153583000	-1.899149000
1	0.873334000	-2.215324000	-3.235562000
1	-0.852451000	-2.321954000	-2.851244000
1	-0.146146000	-4.369064000	-1.729999000
1	1.481946000	-3.721783000	-1.454204000
6	0.416077000	-3.472444000	-1.458636000
6	0.153825000	-2.284366000	-2.415984000
6	-0.001943000	-2.934707000	-0.063163000
1	-1.043552000	-3.186432000	0.174790000
1	0.636362000	-3.316409000	0.739059000
7	2.978447000	0.577488000	0.527808000
6	3.593449000	0.635737000	-0.698542000
8	3.952874000	-0.372127000	-1.386748000
1	3.519427000	2.279255000	-2.113881000
1	4.865898000	2.344178000	-0.967737000
1	3.370535000	3.836129000	0.239367000

1	1.939410000	3.075663000	-0.481435000
6	2.928792000	2.881412000	-0.055608000
6	3.800061000	2.104360000	-1.072018000
6	2.798214000	1.912999000	1.150543000
1	3.576506000	2.090893000	1.904403000
1	1.822707000	1.986936000	1.638480000
6	-5.079287000	-0.605148000	1.234189000
1	-5.166501000	-1.452806000	0.543044000
1	-5.891788000	-0.678634000	1.967470000
1	-5.223607000	0.317652000	0.659656000
6	3.844396000	-0.976738000	2.276644000
1	3.830634000	-0.224742000	3.074816000
1	3.693872000	-1.961723000	2.734054000
1	4.831616000	-0.963663000	1.801766000

The proposed adduct

6	5.883952000	-0.898570000	1.525162000
1	4.951475000	-0.605521000	1.030760000
6	6.625207000	0.368912000	2.004615000
1	6.005336000	0.827792000	2.786411000
1	7.568599000	0.088168000	2.491626000
6	6.943226000	1.427154000	0.914638000
1	7.581134000	0.981877000	0.142847000
6	7.676922000	2.622420000	1.577355000
1	7.041085000	3.041115000	2.369028000
1	8.572206000	2.229950000	2.078217000
6	8.079801000	3.787153000	0.640816000
1	7.189495000	4.181825000	0.136504000
6	8.731874000	4.930602000	1.466487000
1	8.026996000	5.207532000	2.262222000
1	9.634367000	4.549901000	1.965533000
7	8.968377000	3.333962000	-0.451953000
6	8.725722000	3.597909000	-1.778260000
8	7.745164000	4.271384000	-2.226436000
1	10.143218000	3.589885000	-3.424137000
1	9.417489000	2.017549000	-3.056875000
1	11.489686000	1.712191000	-1.810022000
1	11.658220000	3.458667000	-1.554389000
6	10.942826000	2.630668000	-1.584018000
6	9.824256000	2.933711000	-2.610563000
6	10.196506000	2.532433000	-0.225856000
1	9.936447000	1.494762000	0.019900000
1	10.780388000	2.946213000	0.601627000
7	5.727054000	1.857818000	0.194738000
6	5.541273000	1.654253000	-1.153574000
8	6.345826000	1.038972000	-1.919914000
1	3.664283000	1.664100000	-2.243730000
1	4.450087000	3.243111000	-2.094788000
1	2.901477000	3.488673000	-0.231980000
1	2.834107000	1.729823000	0.012187000
6	3.493245000	2.569968000	-0.220222000

6	4.222090000	2.311268000	-1.562030000
6	4.638261000	2.644808000	0.826139000
1	4.966238000	3.677794000	1.000963000
1	4.353507000	2.207072000	1.787501000
7	6.651150000	-1.638914000	0.492707000
6	6.054271000	-2.221608000	-0.588239000
8	4.814986000	-2.142120000	-0.876044000
1	7.004240000	-2.817913000	-2.443678000
1	6.915981000	-4.082183000	-1.209783000
1	9.184140000	-3.358612000	-0.720921000
1	8.869562000	-1.739858000	-1.372631000
6	8.449021000	-2.552463000	-0.772501000
6	7.097809000	-3.012346000	-1.372295000
6	8.079316000	-2.026233000	0.640112000
1	8.180084000	-2.804121000	1.407402000
1	8.686568000	-1.167645000	0.935853000
6	9.082742000	6.178230000	0.631237000
1	8.183862000	6.611082000	0.174920000
1	9.547211000	6.945609000	1.262667000
1	9.786129000	5.929623000	-0.172413000
6	5.546092000	-1.823441000	2.719515000
1	6.454804000	-2.144201000	3.242805000
1	4.910241000	-1.290087000	3.435557000
1	5.008072000	-2.713334000	2.375654000
78	-5.084642000	-1.839403000	-0.444358000
17	-5.135169000	-3.020947000	1.673165000
17	-4.931843000	-3.957668000	-1.595219000
17	-7.497754000	-1.956119000	-0.538052000
17	-5.083616000	-0.696062000	-2.584453000
6	-5.507371000	2.450133000	1.804476000
6	-4.611916000	2.290190000	0.727441000
6	-4.494623000	1.042420000	0.108010000
7	-5.235855000	-0.024310000	0.528860000
6	-6.103345000	0.108430000	1.576640000
6	-6.247381000	1.332053000	2.236098000
1	-3.993799000	3.105648000	0.371038000
1	-3.826763000	0.885166000	-0.726771000
1	-6.660961000	-0.770576000	1.864916000
1	-6.931261000	1.403039000	3.072876000
6	-0.224546000	-1.727587000	-0.258311000
6	-0.995214000	-1.463728000	0.892158000
6	-2.388974000	-1.498984000	0.816076000
7	-3.022226000	-1.765898000	-0.366576000
6	-2.295514000	-2.010647000	-1.496071000
6	-0.897197000	-1.998519000	-1.467164000
1	-0.524511000	-1.230469000	1.839241000
1	-3.010197000	-1.325466000	1.683269000
1	-2.849297000	-2.209604000	-2.401997000
1	-0.359232000	-2.180962000	-2.390083000
6	1.278838000	-1.565993000	-0.192243000
8	1.730814000	-0.439932000	0.201429000
6	-5.603105000	3.740154000	2.585064000

8	-5.361075000	3.722285000	3.831726000
7	2.089454000	-2.589326000	-0.575141000
1	3.106215000	-2.385348000	-0.604805000
7	-5.920261000	4.897113000	1.925368000
1	-5.900582000	5.735394000	2.503834000
6	-6.431135000	5.054902000	0.551762000
1	-6.224192000	4.158126000	-0.031222000
1	-5.925837000	5.900855000	0.079550000
6	-7.952749000	5.306668000	0.595038000
1	-8.503343000	4.449384000	0.988610000
1	-8.208451000	6.214802000	1.145881000
6	1.689070000	-3.975968000	-0.864956000
1	2.232031000	-4.321264000	-1.749100000
1	0.622034000	-4.030245000	-1.089167000
6	1.936357000	-4.942698000	0.301536000
1	1.525713000	-4.578908000	1.245764000
1	1.550398000	-5.938187000	0.069220000
8	3.428860000	-5.025181000	0.424611000
8	-8.307537000	5.496947000	-0.845946000
7	-9.734845000	5.777467000	-1.055719000
8	-10.481107000	5.824599000	-0.034626000
8	-10.033926000	5.938169000	-2.266412000
7	3.872041000	-5.939135000	1.480052000
8	2.984982000	-6.558771000	2.138357000
8	5.124513000	-5.991432000	1.597100000

Theoretical IR spectra of a platinum complex, a portion of a copolymer and an adduct

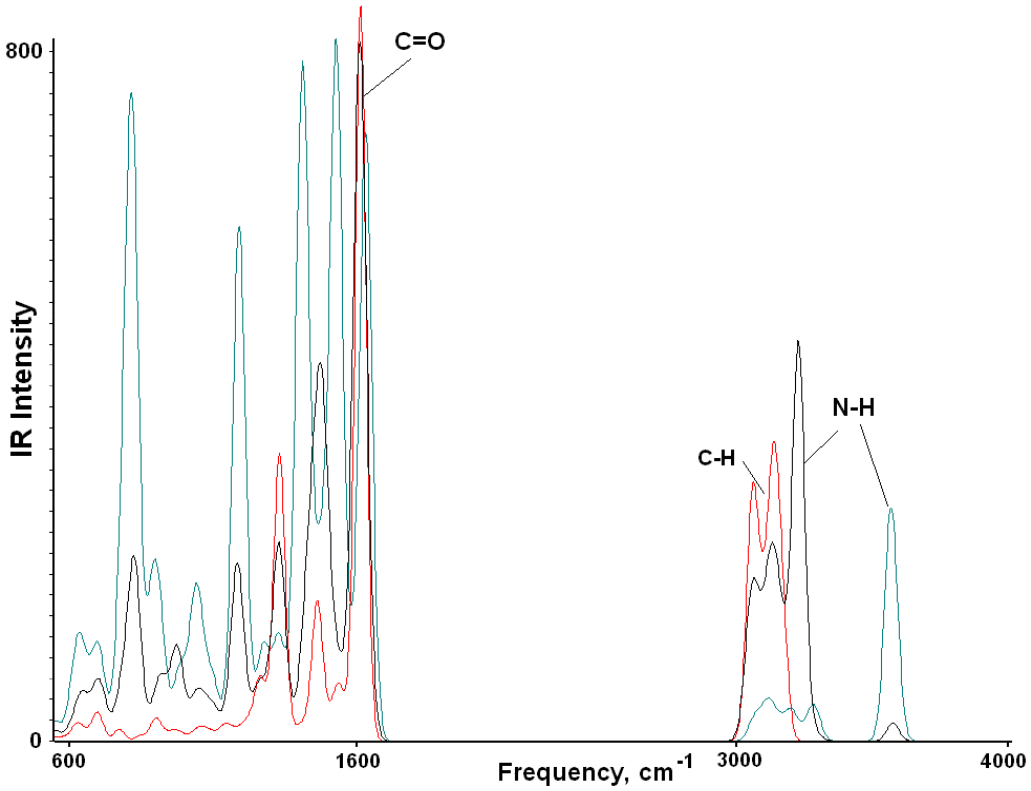


Figure S7 Theoretical IR spectra of a complex of platinum (green), a portion of a copolymer (red) and an adduct (black).

Theoretical spectra confirmed the assumption on the structure of the Pt^{IV} complex copolymer adduct. First of all, a single peak is of interest within the region of 3300 cm^{-1} in the spectrum of the platinum complex, corresponding to the stretching vibrations of the N–H group. It is also present in the theoretical spectrum at 3558 cm^{-1} (thus, the scaling factor is 1.08). It shifts by 327 cm^{-1} in the simulated spectrum of the adduct, and falls into the region of C–H bonds stretching vibration. The small shift of the absorption band of the C=O group vibration in VP moiety is apparently due to the hydrated state of the initial copolymer and its characteristic shift of absorption band in its IR spectrum.

CVA encapsulated Pt(IV)C in aqueous phosphate buffer, DMSO, and initial Pt(IV)C in DMSO

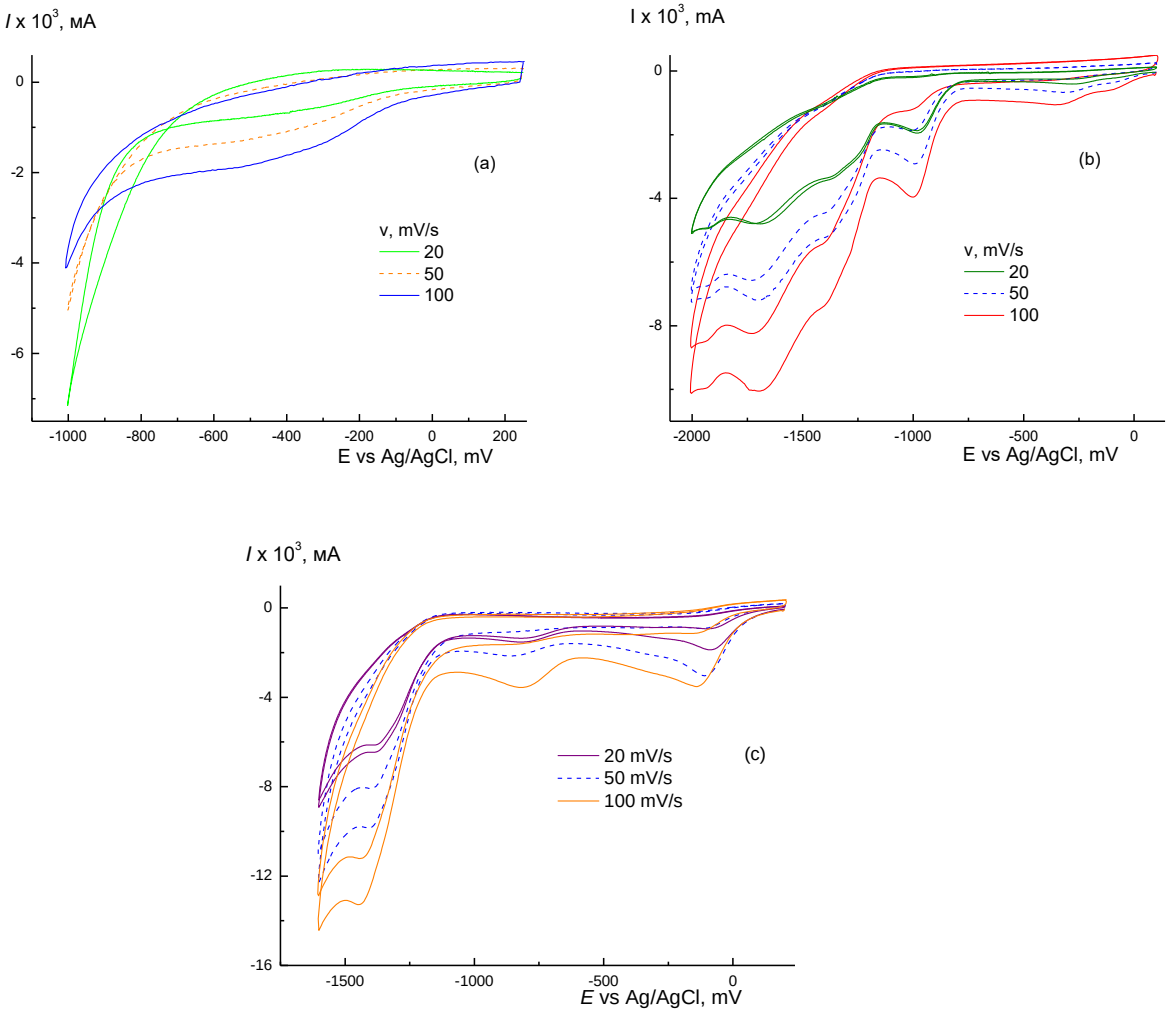


Figure S8 CVA curves recorded on GC-electrode at different scan rates *v* for (*a*) encapsulated Pt^{IV} complex in aqueous phosphate buffer solution + 0.5 KCl, (*b*) in DMSO + 0.1 M $TBAPF_6$, and (*c*) initial Pt(IV) complex in DMSO + 0.1 M $TBAPF_6$.

Table S1 The viability of A-172 cells after 48 h incubation with polymer particles **1**–**3**.

Concentration/μg ml^{-1}	Part of living cells (%)
Polymer particle **1**	
0	100.00 ± 5.62
7	104.59 ± 3.95
70	95.64 ± 6.09
700	95.46 ± 9.10
Polymer particle **2**	
0	100.00 ± 3.56
7	102.92 ± 8.13
70	99.56 ± 6.75
700	98.37 ± 7.23
Polymer particle **3**	
0	100.00 ± 7.64
7	97.72 ± 2.38
70	94.79 ± 6.07
700	92.93 ± 6.50

References

S1 Gaussian, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision B.01*, Gaussan Inc., Wallingford CT, 2009.

S2 *Chemcraft – graphical software for visualization of quantum chemistry computations*. https://www.chemcraftprog.com

S3 B. S. Fedorov, M. A. Fadeev, G. I. Kozub, S. M. Aldoshin, Z. G. Aliyev, L. O. Atovmyan, N. P. Konovalova, T. E. Sashenkova, T. A. Kondratieva, S. V. Blokhina, *Pharm. Chem. J.*, 2009, **43** (3), 134 [*Khim.-Farm. Zh.*, 2009, **43** (3), 12].

S4 B. S. Fedorov, M. A. Fadeev, G. I. Kozub, A. N. Chekhlov, N. P. Konovalova, T. E. Sashenkova, E. I. Berseneva, O. V. Dobrokhotova, L. V. Tatyanenko, *Russ. Chem. Bull.*, *Int. Ed.*, 2011, **60**, 1181 [*Izv. Akad. Nauk. Ser. Khim.*, 2011, **60**, 1155].

S5 S. V. Kurmaz, V. D. Sen', A. V. Kulikov, D. V. Konev, V. A. Kurmaz, A. A. Balakina, A. A. Terent'ev, *Russ. Chem. Bull., Int. Ed.*, 2019, **68**, 1769 [*Izv. Akad. Nauk. Ser. Khim.*, 2019, **68**, 1769].

S6 S. V. Kurmaz, T. N. Rudneva, N. A. Sanina, *Mendeleev Commun.*, 2018, **28**, 73.

S7 S. V. Kurmaz, N. A. Obraztsova, *Mendeleev Commun.*, 2015, **25**, 350.

S8 S. V. Kurmaz, N. A. Obraztsova, A. A. Balakina, A. A. Terent'ev, *Russ. Chem. Bull., Int. Ed.*, 2016, **65**, 2097 [*Izv. Akad. Nauk. Ser. Khim.*, 2016, **65**, 2097].

S9 V. Kurmaz, V. Yu. Gak, V. A. Kurmaz, D. V. Konev, *Russ. J. Phys. Chem.*, 2018, **92**, 329 [*Zh. Fiz. Khim.*, 2018, **92**, 293].

S10 B. S. Fedorov, M. A. Fadeev, G. I. Kozub, N. P. Konovalova, L. M. Volkova, *RU Patent 2245328*, 2004.

S11 A. G. Krivenko, A. S. Kotkin, V. A. Kurmaz, *Russ. J. Electrochem.*, 2005, **41**, 137.

S12 S. V. Kurmaz, N. A. Obraztsova, E. O. Perepelitsina, G. V. Shilov, D. V. Anokhin, E. V. Pechnikova, *Materials Today Commun.*, 2015, **4**, 130.

S13 S. V. Kurmaz, N. A. Obraztsova, E. N. Kabachkov, *Colloid Polymer Sci.*, 2016, **294**, 2087.