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Spectroscopic and Electrochemical Properties of Mixed-Ligand Cycloplatinated Complexes Based on 2-(2-Thienyl)Pyridine and 2-Phenylpyridine with 1,10-Phenantroline and Its 1,4-Diazine Derivatives

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Abstract—A comparative study of dipyrido- and dibenzo-substituted 1,4-diazines {dipyrido[f,h]quinoxaline (dpq), dipyrido[*a,c*]phenazine (dppz), 6,7-dicyanodipyrido[*f,h*]quinoxaline (dicnq), dibenzo[*f,h*]quinoxaline, dibenzo[*a,c*]phenazine, 6,7-dicyanodibenzo[*f,h*]-quinoxaline}, *o*-phenantroline (phen), and also of the complexes $[Pt(N\^{}C)(N\^{}N)]^+$ [$(N\^{}C)^-$ are depronorated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine; (N^N) is ethylenediamine, phen, dpq, dppz, dicnq] was carried out by the methods of ^{1}H NMR, electronic absorption, and emission spectroscopy and by cyclic voltammetry. It was found that in frozen solutions of $[Pt(N\^{}C)\cdot(N\^{}N)]^+$ complexes the photoexcitation energy decay from two lowest in energy electronic excited states has isolated character and is localized on {Pt(N^C)} and {Pt(N^N)} metal-complex fragments: $(d–\pi^*_{N\^{}C})$ and $(d–\pi^*_{phen})$ [(N^N) = phen, dpq, dicnq)] or $(d–\pi^*_{N\^{}C})$ and $(\pi–\pi^*_{diaz})$ [(N^N) = dppz]. Thermal quenching of the luminescence from the $(d–\pi^*_{phen})$ and $(\pi–\pi^*_{diaz})$ states gives rise to luminescence of the complexes in liquid solutions at 293 K only from the $(d–\pi^*_{N\^{}C})$ state.

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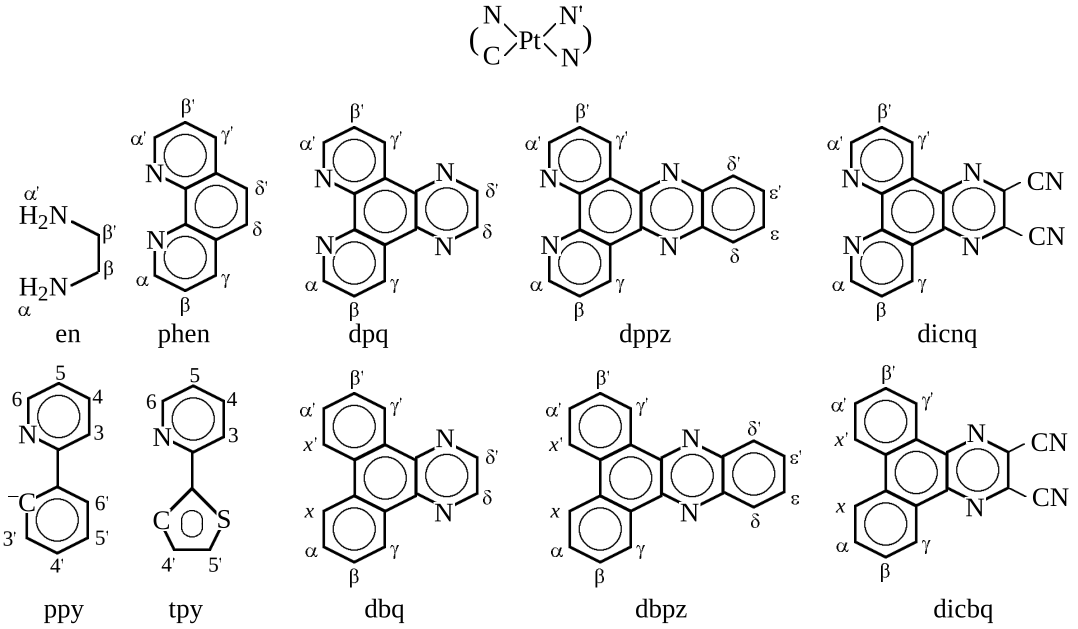
The development of the chemistry of molecular-organized metal–complex systems, capable of directed transport and accumulation of charge or energy on a reaction center owing to a spatial and structural organization of individual photo- and electroactive components determines interest to the complexes with long-living excited states and reversible processes of outer-sphere charge transfer, which able to function as structural components of the molecular-organized systems with variable optical and electrochemical properties [1, 2].

It has been shown previously [3, 4] that ethylenediamine (en) cycloplatinated complexes $[Pt(N\^{}C)en]^+\cdot$ [(N^C) designates deprotonated forms of phenyl-, thienyl- and benzo-substituted pyridines] are effectively luminescenting substances not only in frozen (77 K), but also in liquid (293 K) solutions and are characterized by reversible one-electron reduction processes. Within the limits of the model of localized molecular orbitals [5] and Koopmans theorem [6], optical and electrochemical properties of the complexes are determined by the metal-centered d_π character of the highest occupied molecular orbital and by the ligand-centered $\pi^*_{C\^{}N}$ character of the lowest unoccupied molecular orbital. This allows obtaining complexes with variable optical and electrochemical parameters by changing nature of the cyclometallated ligands. Replacement of aliphatic ethylene diamine by heterocyclic diimine (N^N) ligand possessing its own low-energy unoccupied π* orbitals expands a possibility of modification of the optical and electrochemical characteristics of cycloplatinated complexes and favors their intercalating action in reactions with nucleic acids [7].

In this work we represent the results of comparative study of spectroscopic and electrochemical properties of dipyrido- and dibenzo-substituted 1,4-diazines {dipyrido[*f,h*]quinoxaline (dpq), dipyrido[*a,c*]-phenazine (dppz), 6,7-dicyanodipyrido[*f,h*]quinoxaline (dicnq), dibenzo [*f,h*] quinoxaline (dbq), dibenzo[*a,c*]-phenazine (dbpz), 6,7-dicyanodibenzo[*f,h*]quinoxaline (dicbq)}, 1,10-phenantroline (phen), and also of mixed-ligand cycloplatinated $[Pt(N\^{}C)(N\^{}N)]^+$ complexes [(N^C) means deprotonated forms of 2-phenylpyridine (ppy) and 2-(2-thienyl)pyridine (tpy) and (N^N) designates etylenediamine (en), phen, dpq, dppz, dicnq].



Proton chemical shifts (δ) in NMR spectra, maxima of absorption bands (λ_{max}), and corresponding extinction coefficients (ε), maxima of luminescence bands (λ'_{max}), and also half-wave potentials ($E_{1/2}$) and differences between potentials of peak currents (ΔE) in voltammograms of electroreduction processes for diryrido- and dibenzo-substituted 1,4-diazines are given in Table 1.

Specificity of electronic structure of 1,4-diazine derivatives of 1,10-phenantroline (dpq, dppz, dicnq) is determined by the presence of two heterocycles, phenantroline and diazine, in their composition. Comparison of spectroscopic and electrochemical characteristics of dpq, dppz, and dicnq with both 1,10-phenantroline and dibenzo-substituted 1,4-diazines (dbq, dbpz, dicbq) points to a weak electronic interaction between the phenantroline and diazine parts of the (N^N) ligands, which agrees with the results of quantum-chemical calculations of dipyrido[*a,c*]phenazine [8]. The ^{1}H NMR spectroscopy data point to a weak influence of the nature of diazine substituents on the proton chemical shifts of phenantroline parts of dipyrido-substituted 1,4-diazines [$\delta(H^{\alpha})$ 9.25±0.11,

Table 1. Spectroscopic and electrochemical parameters of 1,4-diazine derivatives of 1,10-phenantroline and phenanthrene

Compound	δ, ppm^a					λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1})^b	λ_{max}, nm^c	$-E_{1/2}$m V (ΔE, mV)^{b,d}
	H^x	H^{α}	H^{β}	H^{γ}	$H^{\delta\varepsilon}$			
phen	–	9.08	7.71	8.43	7.91	270 (28.1)	459, 490, 531	2.51 (60)
dppz	–	9.14	7.86	9.44	8.27/7.99	268 (27.3), 363 (10.4), 378 (7.9)	545, 559,^{e} 589, 640^e	1.61 (60), 2.49 (60)
dpq	–	9.24	7.96	9.45	9.17	276^e (12.1), 336^e (3.2)	429,^{e} 455, 476, 518^e	2.00 (60), 2.53^f
dicnq	–	9.36	8.04	9.41	–	265 (43.6), 307 (23.1), 364^e (7.4)	466,^{e} 478, 517, 573^e	1.09 (70), 2.10^d, 2.57^d
dbpz	8.80	7.91	7.83	9.32	8.36/8.00	279 (33.9), 306 (9.3), 374 (14.0), 392 (14.9)	550, 563, 594, 612^e	1.57 (160), 2.17^f
dbq	8.83	7.87	7.82	9.13	9.04	253 (35.5), 305 (12.0), 338 (9.5), 353 (8.8)	442, 459, 470, 492, 506	2.12 (70)
dicbq	8.92	8.05	7.93	9.08	–	271 (15.4), 318 (14.4), 368 (6.7)	469, 489,^{e} 500, 529	1.03 (70)

[a] δ relative to $Si(CH_3)_4$, $(CD_3)_2SO$, 293 K. [b] DMF, 293 K. [c] DMF–toluene, 1:1, 77 K. [d] $E_{1/2}$ relative to the Fc^+/Fc redox system. [e] Shoulder. [f] Peak-current potential at the potential scanning rate of 100 mV s^{-1}.

$\delta(H^{\beta})$ 7.95±0.09, $\delta(H^{\gamma})$ 9.43±0.02 ppm], a closeness of the chemical shifts of H^{α} and H^{β} protons and similar signals for 1,10-phenantroline ($\Delta\delta < 0.2 \pm 0.1$ ppm), and also a slight change in chemical shifts of H^{δ} and H^{ε} diazine protons for dipyrido-substituted 1,4-diazines compared to the corresponding dibenzo derivatives ($\Delta\delta < 0.0 \pm 0.1$ ppm). The reduction in the chemical shifts of H^{α} and H^{β} protons in the series dicnq > dpq > dppz > phen points to a regular reduction in the basicity of pyridine nitrogen atoms on the introduction of diazine substituents with acceptor properties.

Within the framework of the model of localized molecular orbitals [5] the electrochemical and optical properties of dipyrido-substituted 1,4-diazines are determined by the electro- and photo-stimulated electron transfer involving low-energy unoccupied π^* orbitals mainly localized on poorly interacting phenantroline (π^*_{phen}) and diazine (π^*_{diaz}) parts of ligands. Reduction voltammograms of 1,10-phenantroline and its 1,4-diazine derivatives are characterized by one-electron reduction waves with practically invariable a half-wave potential (E –2.53±0.03 V) (phen, dppz) or a peak current (dpq, dicnq) related to the electron transfer on redox orbitals of π^*_{phen} ligands. At the same time the presence of additional anode-shifted reversible one-electron reduction waves is characteristic for diazine derivatives of 1,10-phenantroline. Their half-wave potentials are close ($\Delta E_{1/2}$ 0.07±0.04 V) to the potentials of one-electron reduction waves of corresponding dibenzo derivatives of 1,4-diazines. It allows us to assign this reduction wave of diazine derivatives of 1,10-phenantroline to the electron transfer on the lowest in energy redox orbitals of π^*_{diaz} ligands. The presence of π-acceptor benzo (dppz) and cyano (dicnq) substituents in the diazine parts of the ligands gives rise to the reduction in the energy of the π^*_{diaz} redoxorbital and results in the anodic displacement of the first-wave potential of the ligand reduction in the series dicnq > dppz > dpq.

A comparative study of electron absorption spectra of dipyrido- and dibenzosubstituted 1,4-diazines, and also of 1,10-phenantroline confirms the conclusion on the weak electronic interaction between the phenantroline and diazine parts of the (N^N) ligands. An evidence consists in the only slight changes in the energy ($\nu_{\max}$ 37.1±0.6 kK) and efficiency [ε $(30 \pm 0.9) \times 10^3$ $\mathrm{l\,mol^{-1}\,cm^{-1}}$] of high-energy spin-allowed optical (π–π^*) transitions localized mainly on the phenantroline parts of the (N^N) ligands, and also in the closeness of long-wave ($\lambda > 300$ nm) absorption bands and of vibration-structured low-temperature (77 K) luminescence spectra of dipyrido- and dibenzo-substituted diazines caused by the spin-allowed and spin-forbidden optical (π–π^*) transitions, respectively, mainly localized on the diazine parts of the ligands.

The ^{1}H NMR spectra of the $[\mathrm{Pt(N^\wedge C)(N^\wedge N)}]^+$ complexes contain the proton signals from deprotonated forms of cyclometallated (N^C) and chelated (N^N) ligands. The values of coordination-induced proton chemical shifts of the ligands ($\Delta\delta = \delta_{\mathrm{comp}} - \delta_{\mathrm{lig}}$), reflecting changes in the electronic density of ligands due to a donor-acceptor ligand → metal interaction, are given in Table 2.

The data obtained point to the following. (1) The increase in the shifts $\Delta\delta$ of the H^6 and $H^{3'/4'}$ protons of cyclometallated ligands ppy and tpy on the substitution of heterocyclic ligands (phen, dpq, dppz, and dicnq) for ethylenediamine points to the strengthening of the donor–acceptor interaction of Pt(II) with the both pyridine and carbanionic parts of the (N^C) ligands. Such values of $\delta(H^6)$ (0.32±0.04 ppm) of the complexes show that the decrease in the electron density on the pyridine part of (N^C) ligands is practically independent of the nature of (N^N) heterocyclic ligands and of the carbanionic parts of (N^C) ligands. (2) In accordance with the coordination mode the complex formation of diazine derivatives of 1,10-phenantroline results in a decrease in the electron density mainly localized on the phenantroline parts of the ligands [$\Delta\delta(H^{\alpha})$ 0.53±0.15 ppm], whereas the change in the electronic density on the diazine part of the ligands spatially distant from the coordination center is much less [$\Delta\delta(H^{\delta})$ 0.20±0.03 ppm]. In accordance with a weaker trans-influence of the pyridine parts of (N^C) ligands compared to the carbanionic part in Pt(II) complexes [9], the α/α' and β/β' protons of (N^N) ligands located, respectively, in the trans- and *cis*-positions to the pyridine part of (N^C) ligands, are characterized by various $\Delta\delta$ values. (3) Unlike the complexes with ethylenediamine and 1,10-phenantroline ligands, the complexes with diazine derivatives of 1,10-phenantroline are characterized by the absence of platinum satellites resulted from the spin-spin interaction of the ^{195}Pt nucleus with protons of cyclometallated and chelated ligands. It is caused by a strong anisotropy of the platinum chemical shift in a square-planar environment and by the corresponding type II scalar relaxation of the protons spin-bound with ^{195}Pt [10]. The spatial extent of diazine ligands determines a reduction in the time of molecular reorientation of the complexes that results in broadening of the platinum satellites and their seeming absence in the ^{1}H NMR spectra.

Within the framework of the model of localized molecular orbitals [5] electro- and photo-stimulated processes in cycloplatinated complexes are classified

Table 2. Coordination-induced chemical shifts [$\Delta\delta = \delta_{comp} - \delta_{lig}$, ppm, relative to $(CH_3)_4Si$] (^{195}Pt–^1H coupling constants, *J*, Hz, of protons of ligands in dimethyl sulfoxide solutions of $[Pt(C^\wedge N)(N^\wedge N)]^+$) complexes

Complex	Hydrogen atom of (C^N) and (N^N) ligands												
	3	4	5	6	3'	4'	5'	6'	α/α'	β/β'	γ/γ'	δ/δ'	ε/ε'
[Pt(ppy)en]$^{+a}$	0.09	0.16	–0.08	–0.08 (37)	–0.21	–0.31	–0.35	–0.30	3.20/2.37 (52/29)	1.41/1.41	–	–	–
[Pt(ppy)phen]$^{+a}$	0.18	0.31	0.00	0.31	0.04	0.07	–0.21	–0.26	0.85/0.41 (44/–)	0.51/0.39	0.55/0.55	0.39/0.38	–
[Pt(ppy)dpq]$^+$	0.15	0.40	–0.06	0.30	–0.12	0.10	–0.35	–0.53	0.53/0.34	0.51/0.36	0.32/0.32	0.22/0.22	–
[Pt(ppy)dppz]$^+$	0.21	0.41	–0.10	0.32	–0.08	0.10	–0.21	–0.45	0.39/0.37	0.48/0.40	0.39/0.39	0.20/0.20	0.20/0.20
[Pt(ppy)dicnq]$^+$	0.10	0.39	–0.10	0.28	–0.14	0.09	–0.37	–0.59	0.37/0.33	0.38/0.30	0.49/0.36	–	–
[Pt(tpy)en]$^{+a}$	0.06	0.03	0.27	–0.17 (37)	–	0.02	0.00	–	3.26/2.40 (51/30)	1.37/1.37	–	–	–
[Pt(tpy)phen]$^{+a}$	–0.22	0.53	0.05	0.35	–	0.34	0.06	–	0.83/0.28 (40/24)	0.30/0.20	0.50/0.50	0.30/0.30	–
[Pt(tpy)dpq]$^+$	–0.28	0.32	0.06	0.26	–	0.46	0.22	–	0.64/0.23	0.43/0.29	0.29/0.27	0.21/0.20	–
[Pt(tpy)dppz]$^+$	–0.16	0.39	0.13	0.34	–	0.53	0.28	–	0.77/0.34	0.57/0.42	0.41/0.41	0.16/0.16	0.19/0.19
[Pt(tpy)dicnq]$^+$	–0.07	0.40	0.05	0.40	–	0.60	0.33	–	0.47/0.30	0.47/0.35	0.62/0.42	–	–

[a] CD_3OD.

Table 3. Parameters of electronic absorption spectra and voltammograms of $[Pt(N^\wedge C)(N^\wedge N)]^+$ complexes in dimethylformamide (DMF) solutions

Complex	Absorption, λ_{max}, nm ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)			Reduction, $-E_{1/2}$m V (ΔE, mV)			Oxidation,[a] E_p, V, d_{Pt}
	$^1(\pi-\pi^*)$	$^1(d-\pi^*_{C^\wedge N})$	$^1(d-\pi^*_{phen})$	π^*_{phen}	π^*_{diaz}	$\pi^*_{N^\wedge C}$	
[Pt(ppy)en]$^+$	325 [4.5]	375 [1.8]	–	–	–	2.22 (75)	0.84
[Pt(tpy)en]$^+$	295 [8.2], 310^b [7.3], 325^b [5.9]	401 [2.4]	–	–	–	2.21 (75)	0.89
[Pt(ppy)phen]$^+$	274 [33.0]	379 [5.0]	416 [2.0]	1.53^a	–	2.01(100)	0.62
[Pt(tpy)phen]$^+$	283 [29.9], 355 [10.3]	372^b [9.1]	436^b [1.8]	1.49 (60)	–	1.99 (60)	0.59
[Pt(ppy)dpq]$^+$	273 [40.8], 329^b [14.9]	377 [8.0]	418^b [1.2]	1.40 (60)	2.01^{a,c}	2.01^{a,c}	>0.9^d
[Pt(tpy)dpq]$^+$	277 [32.1], 356 [9.2]	375 [5.0]	436^b [0.8]	1.40 (60)	2.03^a	1.90 (60)	>0.9^d
[Pt(ppy)dppz]$^+$	279 [50.0], 364 [18.9], 379^e [18.5]	379^e [18.5]	415^b [1.0]	1.29 (60)	1.60 (60)	2.04 (70)	>0.9^d
[Pt(tpy)dppz]$^+$	282 [41.4], 362 [12.8], 380^e [11.9]	380^e [1.9]	440^b [0.7]	1.23 (60)	1.57 (60)	1.99 (70)	>0.9^d
[Pt(ppy)dicnq]$^+$	306^b [24.9], 349^b [10.8], 370^e [13.4]	370^e [13.4]	417^b [1.3]	1.98^{a,c}	1.16^c (60)	1.98^{a,c}	0.43
[Pt(tpy)dicnq]$^+$	274 [42.7], 301^b [34.2], 363^e [11.8]	363^e [11.8]	444^b [0.9]	1.98^{a,c}	0.96^c (60)	1.98^{a,c}	0.40

[a] Potential of a peak current at the potential scanning rate of 100 mV s^{-1}. [b] Shoulder. [c] Overlapping of two one-electron reduction waves. [d] Oxidation outside electrochemical stability of the solvent. [e] Overlapping of the absorption bands $^1(\pi-\pi^*)$ and $^1(d-\pi^*)$.

according to the nature of participating orbitals into metal- and ligand-centered, a similarity in the orbital nature of spectroscopic and redox orbitals of the complexes being observed [4] when Koopmans theorem is obeyed [6]. The results of studying the influence of the nature of cyclometallated and chelated ligands on the electrochemical and optical properties of $[Pt(N^\wedge C) \cdot (N^\wedge N)]^+$ complexes are presented in Tables 3 and 4.

Electroreduction voltammograms of the complexes are characterized by one-electron quasireversible reduction waves (Fig. 1) caused by the ligand-centered electron transfer onto unoccupied π* antibonding orbitals of (N^C) cyclometallated and (N^N) chelated ligands. The substitution of 1,10-phenantroline for ethylenediamine in $[Pt(N^\wedge C)(N^\wedge N)]^+$ complexes results not only in anodic shift of the half-wave reduc-

Table 4. Luminescent characteristics of $[Pt(N\hat{}C)(N\hat{}N)]^+$ complexes

Complex	DMF–toluene, 1:1, 77 K, λ_{max}, nm (τ, μs)	DMF, 293 K		Assignment
		λ_{max}, nm	τ, μs	
$[Pt(ppy)en]^+$	481, 498, 508, 517 (15)	487, 518, 567[a]	2	$^3(d–\pi^*_{N\hat{}C})$
$[Pt(ppy)phen]^+$	509, 542, 570	–	–	$^3(d–\pi^*_{phen})$
		494, 525	6	$^3(d–\pi^*_{N\hat{}C})$
$[Pt(ppy)dpq]^+$	515, 545, 600, 641[a]	–	–	$^3(d–\pi^*_{phen})$
	489	498, 533, 574[a]	4	$^3(d–\pi^*_{N\hat{}C})$
$[Pt(ppy)dicnq]^+$	510, 533, 552, 571	–	–	$^3(d–\pi^*_{phen})$
	486, 498[a]	498, 530, 572[a]	3	$^3(d–\pi^*_{N\hat{}C})$
$[Pt(ppy)dppz]^+$	549, 598	–	–	$^3(\pi–\pi^*_{diaz})$
	484, 520[a]	493, 528, 572[a]	4	$^3(d–\pi^*_{N\hat{}C})$
$[Pt(tpy)en]^+$	556, 577, 590, 603[a] (20)	561, 598	10	$^3(d–\pi^*_{N\hat{}C})$
$[Pt(tpy)phen]^+$	510, 521,[a] 548	–	–	$^3(d–\pi^*_{phen})$
	576, 591,[a] 625, 650[a]	574, 612	9	$^3(d–\pi^*_{N\hat{}C})$
$[Pt(tpy)dpq]^+$	506,[a] 543[a]	–	–	$^3(d–\pi^*_{phen})$
	574, 618	578, 618	12	$^3(d–\pi^*_{N\hat{}C})$
$[Pt(tpy)dppz]^+$	549	–	–	$^3(\pi–\pi^*_{diaz})$
	572, 593	567, 620	16	$^3(d–\pi^*_{N\hat{}C})$
$[Pt(tpy)dicnq]^+$	505,[a] 546[a]	–	–	$^3(d–\pi^*_{phen})$
	574, 616[a]	571, 583,[a] 622	9	$^3(d–\pi^*_{N\hat{}C})$

[a] Shoulder.

tion potential ($\Delta E_{1/2}$ ~0.2 V), which is expected for the electron transfer on the $\pi^*_{N\hat{}C}$ orbital of mixed-ligand cycloplatinated complexes according to electrochemical parameters E_L of chelated (N^N) ligands (E_{phen} 0.52, E_{en} 0.10 V) and correlation ratio $E_{1/2} = 0.55\Sigma E_L - 2.265$ found previously [11], but also to the occurrence of an additional wave (E ~–1.5 V] resulted from the electron transfer on the π^* orbital of 1,10-phenantroline. The data of ^{1}H NMR spectroscopy point to an effective reduction of electronic density of the phenantroline ligand as a result of the phen → Pt(N^C) donor-acceptor interaction [$\delta(H^\alpha)$ ~0.8 ppm]. In accordance with these data, the complex formation leads to lowering the energy of the π^*_{phen} orbital and to the anodic shift (ΔE ~1 V) of the potential of the ligand-centered reduction of $[Pt(N\hat{}C)phen]^+$ complexes in comparison to free 1,10-phenantroline. The presence of two π^* orbitals, weakly interacting with one another and localized on the phenantroline and diazine parts of dipyrido-substituted diazine ligands, determines the presence of three one-electron reduction waves of $[Pt(N\hat{}C)(N\hat{}N)]^+$ complexes assigned to the ligand-centered electron transfer on unoccupied π^* orbitals of diazine and cyclometallated ligands. In accordance withthe fact that the donor-acceptor interaction of the pyridine parts of cyclometallated ligands with Pt(II) does not depend on the nature of their carbo-anion parts (ppy and tpy) and on the character of a heterocyclic (N^N) ligand (phen, dpq, dppz, and dicnq) [$\Delta\delta(H^6)$ 0.32 ± 0.04 ppm] the ligand-centered reduction of $[Pt(N\hat{}C)(N\hat{}N)]^+$ complexes involving π^* orbitals of cyclometallated ligands occurs at a practically constant potential (E –1.99 ± 0.04 V). A comparison of reduction voltammograms for the complexes and free dipyrido-substituted diazines shows that the potential of the ligand-centered process caused by the electron transfer involving these orbitals changes only slightly (ΔE 0.05 ± 0.05 V) owing to a low efficiency of the interaction of spatially distant π^*_{diaz} orbitals of the (N^N) ligands and Pt(II). The anodic shift of the potential of the ligand-centered reduction of the complexes involving π^*_{phen} orbitals of dipyrido-substituted (N^N) ligands in the series dppz > dpq> dicnq is connected with weakening the donor-acceptor interaction of the ligands with Pt(II) owing to a decrease in the basicity of pyridine nitrogen atoms.

Unlike quasireversible waves of the ligand-centered reduction, the voltammograms of the oxidation have the irreversible metal-centered character typical for cycloplatinated complexes [3, 4, 11] owing to the formation of such primary products of the electrochemical process as highly reactive Pt(III) complexes exposed to a subsequent fast chemical reaction.

A comparison of the electronic absorption spectra

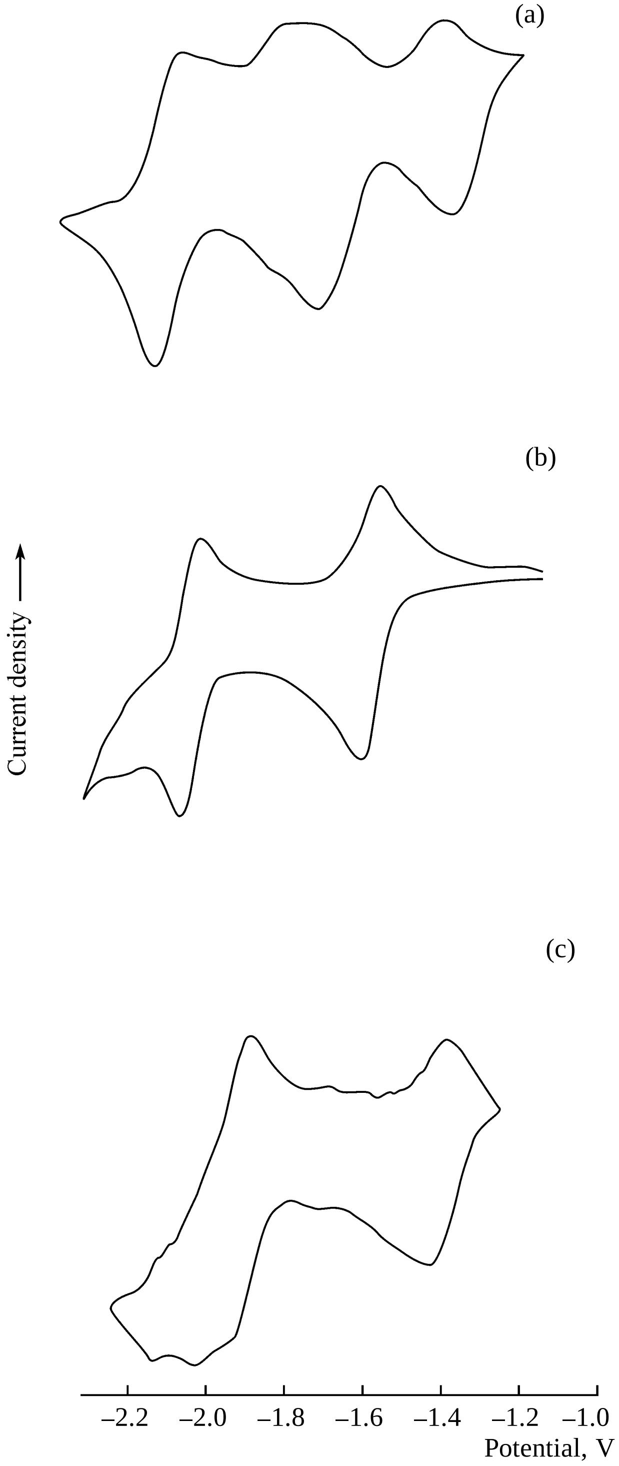


Fig. 1. Reduction voltammograms for complexes. (a) $[\mathrm{Pt(tpy)dppz}]^+$, (b) $[\mathrm{Pt(tpy)phen}]^+$, (c) $[\mathrm{Pt(tpy)dpq}]^+$.

of $[\mathrm{Pt(N{\wedge}C)(N{\wedge}N)}]^+$ complexes (Fig. 2) with the spectra of (N^N) heterocyclic ligands (Table 1) and $[\mathrm{Pt(N{\wedge}C)en}]^+$ shows the presence of three types of spin-allowed optical transitions of various orbital nature: π–π^* intraligand highly intensive [$\varepsilon \sim 10^4$ l mol^{-1} cm^{-1}] transitions, d–$\pi^*_{\mathrm{N{\wedge}C}}$ less intensive and lower in energy transitions of metal → ligand charge transfer [ν 26.6 ± 0.2 kK, ε $(7 \pm 2) \times 10^3$ l mol^{-1} cm^{-1}], and d–$\pi^*_{\mathrm{N{\wedge}N}}$ transitions [ν 23.4 ± 0.7 kK, ε $(1.3 \pm 0.5) \times 10^3$ l mol^{-1} cm^{-1}]. The overlapping of the wave functions mainly localized on Pt(II) d orbitals with $\pi^*_{\mathrm{N{\wedge}C}}$ and π^*_{phen} orbitals of cyclometallated and chelated ligands differs from the overlapping of spatially distant π^*_{diaz} orbitals of diazine derivatives of 1,10-phenantroline, which suggests that the extinction coefficients of the corresponding optical transitions should be different: $\varepsilon(d\text{–}\pi^*_{\mathrm{N{\wedge}C}}) \sim \varepsilon(d\text{–}\pi^*_{\mathrm{phen}}) >> \varepsilon(d\text{–}\pi^*_{\mathrm{diaz}})$. As a consequence, the long-wave absorption bands of the complexes were assigned to d–$\pi^*_{\mathrm{N{\wedge}C}}$ and d–π^*_{phen} charge-transfer metal → ligand transitions.

The comparison of the parameters of electronic absorption spectra and electrochemical characteristics of the complexes shows that, in spite of the overlap of individual absorption bands and reduction waves, a correspondence between energy differences of spectroscopic [$\nu_{\mathrm{max}}(d\text{–}\pi^*_{\mathrm{N{\wedge}C}}) - \nu_{\mathrm{max}}(d\text{–}\pi^*_{\mathrm{phen}}) = 0.4 \pm 0.1$ eV] and redox [$E_{1/2}(\pi^*_{\mathrm{N{\wedge}C}}) - E_{1/2}(\pi^*_{\mathrm{phen}}) = -0.52 \pm 0.06$ V] orbitals is observed. This fact confirms applicability of the model of localized molecular orbitals for joint interpretation and forecasting of optical and electrochemical properties of the family of $[\mathrm{M(N{\wedge}C)(N{\wedge}N)}]^+$ complexes.

The luminescence of the $[\mathrm{Pt(N{\wedge}C)en}]^+$ complexes both in frozen (77 K) and in liquid (293 K) solutions is caused by a spin-forbidden radiation process of the photoexcitation energy degradation from the lowest in energy d–$\pi^*_{\mathrm{N{\wedge}C}}$ excited electronic state. The luminescence decay obeys an exponential kinetics and has energies {E^{00} 18.0 and 20.8 kK for $[\mathrm{Pt(tpy)en}]^+$ and $[\mathrm{Pt(ppy)en}]^+$} and vibration frequencies (ν_{vibr} 0.68, 1.07, and 1.43 kK) characteristic of purely electronic transitions [3, 4]. Contrastingly, the character of the luminescence of $[\mathrm{Pt(N{\wedge}C)(N{\wedge}N)}]^+$ complexes with (N^N) heterocyclic ligands depends on the ligand nature and temperature (Figs. 3 and 4). The low-temperature luminescence of $[\mathrm{Pt(N{\wedge}C)dppz}]^+$ complexes is characterized by a non-exponential decay kinetics, whereas the vibration-structured luminescent spectra are determined by a superposition of vibronic transitions from two excited electronic states: the charge transfer state {π–$\pi^*_{\mathrm{N{\wedge}C}}$, E^{00} ~17.4 and 20.66 kK for $[\mathrm{Pt(tpy)dppz}]^+$ and $[\mathrm{Pt(ppy)dppz}]^+$, ν_{vibr} 1.43 kK} and the intraligand state (π–π^*_{diaz}, E^{00} 18.22 kK, ν_{vibr} ~1.3 kK), parameters of these states being close to the luminescence characteristics of the $[\mathrm{Pt(N{\wedge}C)en}]^+$ complexes and of the free dppz ligand (E^{00} 18.35 kK, ν_{vibr} 1.36 kK). The luminescence of the frozen solutions of $[\mathrm{Pt(N{\wedge}C)(N{\wedge}N)}]^+$ complexes [(N^N) = phen,

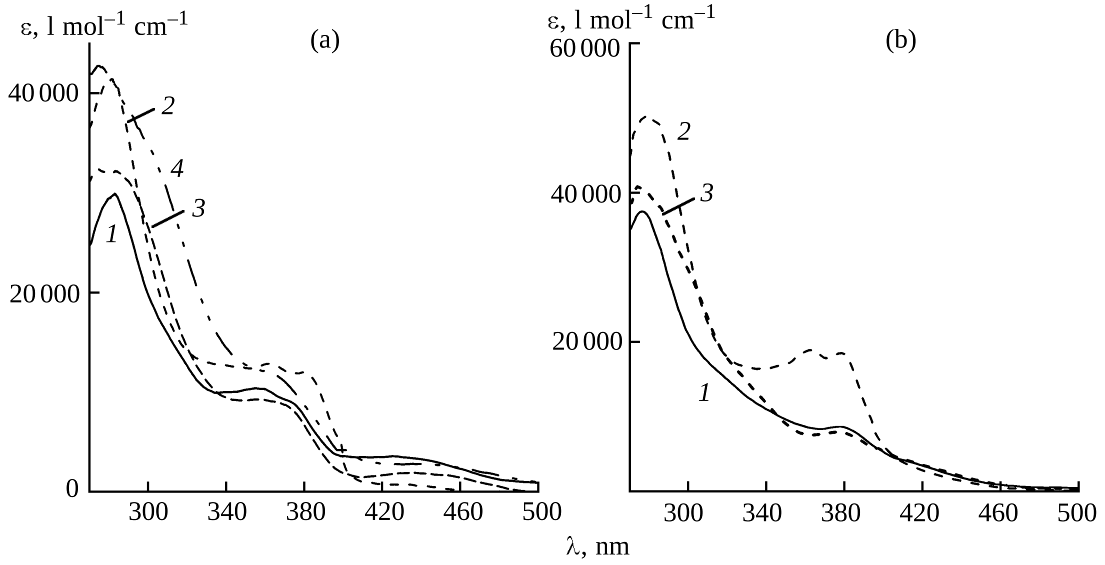


Fig. 2. Electronic absorption spectra of $[Pt(C\^N)(N\^N)]^+$, DMF, 293 K. (C^N): (a) ppy, (b) tpy; (N^N): (*1*) phen, (*2*) dpq, (*3*) dppz, (*4*) dicnq.

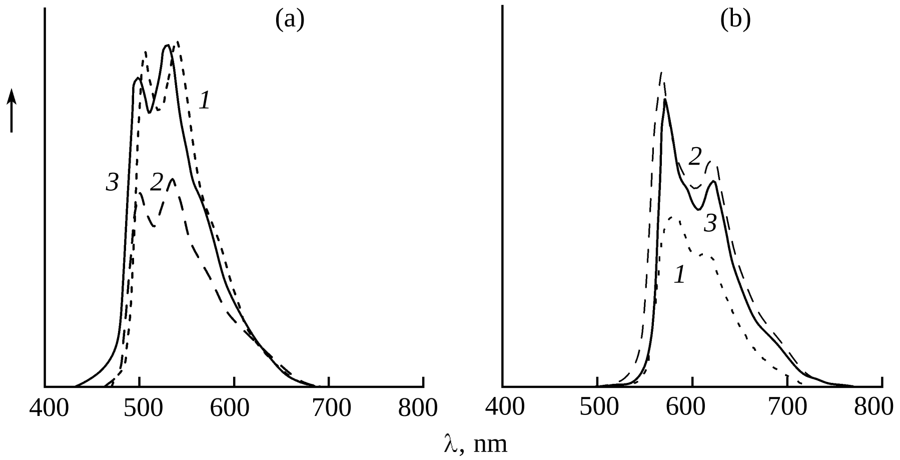


Fig. 3. Luminescence spectra of $[Pt(C\^N)(N\^N)]^+$, DMF, 293 K. (C^N): (a) ppy, (b) tpy; (N^N): (*1*) dpq, (*2*) dppz, (*3*) dicnq.

dpq, dicnq] is also characterized by a non-exponential decay kinetics and by a superposition of two types of vibronic transitions from the charge-transfer states localized on {Pt(N^C)} and {Pt(N^N)} metal-complex fragments: d–π–$\pi^*_{N\^C}$, E^{00} 17.6±0.3 and 20.6±0.1 kK for [Pt(tpy)] and [Pt(ppy)], ν_{vibr} 1.3±0.1 kK and d–π^*_{phen}, E^{00} 19.6±0.1 kK, ν_{vibr} 1.4±0.2 kK. The parameters of the luminescence from the d–π^*_{phen} state localized on {Pt(N^N)} fragments of the complexes agree with the characteristics of the luminescence of the $Pt(phen)(CH_3)_2$ complex in a frozen (77 K) solution in diethyl ether (E^{00} 18.90 kK, ν_{vibr} 1.30 kK) assigned to the transition from the d–π^*_{phen} excited state [12].

Thus, the study of the low-temperature luminescence shows that, owing to a weak electronic interaction between {Pt(N^C)} and {Pt(N^N)} fragments of $[Pt(N\^C)(N\^N)]^+$ complexes with dipyrimidine (N^N) ligands, the degradation of their photoexcitation energy occurs from two lowest in energy electronic excited states localized on each of the fragments (Fig. 4).

In accordance with the weak interaction of the excited states of electrons localized on {Pt(N^C)} and {Pt(N^N)} fragments, the luminescence of $[Pt(N\^C)\cdot(N\^N)]^+$ complexes in liquid solutions (293 K) irrespective of the nature of heterocyclic ligands (N^N) is characterized by a monoexponential decay kinetics with close values of both kinetic and energy characteristics {τ 4±3 μs, ν_{max} 22.2±0.1 and 18.9±0.1 kK

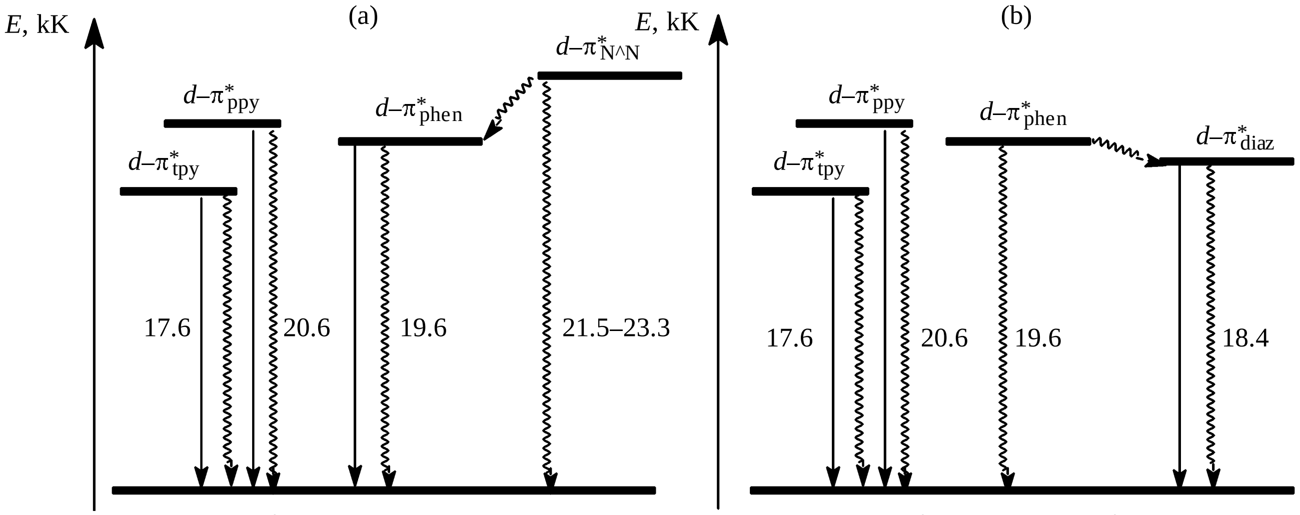


Fig. 4. Energy diagram of radiative (solid line) and nonradiative (wavy line) processes of the degradation of photoexcitation energy in frozen solutions of $[\mathrm{Pt(N^\wedge C)(N^\wedge N)}]^+$ complexes. (N^N): (a) phen, dpq, dicnq; (N^N): (b) dppz.

for $[\mathrm{Pt(ppy)(N^\wedge N)}]^+$; τ 12±3 μs, $\nu_{\max}$ 17.5±0.1 and 16.2±0.1 kK for $[\mathrm{Pt(tpy)(N^\wedge N)}]^+$}, which slightly differ from the luminescence parameters of $[\mathrm{Pt(N^\wedge C)en}]^+$ complexes (Table 4). It allows us to assign the luminescence to the spin-forbidden optical transition from the d–$\pi^*_{\mathrm{N^\wedge C}}$ state and points to a different efficiency of temperature quenching the luminescence involving isolated states localized on {Pt(N^C)} and {Pt(N^N)} metal-complex fragments.

The combination of optical and electrochemical parameters of $[\mathrm{Pt(N^\wedge C)(N^\wedge N)}]^+$ complexes with 1,4-diazine derivatives of 1,10-phenantroline in liquid (293 K) solutions shows the presence of the both long-living excited d–$\pi^*_{\mathrm{N^\wedge C}}$ states of electrons localized on a [Pt(N^C)] fragment and a reversible electroreduction. The long-living excited states have the energy of a purely electronic transition and the life time determined by the nature of a cyclometallated (N^C) ligand, whereas the reversible electroreduction results from the electron transfer on spatially distant π^*_{diaz} redox orbitals of a chelated (N^N) ligand with potentials depending on the nature of a diazine substituent of 1,10-phenantroline. It allows us to consider these complexes with predicted optical and electrochemical parameters as perspective components of molecular-organized metal complex systems with a directed spatial charge phototransfer.

EXPERIMENTAL

The ^{1}H NMR spectra and the electronic absorption spectra were taken on a Bruker AC-200F spectrophotometer and an SF-2000 spectrometer at 298 K in $(\mathrm{CD_3})_2\mathrm{SO}$ and DMF solutions, respectively. The luminescence experiments were carried out on an SDL-2 spectrometer and a KSVU-1 installation with a pulse photoexcitation laser (LGI-21, λ 337 nm) at 77 K in glassy DMF–toluene (1:1) matrixes and at 298 K in DMF [13]. The parameters of cyclic voltammograms were determined on a modified SBA-1B installation at 298 K in a three-electrode cell with separate compartments of working (Pt), auxiliary (Pt), and reference (Ag) electrodes in the presence of a 0.1 M $[\mathrm{N(C_4H_9)_4}]\mathrm{ClO_4}$ solution in DMF [11]. Half-wave and current peak potentials are given in relation to the ferrocenium-ferrocene redox system.

Dipyrido- and dibenzo-substituted 1,4-diazines were obtained by the condensation of 1,10-phenantroline-5,6-dion and 9,10-phenanthraquinone with corresponding diamines–ethylenediamine (dpq and dbq), 1,10-phenylenediamine (dppz and dbpz), and diaminomaleonitrile (dicnq and dicbq) [14–16]. Complexes $[\mathrm{Pt(N^\wedge C)en}]\mathrm{ClO_4}$ were synthesized by the technique [17], and $[\mathrm{Pt(N^\wedge C)(N^\wedge N)}]\mathrm{NO_3}$ [(N^N) = dpq, dppz, dicnq] by the modified technique [7].

(Ethylenediamine)[2-(2-pyridyl)thiophene-3-ido]platinum(II) perchlorate $[\mathrm{Pt(tpy)en}]\mathrm{ClO_4}$. Yield 60%. ^{1}H NMR spectrum ($\mathrm{CD_3OD}$), δ, ppm (J, Hz): 8.48 (H^6, $^3J_{\mathrm{HH}}$ 5.8, $^4J_{\mathrm{HH}}$ 1.4, $^5J_{\mathrm{HH}}$ 0.8, $^3J_{\mathrm{PtH}}$ 37), 7.99 (H^4, $^3J_{\mathrm{HH}}$ 7.8, $^4J_{\mathrm{HH}}$ 1.5), 7.62 ($\mathrm{H}^{5'}$, $^3J_{\mathrm{HH}}$ 4.8), 7.55 (H^3, $^3J_{\mathrm{HH}}$ 8.0, $^4J_{\mathrm{HH}}$ 1.2, $^5J_{\mathrm{HH}}$ 0.8), 7.15 (H^5, $^3J_{\mathrm{HH}}$ 5.8, 7.6, $^4J_{\mathrm{HH}}$ 1.5), 7.11 ($\mathrm{H}^{4'}$, $^3J_{\mathrm{HH}}$ 4.7, $^3J_{\mathrm{PtH}}$ 17), 5.94 (H^α, $^3J_{\mathrm{PtH}}$ 51), 5.10 ($\mathrm{H}^{\alpha'}$), 2.81 ($\mathrm{H}^{\beta,\beta'}$, $^4J_{\mathrm{PtH}}$ 28).

(1,10-Phenantroline)[2-(2-pyridyl)thiophene-3-ido]platinum(II) nitrate $[\mathrm{Pt(tpy)phen}]\mathrm{NO_3}$. Yield 40%. ^{1}H NMR spectrum ($\mathrm{CD_3OD}$), δ, ppm (J, Hz):

9.92 (H$^{\alpha}$, $^3J_{\mathrm{HH}}$ 5.9, $^3J_{\mathrm{PtH}}$ 40), 9.38 (H$^{\alpha'}$, $^3J_{\mathrm{HH}}$ 4.9, $^3J_{\mathrm{PtH}}$ 24), 8.96 (H$^{\gamma\gamma'}$, $^3J_{\mathrm{HH}}$ 7.9), 8.77 (H^{6}, $^3J_{\mathrm{HH}}$ 5.9), 8.27 (H$^{\delta\delta'}$), 8.07 (H$^{\beta}$, $^3J_{\mathrm{HH}}$ 5.9, 7.9), 7.97 (H$^{\beta'}$, $^3J_{\mathrm{HH}}$ 6.9, 7.9), 8.25 (H^{4}, $^3J_{\mathrm{HH}}$ 7.2), 7.50 (H^{3}, $^3J_{\mathrm{HH}}$ 7.6), 7.68 (H$^{5'}$, $^3J_{\mathrm{HH}}$ 4.8), 7.43 (H$^{4'}$, $^3J_{\mathrm{HH}}$ 5.0), 7.23 (H^{5}, $^3J_{\mathrm{HH}}$ 6.9).

(Dipyrido[*f,h*]quinoxaline)[2-(2-pyridyl)thiophene-3-ido]platinum(II) nitrate [Pt(tpy)(dpq)]NO$_3$. Yield 34%. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.90 (H$^{\alpha}$, $^3J_{\mathrm{HH}}$ 3.8), 9.74 (H$^{\gamma}$, $^3J_{\mathrm{HH}}$ 8.5), 9.72 (H$^{\gamma'}$, $^3J_{\mathrm{HH}}$ 8.5), 9.47 (H$^{\alpha'}$, $^3J_{\mathrm{HH}}$ 3.8), 9.38 (H$^{\delta}$), 9.37 (H$^{\delta'}$), 8.77 (H^{6}, $^3J_{\mathrm{HH}}$ 5.7), 8.39 (H$^{\beta'}$, $^3J_{\mathrm{HH}}$ 4.0, 7.9), 8.25 (H$^{\beta}$, $^3J_{\mathrm{HH}}$ 4.0, 7.9), 8.00 (H^{4}), 7.79 (H$^{5'}$, $^3J_{\mathrm{HH}}$ 4.8), 7.48 (H^{3}, $^3J_{\mathrm{HH}}$ 7.0), 7.44 (H$^{4'}$, $^3J_{\mathrm{HH}}$ 4.8), 7.27 (H^{5}, $^3J_{\mathrm{HH}}$ 6.7).

(Dipyrido[*a,c*]phenazine)[2-(2-pyridyl)-thiophene-3-ido]platinum(II) nitrate [Pt(tpy)(dppz)]·NO$_3$. Yield 36%. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.91 (H^{a}, $^3J_{\mathrm{HH}}$ 5.0), 9.85 (H$^{\gamma\gamma'}$), 9.48 (H$^{\alpha'}$), 8.85 (H^{6}, $^3J_{\mathrm{HH}}$ 5.6), 8.43 (H$^{\beta,\delta,\delta'}$), 8.28 (H$^{\beta'}$), 8.18 (H$^{\varepsilon,\varepsilon'}$, $^3J_{\mathrm{HH}}$ 3.5, 6.5), 8.07 (H^{4}), 8.00 (H^{4}), 7.85 (H$^{5'}$, $^3J_{\mathrm{HH}}$ 5.0), 7.60 (H^{3}, $^3J_{\mathrm{HH}}$ 8.7), 7.51 (H$^{4'}$, $^3J_{\mathrm{HH}}$ 4.8), 7.34 (H^{5}).

(6,7-Dicyanodipyrido[*f,h*]quinoxaline)[2-(2-pyridyl)thiophene-3-ido]platinum(II) nitrate [Pt(tpy)(dicnq)]NO$_3$. Yield 30%. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.13 (H$^{\gamma}$), 9.83 (H$^{\alpha,\gamma'}$), 9.66 (H$^{\alpha'}$), 8.91 (H^{6}), 8.51 (H$^{\beta}$), 8.39 (H$^{\beta'}$), 8.08 (H^{4}, $^3J_{\mathrm{HH}}$ 8.0), 7.90 (H$^{5'}$, $^3J_{\mathrm{HH}}$ 5.0), 7.69 (H^{3}, $^3J_{\mathrm{HH}}$ 8.0), 7.58 (H$^{4'}$, $^3J_{\mathrm{HH}}$ 4.8), 7.36 (H^{5}).

(Ethylenediamine)[2-(2-pyridyl)phenyl-1-ido]-platinum(II) perchlorate [Pt(ppy)en]ClO$_4$. Yield 65%. ^{1}H NMR spectrum (CD$_3$OD), δ, ppm (*J*, Hz): 8.50 (H^{6}, $^3J_{\mathrm{HH}}$ 5.8, $^4J_{\mathrm{HH}}$ 1.5, $^5J_{\mathrm{HH}}$ 0.7, $^3J_{\mathrm{PtH}}$ 37), 8.00 (H^{4}, $^3J_{\mathrm{HH}}$ 7.8), 7.87 (H^{3},$^3J_{\mathrm{HH}}$ 7.5), 7.59 (H$^{6'}$, $^3J_{\mathrm{HH}}$ 5.9, $^4J_{\mathrm{HH}}$ 3.2), 7.24 (H$^{3'}$, $^3J_{\mathrm{HH}}$ 5.8), 7.10 (H$^{4',5'}$), 5.88 (H$^{\alpha}$, $^3J_{\mathrm{PtH}}$ 52), 5.05 (H$^{\alpha'}$, $^3J_{\mathrm{PtH}}$ 29), 2.84 (H$^{\beta,\beta'}$).

(1,10-Phenantroline)[2-(2-pyridyl)phenyl-1-ido]-platinum(II) nitrate [Pt(ppy)phen]NO$_3$. Yield 45%. ^{1}H NMR spectrum (CD$_3$OD), δ, ppm (*J*, Hz): 9.94 (H$^{\alpha}$, J_{HH} 5.8, $^3J_{\mathrm{PtH}}$ 44.5), 9.50 (H$^{\alpha'}$, $^3J_{\mathrm{HH}}$ 4.2), 9.01 (H$^{6,\gamma}$,$^{\gamma'}$), 8.34 (H$^{\delta}$), 8.33 (H$^{\delta'}$), 8.28 (H$^{\beta}$, $^3J_{\mathrm{HH}}$ 5.3, 8.0), 8.16 (H$^{\beta'}$, $^3J_{\mathrm{HH}}$ 8.0), 8.15 (H^{4}, $^3J_{\mathrm{HH}}$ 7.0), 7.96 (H^{3}, $^3J_{\mathrm{HH}}$ 7.6, $^4J_{\mathrm{HH}}$ 1.5), 7.62 (H$^{6'}$, $^3J_{\mathrm{HH}}$ 7.6, $^4J_{\mathrm{HH}}$ 1.5), 7.49 (H$^{3'}$, $^3J_{\mathrm{HH}}$ 5.0), 7.48 (H$^{4'}$, $^3J_{\mathrm{HH}}$ 8.7), 7.31 (H^{5}, $^3J_{\mathrm{HH}}$ 7.9, $^4J_{\mathrm{HH}}$ 1.4), 7.24 (H$^{5'}$, $^3J_{\mathrm{HH}}$ 7.5, $^4J_{\mathrm{HH}}$ 1.5).

(Dipyrido[*f,h*]quinoxaline)[2-(2-pyridyl)phenyl-1-ido]platinum(II) nitrate [Pt(ppy)(dpq)]NO$_3$. Yield 35%. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.77 (H$^{\alpha,\gamma,\gamma'}$), 9.58 (H$^{\alpha'}$, $^3J_{\mathrm{HH}}$ 3.3), 9.39 (H$^{\delta,\delta'}$), 9.05 (H^{6}, $^3J_{\mathrm{HH}}$ 5.7), 8.47 (H$^{\beta'}$), 8.32 (H$^{\beta}$), 8.19 (H^{4}, $^3J_{\mathrm{HH}}$ 7.6), 8.04 (H^{3}, $^3J_{\mathrm{HH}}$ 8.6), 7.60 (H$^{6'}$, $^3J_{\mathrm{HH}}$ 7.6), 7.52 (H$^{4'}$, $^3J_{\mathrm{HH}}$ 5.7), 7.37 (H$^{3'}$, $^3J_{\mathrm{HH}}$ 7.6), 7.23 (H^{5}, $^3J_{\mathrm{HH}}$ 7.5), 7.14 (H$^{5'}$, $^3J_{\mathrm{HH}}$ 7.6).

(Dipyrido[*a,c*]phenazine)[2-(2-pyridyl)-phenyl-1-ido]platinum(II) nitrate [Pt(ppy)(dppz)]NO$_3$. Yield 40%. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.83 (H$^{\gamma,\gamma'}$, $^3J_{\mathrm{HH}}$ 7.6), 9.53 (H$^{\alpha}$, $^3J_{\mathrm{HH}}$ 4.0), 9.21 (H$^{\alpha'}$, $^3J_{\mathrm{HH}}$ 3.8, $^4J_{\mathrm{HH}}$ 1.9), 9.02 (H^{6}, $^3J_{\mathrm{HH}}$ 5.7), 8.43 (H$^{\beta,\beta',\delta,\delta'}$), 8.19 (H$^{\varepsilon,\varepsilon',4}$), 8.09 (H^{3}), 7.68 (H$^{6'}$, $^3J_{\mathrm{HH}}$ 7.6), 7.52 (H$^{4'}$, $^3J_{\mathrm{HH}}$ 7.6, 5.7), 7.41 (H$^{3'}$, $^3J_{\mathrm{HH}}$ 7.6), 7.28 (H$^{5'}$, $^3J_{\mathrm{HH}}$ 7.6), 7.18 (H^{5}, $^3J_{\mathrm{HH}}$ 7.6).

(6,7-Dicyanodipyrido[*f,h*]quinoxaline)[2-(2-pyridyl)phenyl-1-ido]platinum(II) nitrate [Pt(ppy)·(dicnq)]NO$_3$. Yield 30%. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.90 (H$^{\gamma}$), 9.77 (H$^{\gamma'}$), 9.73 (H$^{\alpha}$), 9.69 (H$^{\alpha'}$), 8.98 (H^{6}, $^3J_{\mathrm{HH}}$ 5.7), 8.42 (H$^{\beta}$), 8.34 (H$^{\beta'}$), 8.18 (H^{4}, $^3J_{\mathrm{HH}}$ 7.6), 7.98 (H^{3}, $^3J_{\mathrm{HH}}$ 5.0), 7.54 (H$^{6'}$, $^3J_{\mathrm{HH}}$ 7.6), 7.51 (H$^{4'}$, $^3J_{\mathrm{HH}}$ 5.7), 7.35 (H$^{3'}$, $^3J_{\mathrm{HH}}$ 6.0), 7.19 (H^{5}, $^3J_{\mathrm{HH}}$ 7.6), 7.12 (H$^{5'}$, $^3J_{\mathrm{HH}}$ 7.0).

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