

"Luminescent Pt(II) Complexes of Tridentate Cyclometalating 2,5-Bis(aryl)-pyridine Ligands"

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Received Eur.J.Inorg.Chem.

Key Topic: Structure-Luminescence Correlations

Synopsis:

Platinum(II) complexes of bis-cyclometalated 2,5-bis(aryl)-pyridine ligands show orange phosphorescence in solution and solid with moderate quantum yields up to 0.45 in PMMA matrix. Structural modifications on the periphery of the 2-phenyl-6-(thiophen-2-yl)pyridine ligands have remarkable impact on the quantum yields, while the emission energies vary only moderately.

Graphical abstract:



Keywords: Platinum / Heteroaromatic Ligands / Cyclometalation / Triplet Emission / Electrochemistry

Abstract Biscyclometalated Pt(II) complexes of dianionic 2,5-bis(aryl)-pyridine ligands (L¹⁻⁶)²⁻ carrying various cyclometalating or pending aryl groups have been synthesised in two steps. Reaction of the H₂L proto-ligands with K₂[PtCl₄] in acetic acid gave the mono-cyclometalated complexes [Pt(HL)Cl]₂. Heating of these complexes in hot DMSO (dimethyl sulfoxide) yielded the double-cyclometalated DMSO complexes $[Pt(L^{1-6})(DMSO)]$. Reaction of $[Pt(L^4)(DMSO)]$ with N,N-dimethylimidazolium iodide in the presence of KOtBu as base gave the carbene complex $[Pt(L^4)(Me_2Imd)]$. Detailed photophysical studies reveal intense orange luminescence of these complexes in CH₂Cl₂ solution with quantum yields up to 0.22, increased quantum yields up to 1.00 in glassy frozen CH₂Cl₂:MeOH (1:1) and up to 0.44 in PMMA matrices. Detailed electrochemistry (including spectroelectrochemistry) reveals reversible ligand-based first reductions at -2.1 to -2.3V, irreversible Pt-centred oxidations at around 0.8 V and electrochemical band gaps of 2.8 to 3.0 eV. Further reduction waves at very negative potentials interfere with solvent (THF with traces of water) discharge and can be traced to Pt-centred reductions for the DMSO complexes but a second ligand-centred reduction for the Me₂Imd complex from UV-vis spectroelectrochemistry. The photo/electrochemical properties can be roughly correlated with the ligand pattern and suggest their application in optoelectronics.

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Introduction

Tridentate cyclometalating ligands such as the prototypical 6-(phen-2-yl)-2,2'-bipyridine (Phbpy)[–] (Scheme 1) have been used in organoplatinum(II) and -palladium(II) chemistry starting from the 1990s.^[1-2] Having the same shape and electron configuration as 2,2':6',2''-terpyridine (terpy)^[3] the anion (Phbpy)[–] provides very stable tridentate binding and the cyclometalation requiring C–H activation of the phenyl core can be carried out at moderate conditions, usually heating suitable Pt(II) or Pd(II) precursors and the C–H functionalised proto-ligands (ligand precursor prior to metalation).^[1-2, 4-14]



Scheme 1. Structural similarities of terpy, (Phbpy)[–] (HPhbpy = 6-phenyl-2,2'-bipyridine), and [–] (PhPyPh)[–] (HPhPyPhH = 2,6-diphenyl-pyridine) Pt complexes (from left to right). Note, that using anionic X[–] coligands (halides, alkyl, aryl, ...) leads to cationic (NNN), neutral (CNN) or anionic (CNC) complexes, while the use of neutral ligands L such as DMSO, pyridines, phosphines, isonitriles, or carbenes leads to neutral (CNC) complexes.

Very soon it was found that many Pt(II) derivatives of the Phbpy ligand show intense luminescence, some even at ambient temperature.^[11, 15-19] One reason lies in the destabilisation of dark metalcentred excited states associated with the Pt(II) dx^2-y^2 orbital when using these very strong carbanionic ligands,^[20] the other reason lies in their rigidity. Consequently the idea came up using tridentate dicarbanionic cyclometalating ligands of the 2,6-di(phen-2-yl)pyridine (¬PhPyPh¬, see Scheme 1) type with Pt(II).^[21-32] Recently, Che et al. employed several derivatives of this ligand type with the aim of providing suitable excited states through variation of the 2,5-aryl groups at the central pyridine unit and they achieved very efficient triplet emitters, which show phosphorescence even at room temperature. One crucial move in their ligand design was the use of thiophene as one of their pending metalated aryl groups, with the complex **4** in Scheme 2 being the most efficient triplet emitter.^[31]



Scheme 2. Chemical structures of the synthesised Pt^{II} complexes [Pt(L¹⁻⁶)(coligand)]. [Pt(L¹)(DMSO)] (1), [Pt(L²)(DMSO)] (2), [Pt(L³)(DMSO)] (3), [Pt(L⁴)(DMSO)] (4), [Pt(L⁵)(DMSO)] (5), [Pt(L⁶)(DMSO)] (6), [Pt(L⁴)(Me₂Imd)] (4a).

We became interested in these complexes and decided not only to re-synthesise and re-investigate the prototypical complex **4** but also extend our study to further derivatives (Scheme 2) with the aim of achieving structure-properties relationships for efficient luminescence in such complexes. Therefore, we also replaced the DMSO coligand in one of the doubly cyclometalated complexes by a strong carbene ligand and studied the outcome of this replacement.

Furthermore, we investigated in detail the electrochemistry of the prototype 4, which has not been done yet, and its new derivatives in view of a possible application in OLEDs. In this contribution, we will report on the synthesis and full characterisation of the ligands and complexes, most of them were novel. We will also report on detailed absorption and emission spectroscopy, the latter carried out at ambient temperature in CH2Cl2 solution, in glassy frozen CH2Cl2/MeOH solution (v:v = 1:1) at 77 K as well as poly(methyl methacrylate) (PMMA) films. These results voltammetry were combined with detailed electrochemical (cyclic and UV-vis spectroelectrochemistry) and preliminary structure-properties relationships were drawn.

Results and Discussion

Preparations and analyses

The preparation of the 2,5-bis(aryl)-pyridine proto-ligands (H_2L^{1-6}) is outlined in the Supporting Information (SI). The complexes were prepared according to a literature method.^[23] In brief, the proto-ligands H_2L^{1-6} were heated with K₂[PtCl₄] in glacial acetic acid which resulted in the formation of yellow-orange materials in excellent yields. The ¹H NMR spectra exhibit typical

satellites of a ${}^{3}J_{\text{Pt-H}}$ coupling of about 60 Hz (${}^{195}\text{Pt}$, $I = \frac{1}{2}$, 33.8% nat. abundance) for the signals of the ortho protons of the Pt bound phenyl group. The reaction products are either Cl-bridges dimers [{Pt(HL¹⁻⁶)}₂(μ -Cl)₂] [^{23]} or monomers [Pt(HL¹⁻⁶)Cl] with S-coordination through the thiophene moiety, as has been suggested earlier for the reaction of HL¹ with K₂[PtCl₄].^[33] Our detailed 2D Pt-H NMR spectroscopy searching evidence for ${}^{x}J_{\text{Pt-H}}$ coupling of the thiophene protons through extensive variation of the assumed coupling constant was not successful (for spectra, see Supporting Information). Standard EI mass spectrometry shows monomers, HR-ESI measurements on a LTQ Orbitrap XL also gave no evidence for the Cl-bridged dimers, but monomeric species. At the same time, none of these methods can unambiguously exclude the presence of dimers and having no evidence for monomers we infer dimeric structures from related complexes without a potentially binding pendant group as e.g. for [{Pt(HPhPyPh)}₂(μ -Cl)₂].^[23] For cryoscopy or ebullioscopy measurements the solubility of the complexes turned out to be too low.

These intermediate complexes were reacted with dimethyl sulfoxide to yield the doubly cyclometalated complexes $[Pt(L^{1-6})(DMSO)]$ in high yields (69 to 95%). The DMSO coligand can easily be exchanged by carbene ligand as has been shown for the conversion from complex **4** to complex **4a**.

Molecular structures in solution (NMR) and in the solid (XRD)

Detailed 1D and 2D ¹H NMR spectroscopy proved the molecular entities of the seven complexes **1-6** and **4a**. Especially, the metalation of the phenyl and the thiophenyl groups is obvious from the platinum satellites at the signals of the corresponding ortho protons with ³*J*_{Pt-H} coupling constants of about 25 Hz (Figure 1). From [Pt(L³)(DMSO)] (**3**) suitable single crystals were obtained from evaporation of a CH₂Cl₂ solution and submitted to X-ray diffraction experiments. The compound was found to crystallise in the monoclinic space group *P*2₁/c. Figure 2 shows the crystal structure. The molecules are arranged in layers along the crystallographic *b*-axis. The intermolecular Pt[…]Pt distance exceeds 5 Å, revealing the absence of such intermolecular interaction. In the molecular structure (Figure 1) the platinum atom is distorted square planar surrounded (C–Pt–C angle of 157.6(9)°). The bond lengths Pt–N (1.99(2) Å), Pt–S_{DMSO} (2.21(1) Å), Pt–C_{thiophene} (2.16(2) Å) and Pt–C_{phenyl} (2.02(3) Å) accord with those of similar structures.^[24, 31]



Figure 1. Low field part of the ¹H NMR spectrum of $[Pt(L^3)(DMSO)]$ (3) measured in CD₂Cl₂ at 300 MHz)left). Molecular structure (50% probability of ellipsoids, hydrogen atoms were omitted for clarity, right).



Figure 2. Crystal structure of $[Pt(L^3)(DMSO)]$ (3) viewed along the crystallographic b axis.

UV-vis absorption and emission spectroscopy

Photophysical data of all complexes $[Pt(L^{1-6})(DMSO)]$ (**1-6**) and $[Pt(L^4)(Me_2Imd)]$ (**4a**) are summarised in Table 1. In Figure 3 absorption and emission spectra of complexes **1-4** in CH₂Cl₂ at room temperature are shown, Figure 4 includes the spectra of complexes **4-6** and **4a**. Our data for complex **4** matches with the results of Che et al.^[31] with the exception of the quantum yield. Different measurement methods are very probably responsible for this deviation.

All complexes show absorption bands between 250-300 ($\epsilon \approx 20000-50000 \text{ L mol}^{-1} \text{ cm}^{-1}$) which are assigned to transitions with predominantly ligand character (IL = intraligand). According

to literature^[31-32] the moderate absorption bands at 350-400 nm ($\epsilon \approx 10000$ -30000 L mol⁻¹ cm⁻¹) can be assigned to mixed ¹MLCT/³IL transitions of [(5d)Pt $\rightarrow \pi^*(C^N^C)$] and weak absorption bands >440 nm are assigned to transitions with mixed ³MLCT/³IL character.



Figure 3. Absorption and emission spectra of complexes $[Pt(L^{1-4})(DMSO)]$ (1-4) in CH₂Cl₂ at 298 K with the inset showing the long-wavelength absorption bands.



Figure 4. Absorption and emission spectra of complexes $[Pt(L^{4-6})(DMSO)]$ (4-6) and $[Pt(L^4)(Me_2Imd)]$ (4a) in CH_2Cl_2 at 298 K.

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Upon excitation at $\lambda_{ex} = 350-450$ nm, complexes **1-6** and **4a** in CH₂Cl₂ show orange phosphorescence ($\lambda_{em} = 579-595$ nm; $\Phi = 0.05-0.22$). Even complex **1**, with the most simplified ligand structure, is emissive in CH₂Cl₂ solution with a quantum yields of $\Phi = 0.06$. These quantum yields are remarkably high for such C^N^C complexes which are frequently non-emissive in solution and we ascribe these improved luminescence properties to the presence of the thiophene unit. The reason why the thiophenyl complexes are superior in quantum yields over phenyl, naphthyl, carbazole, or fluorenyl containing derivatives as described in Che's paper ^[31] is not yet clear. Both absorption and emission energies are generally red-shifted for thiophenyl derivatives compared with the other complexes,^[31] and the more efficient luminescence is either the simple consequence of the energy-gap law or might be due to a slightly different excited state. TD-DFT calculations on a reasonable level (TD-B3LYP/6-31G(d)-LANL2DZ) were able to reproduce qualitatively the observed red-shifts and suppose a slightly different character of the excited states with varying contributions of ³MLCT and ³IL (π - π^*).^[32]

Exchange of a cyclometalating phenyl group by a naphthyl unit leads to slightly enhanced radiative rate constants (k_r) for complexes 2, 4 and 4a in solution. Recent calculations on [Pt(Phbpy)Cl] showed that an extension of the π conjugation of the lateral aryl ring prevents distortion of the excited triplet state, thus increasing the k_r values.^[36] The non-radiative constants (k_{nr}) are generally lower with naphthyl units, and in the case of complexes 4 and 4a a significant enhancement of k_{nr} can be attributed to the exchange of DMSO by carbene as the ancillary ligand. Che et al. observed an enhanced Φ upon replacement of DMSO with an isocyanide ligand and suggested that the good σ -donating ability of isocyanides leads to destabilisation of metal-centred quenching states.^[31] The same effect in complex 4a was expected due to the strong σ -donating capabilities of Me₂Imd, but the quantum yield of 4a is markedly lower in solution than that of 4. The increased k_{nr} value observed in this case suggested that the radiationless decay favoured by a higher density of vibrational states introduced by Me₂Imd played a more significant role, even when compared to the complexes bearing an ancillary DMSO. In contrast, the phenyl groups at the 4-position of the pyridine on complexes 3, 4 and 4a did not markedly affect the values of the radiative and nonradiative constants. Interestingly, the insertion of p-methoxy (5) and p-fluoro (6) substituents at the phenyl ring lead to decreased k_r values in solution, without significantly affecting the radiationless deactivation rate constants. (TD)DFT studies are planned to explain their role.

Results of equimolar low complex concentrations ($c = 16 \mu \text{mol g}^{-1}$) are shown in Table 1. We observed that the emission maxima and quantum yields in PMMA matrices are only marginally sensitive to complex concentration (spectra shown in the SI), even though platinum(II) complexes can potentially interact through co-planar stacking. Consequently, the energy of the highest

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occupied molecular orbital (HOMO) is raised and the energy of the lowest unoccupied molecular orbital (LUMO) is reduced resulting in a bathochromic shift of emission bands.^[34-35] Instead, we do not observe such marked concentration-dependent excimer formation and ascribe the slight red-shifts to changes in polarity of the environment. In PMMA matrices and glassy frozen $CH_2Cl_2/MeOH$ mixtures (v:v = 1:1) the quantum yields are increased due to reduced radiationless deactivation by suppressed molecular vibrations and solvent coupling, whereas the emission energies are similar in accordance with a predominant ligand centred character of the emissive triplet state.

					(<i>)</i> :	1				D) () (b]	· · · · · ·
						glassy, 77 K ^[d]				PMMA	
	$\lambda_{abs}^{[b]}(\varepsilon)$	$\lambda_{em}^{[b]}$	$arPhi^{[b]}$	$k_{\rm r}^{\rm [b]}$	$k_{\rm nr}$ ^[b]	$\lambda_{\rm em}^{[c]}(\tau)$	$arPhi^{[c]}$	$k_{\rm r}^{\rm [c]}$	$k_{\rm nr}^{\rm [c]}$	$\lambda_{\rm em}^{\rm [d]}$	$arPhi^{[d]}$
		(τ)		-				-			
1	252 (2.5), 269 (2.6),	586	0.06	2.1	32.4	577	0.31	1.6	3.5	584, 633,	0.25
	295sh (1.2), 335 (1.5),	(2.9),		(±0.	(±0.	(20.0),		(±0.3)	(±0.3)	693sh	
	350 (1.7), 464 (0.9),	633,		7)	7)	598,					
	492 (0.1)	693sh				627, 687					
2	270 (3.2), 294 (3.1),	579	0.18	5.5	24.8	568	0.34	1.5	3.0	576, 623,	0.28
	328sh (1.1), 347sh	(3.3),		(±0.	(±0.	(22.3),		(±0.1)	$(\pm$	685sh	
	(1.1), 361 (1.5), 376sh	625,		6)	6)	589,			0.1)		
	(1.0), 396 (0.9), 446	683sh				617, 674					
	(0.1), 474sh (0.1)										
3	252 (2.6), 274sh (3.7),	595	0.09	3.0	30.3	582	1.00	4.2	< 0.2	589, 636,	0.34
	296 (4.2), 339 (2.1),	(3.0),		(±0.	(±0.	(23.7),		(±0.2)		694sh	
	352 (2.1), 470 (1.0),	637,		3)	3)	601,					
	499 (0.1)	696sh				631, 687					
4	273 (5.3), 293 (5.1),	585	0.22	5.6	20.0	572	0.64	2.5	1.4	582, 625,	0.36
	304sh (4.6), 331sh	(3.9),	[e]	(±0.	(±0.	(25.6),		(±0.1)	(±0.1)	682sh	
	(1.9), 365 (1.8), 379sh	629,		3)	3)	591,					
	(1.2), 401 (1.1), 447	694sh				620, 677					
	(0.2), 481 (0.1)										
5	273 (3.7), 296 (3.8),	579	0.06	1.5	23.5	570	1.00	3.5	< 0.2	577, 625,	0.40
	310 (4.0), 330 (3.5),	(4.0),		(±0.	(±1)	(29.0),		(±0.2)		677sh	
	355 (2.6), 377sh (1.2),	625,		3)		587,					
	400 (1.0), 449 (0.2),	688sh				616, 672					
	476 (0.1)										
6	274 (4.5), 294 (4.4),	583	0.05	1.5	27.9	572	0.38	1.3	2.1	583, 626,	0.44
	304sh (4.0), 331sh	(3.4),		(±0.	(±0.	(29.8),		(± 0.1)	(± 0.1)	685sh	
	(1.6), 365 (1.6), 379sh	628,		3)	6)	589,					
	(1.1), 402 (1.0), 452	692sh				620, 675					
	(0.1), 478 (0.1)			_							
4 a	260 (5.1), 282 (5.8),	593	0.06	7	104	578	0.65	4.4	2.4	585, 632,	0.37
	293sh (5.7), 353sh	(0.9),		(±1)	(± 3)	(14.9),		(± 0.3)	(± 0.3)	696sh	
	(1.5), 372 (2.1), 401	638,				601,					
	(1.1), 468 (0.1)	696sh				627, 685					

Table 1. Selected photophysical data of complexes $[Pt(L^{1-6})(DMSO)]$ (1-6) and $[Pt(L^4)(Me_2Imd)]$ (4a).^[a]

[a] Absorption maxima λ_{abs} in nm with absorption coefficient ε in 10000 L mol⁻¹ cm⁻¹; emission maxima λ_{em} in nm, excitation wavelength with τ = triplet state lifetime in μ s. Standard deviations of the fitted lifetime values were negligible for the calculation of the unimolecular deactivation rate constants, excitation wavelength $\lambda_{ex} = 350$ nm for all measurements; Φ = photoluminescence quantum yield. Φ values carried a maximum 5% standard deviation intrinsic to the measurement procedure; radiative k_r and non-radiative k_{nr} rate constants in 10⁴s⁻¹. [b] Determined in deoxygenated CH₂Cl₂ ($c = 2.5 \times 10^{-5}$ mol L⁻¹). [c] Measured in PMMA matrices ($c = 16 \mu$ mol g⁻¹). [d] Measured in glassy frozen (77 K) CH₂Cl₂/MeOH mixtures (v:v = 1:1). [e] Compare a Φ of 0.13 in ref [31].

At 77 K, in glassy frozen solutions, complexes **4** and **4a** show identical Φ and complexes **3** and **5** possess unitary quantum yields. The latter represent a phenyl (**3**) or naphthyl (**5**) metalated core and phenyl or *p*-methoxyphenyl substituents. For these two complexes, the k_r is enhanced upon freezing, whereas for the other examples a drop is observed. A reduced charge-transfer character in the excited state in the absence of solvent reorganisation usually restricts the participation of the metal centre in the excited state and therefore lowers the luminescence rate constant. TD-DFT calculations on a higher level of sophistication than in the previous report by Zhang et al. (TD-B3LYP/6-31G(d)-LANL2DZ)^[32] will be needed to clarify the influence of the substituents on the vertical transitions for complexes **3** and **5** and their relaxation pathway(s).

Electrochemistry

Cyclic voltammograms of complexes **1-6** and **4a** show irreversible oxidations between 0.5-0.8 V, selected plots were shown in Figure 5, data is collected in Table 2. A cathodic shift in the oxidation potential upon substitution of phenyl (**1**) to naphthyl (**2**) is in line with DFT calculations showing contributions of the naphthyl moiety to the HOMO.^[32] First reduction waves occur between -2.06 V and -2.30 V with markedly varying reversibility (Table 2).



Figure 5. Cyclic voltammograms of oxidation and first reduction of complexes $[Pt(L^{1-4})(DMSO)]$ (1-4) measured in 0.1 M nBu₄NPF₆/THF vs. ferrocene/ferrocenium.

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The potentials are slightly anodically shifted for the 4-phenyl-pyridine containing systems **3** to **6** compared to **1** and **2** and the reversibility is higher. Substitution of phenyl to naphthyl (compare **1-2** and **3-4**) has no impact on the potentials but the reversibility of the first reduction increases markedly. The reason is probably a superior stabilisation of negative charge through extension of the π -conjugated system in both cases. According to DFT calculations, the LUMO is predominantly located on the pyridine moiety and the peripheral phenyl,^[32] in line with our results. Substitution at the para position of peripheral 4-phenyl group does not affect markedly the reduction potentials (compare **4-5** and **4-6** in Table 2). An exchange of DMSO against Me₂Imd causes a cathodic shift of both the oxidation and the reduction potentials. This is in line with the expected superior σ -donating ability of this carbene ligand compared with DMSO.

complex	$E_{\rm pa}{\rm Ox1}$	$E_{1/2} (I_{\rm pa}/I_{\rm pc}) \text{ Red1}$	$E_{1/2}$ or E_{pc} Red2	$\Delta E \text{ Ox1-Red1} / \text{eV}$
1	0.67	-2.25 (0.00)	-2.57 irr.	2.92
2	0.79	-2.20 (0.63)	-2.51 irr.	2.99
3	0.78	-2.09 (0.77)	-2.68 irr.	2.87
4	0.81	-2.06 (0.86)	-2.60 rev.	2.87
5	0.81	-2.10 (0.77)	-2.69 irr.	2.91
6	0.81	-2.08 (0.64)	-2.74 irr.	2.89
4 a	0.50	-2.30 (0.85)	-2.98 irr.	2.80

Table 2. Electrochemical data of complexes $[Pt(L^{1-6})(DMSO)]$ (1-6) and $[Pt(L^4)(Me_2Imd)]$ (4a).^[a]

[a] Measured in 0.1 M nBu_4NPF_6/THF vs. ferrocene/ferrocenium at a scan rate of 100 mV/s. Half-wave potentials $E_{1/2}$ in V with current ratio I_{pa}/I_{pc} (1 = reversible, 0 = irreversible), E_{pa} = anionic peak potential in V, E_{pc} = cathodic peak potential in V.

For most of the complexes a second reduction wave can be observed at potentials cathodically shifted to the first by approximately 0.3 V for the complexes 1 and 2 and about 0.6 V for the systems containing the 4-phenyl-pyridine moieties, in line with a pyridine-centred LUMO. For complex **4a** the shift is largest with about 0.7 V. Also, the electrochemical band gaps can be derived from comparison of the first (reversible) reductions and the irreversible oxidations (Table 2). For complexes **1-6** values around 2.9 eV were found, complex **4a** exhibits the smallest value with 2.8 eV. Unfortunately, the lacking reversibility devaluates a bit these very interesting numbers. However, we are confident that the observed irreversibility in the CV measurements is only due to overlay of the reduction waves of the complexes were quite stable.

Spectroelectrochemical UV-vis absorption measurements were conducted for **4** and **4a** (data summarised in Table 3). Absorption spectra of oxidised species **4**⁺ and **4a**⁺ are very similar to **4** and **4a**, indicating that oxidation occurs predominantly at the platinum centre (Figures in the SI). Importantly, the initial spectrum cannot be recovered upon re-reduction in line with the irreversible character of the CV waves. During first reduction of **4** and **4a** new long-wavelength bands with maxima at 816 and 870 nm arise which are typical for a pyridine based reduction^[37-38] and the corresponding species are best described as $[Pt(II)(L^{*3-})(DMSO)]^{*-}$. These absorptions are only slightly red-shifted upon second reduction from **4**^{*-} to **4**²⁻ (Figure 6). In analogy to the complex $[Pt(bpy)(Py)_2]^{2+}$ and related derivatives^[37] the rather similar spectra of **4**^{*-} and **4**²⁻ point to a Pt-based reduction with the products best described as $[Pt(I)(L^{*3-})(DMSO)]^{2-}$ (both containing L^{*3-} as the essential chromophore).

Table 3. UV-vis absorption data of $[Pt(L^4)(DMSO)]^{+/n-}$ (4 ^{+/n-}) and $[Pt(L^4)(Me_2Imd)]^{+/n-}$ (4a ^{+/n-}). ^[a]							
reductio	λ_{abs} / nm	oxida	ation	λ_{abs} / nm			
4	268, 300sh, 350, 383, 431sh 738, 816	4 ⁺	246, 276, 3	307, 392			
4 ²⁻	267, 335sh, 397, 469 843, 916						
4a ⁻	240, 270, 299sh, 319, 360, 407, 771, 870	4 a ⁺	238, 272, 2	294sh, 390, 438sl	h		
4a ²⁻	267, 307sh, 357, 395, 502, 532, 575, 664, 919						

[a] Measured in 0.1 M nBu_4NPF_6/THF , absorption maxima λ_{abs} in nm.



Figure 6. UV-vis absorption spectra recorded during electrochemical reduction of $[Pt(L^4)(DMSO)]$ (4) (green). First reduction from -1.9 V to -2.4 V leading to 4⁻ (blue), second reduction from to -2.5 V to -2.8 V leading to 4²⁻ (pink). Measured in 0.1 M *n*Bu₄NPF₆/THF solution.



Figure 7. UV-vis absorption spectra recorded during electrochemical reduction of $[Pt(L^4)(Me_2Imd)]$ (4a) (green). First reduction from -2.2 V to -2.4 V leading to 4a⁻ (blue), second reduction from -2.7 V to -3.0 V leading to 4a²⁻ (pink). Measured in 0.1 M *n*Bu₄NPF₆/THF solution.

A different behaviour is observed during the second reduction of **4a** containing the N-heterocyclic carbene ligand. A massive spectral change including the blue-shift of the long-wavelength band maxima to 502 and 664 nm (Figure 7) indicate a second ligand-based reduction $[Pt(II)(L^{4-})(MeImd)]^{2-}$ in analogy to observations for complexes $[Pt(bpy)(R)_2]$ with strong carbanionic R⁻ ligands (R = mesityl, phenyl or methyl).^[38]

Conclusions and Outlook

Bis-cyclometalated Pt(II) complexes of dianionic $(CNC)^{2-}$ 2,5-bis(aryl)-pyridine ligands $(L^{1-6})^{2-}$ carrying various aryl substituents have been synthesised in two steps $(H_2L^1 = 2\text{-phenyl-6-(thiophen-2-yl)pyridine}; H_2L^2 = 2-(naphthalen-2-yl)-6-(thiophen-2-yl)pyridine; H_2L^3 = 2,4-diphenyl-6-(thiophen-2-yl)pyridine; H_2L^4 = 2-(naphthalen-2-yl)-4-phenyl-6-(thiophen-2-yl)pyridine; H_2L^5 = 4-(4'-fluorophenyl)-2-(naphthalen-2-yl)-6-(thiophen-2-yl)pyridine; H_2L^6 = 4-(4'-methoxyphenyl)-2-(naphthalen-2-yl)-6-(thiophen-2-yl)pyridine; H_2L^6 = 4-(4'-methoxyphenyl)-2-(naphthalen-2-yl)pyridine). Reaction of the H_2L proto-ligands with K_2[PtCl_4] in acetic acid gave the mono-cyclometalated complexes of the composition [Pt(HL)Cl]_n. The previously assumed monomeric character (n = 1) including S binding of the thiophene group was studied using sophisticated NMR and MS methods. Unfortunately, neither a monomeric (n = 1) nor a dimeric (n = 2) character could be concluded and a dimeric structure can only be inferred from related compounds. Heating these complexes in hot DMSO (dimethyl sulfoxide) yielded the double-cyclometalated DMSO complexes [Pt(L¹⁻⁶)(DMSO)]. Reaction of [Pt(L⁴)(DMSO)] with$ *N*,*N* $-dimethylimidazolium iodide in the presence of KOtBu as base gave the carbene complex [Pt(L⁴)(Me_2Imd)]. Detailed photophysical studies reveal intense orange luminescence of these$

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complexes in CH₂Cl₂ solution with quantum yields up to 0.22, increased quantum yields up to 1.00 in glassy frozen CH₂Cl₂:MeOH (1:1) and up to 0.44 in PMMA matrices and also largely varied excited states lifetimes from 0.9-4.0 µs in CH₂Cl₂ solution and from 14.9-29.8 µs in in glassy frozen CH₂Cl₂:MeOH (1:1). The quite similar emission maxima however, point to the very same excited states regardless of the conditions. Preliminary structure-properties relations include the increase of the radiative constant by extension of the π conjugated system at the metalated ring (phenyl to naphthyl), whereas the insertion of a phenyl substituent at the luminophore only slightly affects the properties. Detailed electrochemistry (cyclic voltammetry and square-wave) reveals ligand-based first reductions ranging from -2.1 to -2.3 with markedly increased reversibility for the 4-phenylpyridine substituted systems, which points to essentially pyridine-centred LUMOs and a description of the reduced complexes as Pt(II) complexes of reduced ligand L*3- [Pt(II)(L*3-)(DMSO)]*-. In contrast to the degree of reversibility, the potentials do not vary markedly upon substitution; the 4phenyl substituted derivatives reveal a slight anodic shift. UV-vis spectroelectrochemistry strongly supports this assignment. Irreversible Pt-centred oxidations at around 0.8 V can be assigned to essentially Pt(II/III) oxidations also in line with the spectroelectrochemistry. Electrochemical band gaps of 2.8 to 3.0 eV can be calculated from the electrochemical data, although the irreversibility of the oxidation waves devaluates the data. Second reduction waves at very negative potentials interfere with solvent (THF with traces of water) discharge and can be traced from UV-vis spectroelectrochemistry to Pt-centred reductions for the DMSO complexes [Pt(I)(L^{•3-})(DMSO)]²⁻ but a second ligand-centred reduction for the Me₂Imd complex $[Pt(II)(L^{4-})(MeImd)]^{2-}$. These electronic descriptions of the reduced complexes with a high negative charge and/or radical character at the ligands are in line with the irreversibility of many reduction waves in these complexes. However, in the absence of protons and hampered possibilities of radical reactions e.g. in solid matrices we are confident that these systems provide high stability in combination with very suitable photo/electrochemical properties suggesting their application in optoelectronics. In future work we will further characterise the reduced and excited states of these complexes by experimental (EPR, transient absorption) and theoretical (highly sophisticated TD-DFT) approaches and will further vary the ligand pattern to refine our preliminary structure-properties relations.

Experimental Section

General Information: Commercially available reagents (solvents and ligands) were used without further purification. Solvents (CH₂Cl₂, THF, toluene, diethyl ether and CH₃CN) were dried using a

MBRAUN MB SPS-800 solvent purification system. For electrochemical measurements THF was distilled over a Na/K alloy prior to use.

The syntheses and analyses of the proto-ligands H_2L^{1-6} is described in the Supporting Information.

Synthesis of monocyclometalated complexes [Pt(HL¹⁻⁶)Cl]₂ – general procedure

Following a literature procedure^[23-24], K_2 [PtCl₄] (208 mg, 0.5 mmol) was added to a solution of H_2L^{1-6} (0.7 mmol, 1.4 eq) in glacial acetic acid (250 mL). The reaction was stirred at 110 °C for 72 h. The orange precipitates were filtered off and washed with glacial acetic acid, water and dried in vacuo.

[**Pt(HL**¹)**Cl**]₂: Yield: 208 mg (0.45 mmol, 90%). $C_{15}H_{10}CINPtS$ (466.84): calcd. C 38.59, H 2.16, N 3.00, S 6.87; found C 38.56, H 2.18, N 3.01, S 6.87%. ¹H NMR (600 MHz, CD₂Cl₂): δ = 8.00 (t, *J* = 7.9 Hz, 1H), 7.76 (dd, *J* = 7.6, 1.3 Hz, *J*_{Pt,H} = 58 Hz, 1H), 7.65-7.58 (m, 3H), 7.51-7.44 (m, 2H), 7.34 (dt, *J* = 10.8, 5.4 Hz, 1H), 7.23-7.16 (m, 2H) ppm. EI-MS(+): m/z = 467 [monomer]⁺, 430 [monomer–HCl]⁺, 237 [H₂L¹]⁺.

[**Pt**(**HL**²)**Cl**]₂: Yield: 253 mg (0.49 mmol, 98%). C₁₉H₁₂ClNPtS (516.94): calcd. C 44.15, H 2.34, N 2.71, S 6.20; found C 44.22, H 2.38, N 2.73, S 6.22%. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.10 (s, $J_{Pt,H}$ = 62 Hz, 1H), 8.04 (t, J = 8.0 Hz, 1H), 7.98 (s, 1H), 7.86-7.76 (m, 3H), 7.69-7.61 (m, 2H), 7.54-7.39 (m, 3H), 7.35 (dd, J = 5.2, 3.7 Hz, 1H) ppm. EI-MS(+): m/z = 517 [monomer]⁺, 480 [monomer–HCl]⁺, 287 [H₂L²]⁺.

[**Pt(HL**³)**Cl**]₂: Yield: 262 mg (0.48 mmol, 97%). C₂₁H₁₄ClNPtS (542.94): calcd. C 46.46, H 2.60, N 2.58, S 5.90; found C 46.42, H 2.66, N 2.61, S 5.91%. ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.87-7.81 (m, 5H), 7.67 (d, *J* = 5.2 Hz, 1H), 7.65-7.56 (m, 5H), 7.40 (dd, *J* = 5.2, 3.7 Hz, 1H), 7.30-7.20 (m, 2H) ppm. EI-MS(+): m/z = 543 [monomer]⁺, 506 [monomer–HCl]⁺, 313 [H₂L³]⁺.

[Pt(HL⁴)Cl]₂: Yield: 579 mg (0.98 mmol, 98%). C₂₅H₁₆ClNPtS (593.00): calcd. C 50.64, H 2.72, N 2.36, S 5.41; found C 50.68, H 2.75, N 2.36, S 5.41%. ¹H NMR: (300 MHz, CD₂Cl₂): δ = 8.05-7.81 (m, *J*_{Pt,H} = 63 Hz, 2H), 7.78-7.68 (m, 5H), 7.61-7.55 (m, 1H), 7.54-7.49 (m, 5H), 7.38-7.28 (m, 2H), 7.25 (dd, *J* = 5.1, 3.8 Hz, 1H) ppm. EI-MS(+): m/z = 593 [monomer]⁺, 556 [monomer–HCl]⁺, 363 [H₂L⁴]⁺.

[Pt(HL⁵)Cl]₂: Yield: 309 mg (0.49 mmol, 99%). C₂₆H₁₈ClNOPtS (623.02): calcd. C 50.12, H 2.91, N 2.25, S 5.15; found C 50.13, H 2.95, N 2.26, S 5.14%. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.24-7.98 (m, *J*_{Pt,H} = 63 Hz, 2H), 7,92 (d, *J* = 1.8 Hz, 1H), 7.85-7.76 (m, 5H), 7.63 (d, *J* = 5.1 Hz, 1H), 7.58 (d, *J* = 3.2 Hz, 1H), 7.52-7.39 (m, 2H), 7.36 (dd, *J* = 5.2, 3.7 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 3.92 (s, 3H) ppm. EI-MS(+): m/z = 623 [monomer]⁺, 586 [monomer–HCl]⁺, 393 [H₂L⁵]⁺.

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[**Pt**(**HL**⁶)**Cl**]₂: Yield: 298 mg (0.49 mmol, 98%). C₂₅H₁₅ClFNPtS (610.99): calcd. C 49.15, H 2.47, N 2.29, S 5.25; found C 49.17, H 2.48, N 2.30, S 5.24%. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.20-7.96 (m, *J*_{Pt,H} = 63 Hz, 2H), 7.91-7.73 (m, 6H), 7.64 (d, *J* = 5.2 Hz, 1H), 7.59 (d, *J* = 3.7 Hz, 1H), 7.45 (dq, *J* = 6.9, 5.5 Hz, 2H), 7.39-7.26 (m, 3H) ppm. EI-MS(+): m/z = 611 [monomer]⁺, 574 [monomer–HCl]⁺, 381 [H₂L⁶]⁺.

Syntheses of doubly cyclometalated complexes [Pt(L¹⁻⁶)(DMSO)]

Following a literature procedure,^[23-24] the monocyclometalated complexes $[Pt(HL^{1-6})Cl]_2$ were dissolved in a small amount of hot dimethyl sulfoxide and small amounts of sodium carbonate were added. The reaction mixture was stirred at 110 °C for 6 h. The raw product was precipitated through addition of several small portions of water, filtered off and washed with water. The material was purified by filtration over aluminium oxide using CH_2Cl_2 as eluent and the products were obtained as yellow-orange solids.

[Pt(L¹)(DMSO)] (1): Yield: 127 mg (0.25 mmol, 75%). $C_{17}H_{15}NOPtS_2$ (508.51): calcd. C 40.15, H 2.97, N 2.75, S 12.61; found C 39.98, H 2.96, N 2.74, S 13.36%. ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.96 (d, J = 7.3 Hz, $J_{Pt,H}$ = 25 Hz, 1H, Hc), 7.61-7.48 (m, 2H, H4/H5'), 7.45 (d, J = 7.6 Hz, 1H, Hf), 7.25 (t, J = 6.8 Hz, 1H, Hd), 7.20-6.96 (m, 4H, He/H3/H5/H4'), 3.66 (s, $J_{Pt,H}$ = 27 Hz, 6H, S-CH₃) ppm. EI-MS(+): m/z = 508 [M]⁺, 430 [M–DMSO]⁺, 237 [L¹]⁺.

[Pt(L²)(DMSO)] (2): Yield: 150 mg (0.27 mmol, 69%). $C_{21}H_{17}NOPtS_2$ (558.57): calcd. C 45.16, H 3.07, N 2.51, S 11.48; found C 44.99, H 3.23, N 2.47, S 11.35%. ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.39 (s, $J_{Pt,H}$ = 28 Hz, 1H, Hc), 7.98 (s, 1H, Hj), 7.76 (t, J = 7.8 Hz, 2H, He/Hh), 7.66 (t, J = 7.9 Hz, 1H, H4), 7.54 (d, J = 4.6 Hz, 1H, H5'), 7.48-7.33 (m, 3H, Hf/Hg/H3), 7.17-7.07 (m, 2H, H4'/H5), 3.73 (s, $J_{Pt,H}$ = 27 Hz, 6H, S-CH₃) ppm. HR-ESI-MS(+): m/z = 580.02724 [M+Na]⁺, 559.04784 [M+H]⁺ (calcd. 559.04778).

[Pt(L³)(DMSO)] (3):Yield: 133 mg (0.23 mmol, 77%). $C_{23}H_{19}NOPtS_2$ (584.61): calcd. C 47.25, H 3.28, N 2.40, S 10.97; found C 46.98, H 3.29, N 2.45, S 11.10%. ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.95 (d, J = 7.3 Hz, $J_{Pt,H}$ = 26 Hz, 1H, Hc), 7.75-7.69 (m, 2H, H2^{+/}/H6⁺⁺), 7.57-7.48 (m, 5H, Hf/H5⁺/H3⁺⁺-H5⁺⁺), 7.32 (s, 1H, H3), 7.29-7.16 (m, 2H, Hd, H5), 7.16-7.03 (m, 2H, He/H4⁺), 3.64 (s, $J_{Pt,H}$ = 27 Hz, 6H, S-CH₃) ppm. EI-MS(+): m/z = 584 [M]⁺, 506 [M–DMSO]⁺, 313 [H₂L³]⁺.

[**Pt(L⁴)(DMSO)**] (**4**): Yield: 255 mg (0.40 mmol, 79%). $C_{27}H_{21}NOPtS_2$ (634.67): calcd. C 51.10, H 3.34, N 2.21, S 10.10; found C 51.35, H 3.39, N 2.28, S 10.10%. ¹H NMR (300 MHz, CD₂Cl₂) δ = 8.38 (s, $J_{Pt,H}$ = 29 Hz, 1H, Hc), 8.03 (s, 1H, Hj), 7.75 (dd, J = 16.3, 7.5 Hz, 4H, He/Hh/H2^{+/}/H6⁺⁺), 7.62-7.50 (m, 5H, H5/H5^{+/}/H3⁺⁺-H5⁺⁺), 7.43-7.30 (m, 3H, Hf/Hg/H3), 7.10 (d, J = 4.6 Hz, $J_{Pt,H}$ = 10

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Hz, 1H, H4'), 3.70 (s, $J_{Pt,H} = 27$ Hz, 6H, S-CH₃) ppm. HR-ESI-MS(+): $m/z = 635.07971 [M+H]^+$ (calcd. 635.07907).

[Pt(L⁵)(DMSO)] (5): Yield: 207 mg (0.31 mmol, 95%). $C_{28}H_{23}NO_2PtS_2$ (664.70): calcd. C 50.60, H 3.49, N 2.11, S 9.65; found C 50.20, H 3.38, N 2.10, S 9.79%.¹H NMR (300 MHz, CD₂Cl₂): δ = 8.42 (s, $J_{Pt,H}$ = 29 Hz, 1H, Hc), 8.09 (s, 1H, Hj), 7.78 (dd, J = 10.3, 8.3 Hz, 4H, He/Hh/H2⁺⁺/H6⁺⁺), 7.63 (d, J = 1.5 Hz, 1H, H5), 7.56 (d, J = 4,7 Hz, 1H, H5⁺), 7.49-7.30 (m, 3H, Hf/Hg/H3), 7.18-7.07 (m, 3H, H4⁺/H3⁺⁺/H5⁺⁺), 3.94 (s, 3H, O-CH₃), 3.75 (s, $J_{Pt,H}$ = 27 Hz, 6H) ppm. EI-MS(+): m/z = 664 [M]⁺, 586 [M–DMSO]⁺, 393 [H₂L⁵]⁺.

[**Pt**(**L**⁶)(**DMSO**)] (6): Yield: 190 mg (0.29 mmol, 89%). $C_{27}H_{20}FNOPtS_2$ (652.66): calcd. C 49.69, H 3.09, N 2.15, S 9.82; found C 49.54, H 2.99, N 2.12, S 9.91%.¹H NMR (300 MHz, CD₂Cl₂): δ = 8.37 (s, $J_{Pt,H}$ = 28 Hz, 1H, Hc), 8.01 (s, 1H, Hj), 7.82-7.68 (m, 4H, He/Hh/H2⁺⁺/H6⁺⁺), 7.53-7.51 (m, 2H, H5/H5⁺), 7.37 (dtd, J = 14.6, 6.9, 1.3 Hz, 2H, Hf/Hg), 7.29-7.21 (m, 3H, H3/H3⁺⁺/H5⁺⁺), 7.09 (d, J = 4.7 Hz, $J_{Pt,H}$ = 10 Hz, 1H, H4⁺), 3.69 (s, $J_{Pt,H}$ = 27 Hz, 6H, S-CH₃) ppm.

Synthesis of [Pt(L⁴)(Me₂Imd)] (4a)

Following a literature procedure^[39] a solution of $[Pt(L^4)(DMSO)]$ (4) (100 mg, 0.16 mmol, 1 eq) in acetonitrile (40 mL) was treated with *N*,*N*-dimethylimidazolium iodide (38 mg, 0.17 mmol, 1.05 eq) and potassium *tert*-butoxide (21 mg, 0.19 mmol, 1.18 eq). The reaction mixture was stirred at 90 °C for 16 h. The solvent was reduced and the orange product was precipitated with water. Yield: 91 mg (0.14 mmol, 88%). C₃₀H₂₄N₃PtS (653.68): calcd. C 55.12, H 3.70, N 6.43, S 4.90; found C 53.75, H 3.72, N 6.11, S 4.95%. ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 8.11$ (s, 1H, Hj), 7.84 (d, *J* = 6.9 Hz, 2H, H2⁺/H6⁺⁺), 7.78 (d, *J* = 7.7 Hz, 1H, Hh), 7.68 (s, 1H, H4), 7.64-7.28 (m, 9H, Hc/He-Hg/H5/H5⁺/H3⁺⁺-H5⁺⁺), 7.13 (s, *J*_{Pt,H} = 12 Hz, 2H, N-HC=CH-N), 6.84 (d, , *J* = 4.5 Hz, *J*_{Pt,H} = 13 Hz, 1H, H4⁺), 3.84 (s, 6H, CH₃) ppm. HR-ESI-MS (+): *m*/z = 652.12584 [M]⁺ (calcd. 652.12601).

Instrumentation: Elemental analysis was obtained using a Hekatech CHNS EuroEA 3000 analyzer. NMR spectra were recorded on a Bruker Avance II 300 MHz spectrometer (1 H: 300.13 MHz) equipped with a BBO ATM 5 mm probe head with z-gradient (1 H/ 19 F X 2 H), or on a Bruker Avance II+ 600 spectrometer (1 H: 400.13 MHz, 13 C: 100.61 MHz) using a TBI 5 mm probe head with z-gradient (1 H 31 P X 2 H). The assignment of the 1 H was obtained from 1 H NOESY and 1 H COSY experiments. All 2D NMR experiments were performed using standard pulse sequences from the Bruker pulse program library. Chemical shifts were relative to TMS. EI-MS in positive mode were determined using a Finnigan MAT 95 spectrometer. If not indicated otherwise, ionisation energy of 20 eV was applied. HR-ESI-MS high resolution measurements were recorded

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with a LTQ-Orbitrap XL spectrometer. UV-vis absorption spectra were recorded on Varian Cary 50 Scan spectrophotometers. Emission spectra at room temperature were recorded on a Spex FluoroMax-3 spectrometer. For emission spectra at 77 K and life time measurements (77 K and 293 K) a PicoQuant FluoTime 300 spectrometer was used. Lifetime analysis was performed using the commercial FluoFit software. The quality of the fit was assessed by minimizing the reduced chi squared function (χ^2). Luminescence quantum yields were determined using a Hamamatsu Photonics absolute PL quantum yield measurement system (C9920-02) equipped with a L9799-01 CW Xenon light source, monochromator, photonic multi-channel analyser and integrating sphere (error of maximum \pm 5% for Φ is estimated). All solvents used were of spectroscopic grade and degassed prior to use. Matrices of complexes in PMMA were prepared by solving complex and PMMA in toluene at different amounts and evaporation of the solvent on a glass substrate (5x5 mm). A PG STAT 30 potentiostat from Metrohm was used for cyclovoltammetric measurements using a three-electrode arrangement consisting of a glassy-carbon working electrode, a platinum counter electrode and a Ag/AgCl reference electrode.

Single crystal structure analysis: The measurement was performed using graphitemonochromatised Mo-K_{α} radiation ($\lambda = 7.1073$ Å) on a STOE IPDS IIT diffractometer (at 293 K). The structure was solved by direct methods (SIR2011)^[40] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014).^[41] Non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The hydrogen atoms were included by using appropriate riding models. Numeric absorption correction was carried out with X-RED^[42] and X-SHAPE.^[43] Full structural information has been deposited with the Cambridge Crystallographic Data Centre, No. CCDC-1528069 for [Pt(L³)(DMSO)]. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Supporting Information (see footnote on the first page of this article): More experimental details, tables and additional figures with NMR spectra, emission spectra, cyclic voltammograms, and spectroelectrochemical UV-vis absorption spectra were provided.

Acknowledgements

We thank Dr. Ingo Pantenburg (University of Cologne) for crystal data collection. We also thank Michael Neihs and Dr. Mathias Schäfer (University of Cologne) for ESI-MS high resolution measurements recorded with an LTQ-Orbitrap XL.

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