Research paper

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Tetradentate N^N°N^N-type luminophores for Pt(II) complexes: Synthesis, photophysical and quantum-chemical investigation

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Abstract

Herein we report on dianionic tetradentate, pyridin-azole-based ligands for luminescent Pt(II) complexes. To improve their solubility in common organic solvents, a hexyl-chain was inserted in the periphery of the luminophoric ligand and different substituents were introduced at the 1*H*-pyrazole moieties including 4-hexylphenyl- (L1), adamantyl- (L2) and 3,5-dimethoxyphenyl (L3) substituents. For the new ligand precursors L1 and L2, the corresponding Pt(II) complexes Pt1 and Pt2 were synthesized and characterized by exact mass spectrometry as well as by ¹H-NMR. L3 was also successfully synthesized and isolated, but due to the limited solubility of the resulting coordination compound, the purification and structural characterization of the corresponding Pt(II) complex Pt3 was not achieved. The absorption and steady-state as well as time-resolved photoluminescence spectra of **Pt1** and **Pt2** were investigated and interpreted employing TD-DFT. We found that the S_1 states for Pt1 and Pt2 can be described mainly as single electron HOMO \rightarrow LUMO excitations with a ¹MP-ILCT character comprising the diazole units and the pyridine rings. At room temperature, **Pt1** and Pt2 show phosphorescence in the green region of the electromagnetic spectrum peaking at 506 nm and 497 nm with photoluminescence quantum yields reaching 17% and 25%, respectively. DFT calculations show that the T₁ states of Pt1 and Pt2 can be mainly described as monoelectronic HOMO-LUMO excitations with predominant ³MP-ILCT character.

Keywords: Pt(II) complex – tetradentate ligands – triplet emitter – steady state and time-resolved spectroscopy – photophysics – NNNN – DFT

Introduction

Photoactive complexes involving the late transition metals (groups 8 - 10) constitute a highly interesting category of compounds for applications in many areas, e.g. photocatalysis^[1,2], bioimaging^{[3–} ^{6]}, optoelectronic sensors^[7–9] and organic light-emitting diodes (OLEDs)^[10–16]. Metal-organic complexes of Re(I)^[13,17], Ru(II)^[18,19], Os(II)^[11,19,20], Ir(III)^[15,21,22], Au(III)^[23-26] and Pt(II)^[22,27-29] have been intensively investigated as triplet emitters. The late transition metals cause a strong spin-orbit-coupling (SOC), due to the *heavy-atom-effect*, leading to an efficient *intersystem crossing* (ISC) and radiative decay from excited triplet states, thus leading to higher external quantum yields in electroluminescent devices.^[30–33] Excited states mostly arise from electronic excitations involving the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) but also energetically close (HOMO-*n*) and (LUMO+*m*) frontier orbitals, as well as combinations thereof. The chromophore, more precisely the energy gap between the HOMO and the LUMO, can be conveniently tuned and the photophysical properties can be set to desired performance.^[34,35] The simplest luminophoric backbone of the chelating chromophore typically includes at least one bidentate ligand with a delocalized π system. Enhanced metal chelate stability can be achieved using multidentate chromophores, such as tri- or tetradentate ligands.^[26,28,35–38] Square-planar cyclometalated complexes of Pt(II) are particularly interesting, due to their doubly occupied d_{z^2} -orbitals which offer the potential for Pt…Pt interactions, which again leads to emerging photophysical properties that can be adjusted by proper modifications to the ligand favouring or suppressing aggregation.^[16,29,39,40] In this sense, the self-assembling behaviour of square-planar transition metal complexes can be manipulated through the nature of the luminophoric backbone.^[41]

Chang et al. reported N^N°N-chelating, azolate-functionalized type ligands for Os(II).^[37] Inspired by their results, we decided to perform studies of the analogous Pt(II) complexes. Initially, we tried to obtain the corresponding species with trifluoromethyl-moieties at the 1*H*-pyrazoles but did not succeed in isolating the desired coordination compound, due to its poor solubility precluding a proper purification and characterization. In this regard, *Liao et al.* were able to attain enhanced solubilities by introducing spiro-arranged moieties to reduce intermolecular π - π stacking.^[42] However, we were interested to investigate in detail the amino-bridged type of luminophores, as well as the corresponding Pt(II) complexes, their solubilities in common organic solvents and aggregation properties (see **Fig. 1**).





Figure 1: Structural formulae of selected N^N°N^N-type ligand precursors published by *Chang et al.*,^[37] *Liao et al.*^[42] and of the structures L1 – L3 presented in this work.

Results and discussion

Synthesis and characterization

To keep the tertiary amine bridge while increasing the solubility, we decided to decorate the bridging *N*-atom with a hexyl-phenyl substituent. Moreover, we tried different moieties at the 1*H*-pyrazole to verify if any of them would lead to a reasonably soluble complex. Thus, adamantyl-, 3,5-dimethoxyphenyl- and 4-hexylphenyl-moieties, were introduced.

The synthesis was carried out by variation of the route previously reported by *Chang et al.* for N^N°N^N-type ligands.^[37] Hence, the acetyl-group of 2-acetyl-6-bromopyridin was protected as dioxolane by reaction with ethylene glycol, followed by a Buchwald-Hartwig-amination of 4-hexylaniline with 2-bromo-6-(2-methyl-1,3-dioxolan-2-yl)pyridine (1) to form the precursor *N*-(4-hexylphenyl)-*N*,*N*-*bis*-(6-(2-methyl-1,3-dioxolan-2-yl)pydid-2-yl)amine (2), which was deprotected with HCl to obtain *N*,*N*-*bis*(acetylpyrid-6-yl)-*N*-(4-hexylphenyl)amine (3). In a one-pot synthesis reported by *Heller et al.*,^[43] **3** was at first allowed to react with lithium *bis*(trimethylsilyl)amide (LiHMDS) to form the corresponding Li-enolate, which was then converted into the keto-species with the desired acid chloride, followed by addition of hydrazine to facilitate the ring closure and resulting in the formation of the desired *bis*(pyridyl-pyrazolate)-based ligand precursors L1 - L3 (Fig. 2). L1 - L3 were combined with Pt(dmso)₂Cl₂ in 2-methoxyethanol to give the corresponding platinum(II) complexes **Pt1 – Pt3**, which displayed limited solubility in common organic solvents (such as DCM, toluene, MeOH, THF, DMF) in correspondence with previous reports by *Chang et al.* and *Liao et al.*^[137,42]



Figure 2: Synthetic route to platinum complexes Pt1 – Pt3.

We were not successful in purifying and characterizing the complex Pt3, as we could not find a proper solvent mixture able to cope with its low solubility. In contrast, suitable purification processes were elaborated for Pt1 and Pt2, and both were characterized. Pt2 shows an overall lower solubility in common organic solvents than Pt1, and a ¹H-NMR-spectrum of Pt2 was acquired in DMSO-d₆ at 90 °C, facilitated by its enhanced solubility at higher temperatures. Thus, the complex was dissolved in DMSO- d_6 at 90 °C and quickly pressed through a syringe filter to obtain a clear solution with the highest possible concentration. This led to a useable ¹H-NMR spectrum, even though the resolution of the peaks is decreased because of the higher temperature. However, it was sufficient to proof the formation of the complex in combination with exact mass spectrometry (EM-MS). A ¹³C-NMR spectrum of Pt2 was also measured but was not suitable for unambiguous assignment, due to the weak signal intensities caused by its low solubility. Apparently, similar properties were observed before, due to the fact that not every complex reported by Liao et al. was characterized by ¹³C-NMR.^[42] In contrast to Pt2, Pt1 has a somewhat higher solubility. Beside EM-MS, a ¹H-NMR spectrum of Pt1 was recorded in methylene chloride- d_2 and chloroform-d at room temperature, respectively, but again no ¹³C-NMR spectrum suitable for assignment was achievable. Single crystal X-ray diffraction could not be obtained for any of the complexes: The low solubility of Pt2 precluded its successful

crystallization, whereas the three hexyl chains of **Pt1**, on the other hand, seem to prevent the formation of crystalline solids for diffractometric analysis.

Photophysical properties and frontier orbitals

Selected photophysical data are summarized in Table 1. Absorption spectra were measured in diluted dichloromethane solutions at room temperature and are shown in Fig. 3 along with the calculated spectra obtained via time dependent density functional theory (TD-DFT). The alkyl chains of the complexes were replaced by hydrogen atoms in order to reduce the computational cost, since they were shown to have a negligible effect on the spectral properties. The computed absorption and emission spectra are found in the electronic supporting information (ESI, Fig. S34 and S35). Also, isosurface plots of the molecular orbitals that are relevant for the description of the excited states can be found in the ESI (Fig. S36). The S_1 states for Pt1 and Pt2 can be mainly described as a monoelectronic HOMO \rightarrow LUMO excitation, while the states at higher energy (S_n) are composed of (multiple) HOMO- $n \rightarrow$ LUMO+m excitations (vide infra). The orbital isosurfaces of Pt1 and Pt2 for the optimized geometry in the electronic ground state show that the LUMOs are largely localized at the pyridine units, whereas the HOMOs are mainly related to the 1H-pyrazoles with a sizeable contribution of the metal centre. Therefore, the lowest excited singlet states of Pt1 and Pt2 can mostly be described as monoelectronic excitations with a metal-perturbed intra-ligand charge-transfer (¹MP-ILCT) character (vide infra). For Pt1 also the peripheral phenyl-moieties participate on the HOMO, HOMO-1, and HOMO-5.

	λ _{abs} [nm]	$\lambda_{ ext{exc}}$ [nm]	λ _{exc^{77K} [nm]}	$\lambda_{\scriptscriptstyle em}$ [nm]	λ _{em} ^{77κ} [nm]	τ ^{Air} [μs]	τ ^{Αr} [μs]	τ ^{77κ} [μs]	${\cal P}_{\sf L}^{\sf Air}$	${\cal P}_{\sf L}{}^{\sf Ar}$	$\Phi_{L^{77K}}$	k _r [10⁴ s⁻¹]	k _{nr} [10 ⁴ s ⁻¹]
Pt1	278, 351	363	347	506, 537	494, 520	2.08 ± 0.03 (1 %), 0.66 ± 0.01 (6 %), 0.155 ± 0.001 (93 %) [0.20 ± 0.03]	9.64 ± 0.06 (42 %), 3.50 ± 0.07 (58 %) [6.1 ± 0.3]	97.3 ± 0.9 (19%), 40.3 ± 0.4 (81%) [51 ± 1]	< 0.02	0.17 ± 0.02	0.92 ± 0.04	Ar: 2.8 ± 0.4 77K: 1.8 ± 0.1	Ar: 13.6 ± 0.6 77K: 0.16 ± 0.08
Pt2	246 278, 342	350	339	497, 515	488, 516	0.506 ± 0.001 (52 %), 0.398 ± 0.002 (48 %) [0.454 ± 0.002]	20.2 ± 0.2 (69 %), 7.5 ± 0.5 (31 %) [16.2 ± 0.6]	131 ± 1 (40 %), 49 ± 1 (60 %) [81 ± 2]	< 0.02	0.25 ± 0.02	0.91 ± 0.04	Ar: 1.5 ± 0.2 77K: 1.12 ± 0.08	Ar: 4.6 ± 0.3 77K: 0.11 ± 0.05

Table. 1: Selected photophysical data for Pt(II)-complexes Pt1 and Pt2.

Excitation and emission spectra were measured for $c = 10^{-5}$ M solutions in dichloromethane at room temperature. Air: measured in airequilibrated $c = 10^{-5}$ M solutions in dichloromethane. Ar: measured in deaerated $c = 10^{-5}$ M solutions in dichloromethane by bubbling the sample with argon. 77K: measured in frozen glassy matrices of dichloromethane/methanol (V:V = 1:1, $c = 10^{-5}$ M) at 77 K. Lifetimes were obtained from the bluest emission maximum, the fitted components are reported with the corresponding relative amplitudes in parentheses. Amplitude-weighted average lifetimes are given in square brackets; average rate constants (k_r and k_{nr}) based on photoluminescence quantum yields and amplitude-weighted average lifetimes.

The experimental absorption spectrum of **Pt1** shows two sets of bands peaking at 278 nm ($\varepsilon = 56510 \text{ M}^{-1} \text{ cm}^{-1}$) and 351 nm ($\varepsilon = 32878 \text{ M}^{-1} \text{ cm}^{-1}$). Additionally, shoulders at 238 nm and 363 nm, respectively, and a weak absorption tail at $\lambda > 380$ nm are observed. According to DFT calculations, the band centred at 278 nm can be ascribed to a S₀ \rightarrow S₁₇ transition, where S₁₇ corresponds predominantly to a HOMO-3 \rightarrow LUMO+2 electronic configuration.



Figure 3: Normalized TD-DFT-calculated absorption spectra for a solution in dichloromethane (black lines) and experimental spectra (red lines; validity range: c = 10⁻⁶ M in dichloromethane, see supporting information **Fig. S33** for more details) for **Pt1** and **Pt2**.

The absorption band of **Pt1** peaking at 351 nm is primarily assigned to two main contributions: a $S_0 \rightarrow S_5$ and a $S_0 \rightarrow S_6$ transition, where the S_5 state mainly has an excited HOMO-2 \rightarrow LUMO configuration and the S₆ state mainly corresponds to a HOMO-2 \rightarrow LUMO+1 monoelectronic excitation. The HOMO-1, HOMO-2, and HOMO-3 of Pt1 exhibit contributions of the metal centre, whereas the LUMO+1 and the LUMO+2 do not show noticeable contributions of the platinum atom. The shoulder at 363 nm corresponds to a $S_0 \rightarrow S_3$ transition and consists predominantly of HOMO \rightarrow LUMO+1 and HOMO- $1 \rightarrow$ LUMO excitations. The absorption tail at 380 nm mainly arises from a S₀ \rightarrow S₁ transition. Therefore, the excited singlet states of Pt1 can be described as monoelectronic excitations with ¹MP-ILCT character. Pt2 shows three absorption bands peaking at 246 ($\epsilon = 12844 \text{ M}^{-1}\text{cm}^{-1}$), 278 ($\epsilon = 12411 \text{ M}^{-1}$ 1 cm⁻¹), and 342 nm (ϵ = 11301 M⁻¹ cm⁻¹), respectively. An additional intense shoulder is located at 367 nm. By DFT calculations, the absorption band peaking at 246 nm can be ascribed to a $S_0 \rightarrow S_{34}$ transition, where the excited state corresponds to a HOMO \rightarrow LUMO+5 configuration. The absorption band peaking at 278 is ascribed to a $S_0 \rightarrow S_{16}$ transition where the excited state corresponds to a HOMO-3 \rightarrow LUMO+2 configuration. The absorption band peaking at 342 nm can be primarily attributed to multiple contributions: $S_0 \rightarrow S_3$, $S_0 \rightarrow S_4$, $S_0 \rightarrow S_5$, and $S_0 \rightarrow S_6$ transitions, where the excited singlet states S₃ − S₆ have mainly HOMO→LUMO+1 (S₃), HOMO-2→LUMO (S₄), HOMO-2→LUMO+1

(S₅), and HOMO-1 \rightarrow LUMO+1 (S₆) monoelectronic excitation character. The shoulder at 367 nm represents the S₀ \rightarrow S₇ transition which can be described as a mixture of HOMO-1 \rightarrow LUMO and HOMO \rightarrow LUMO+1 excitations. Since the orbital pictures show a noticeable participation of the platinum centre in the HOMO, HOMO-2 and HOMO-3 as well as a small contribution in the LUMO+1, the excited singlet states of **Pt2** can also be mostly described as monoelectronic excitations with ¹MP-ILCT character.



Figure 4: a) Normalized excitation spectra (dashed lines, $\lambda_{Em} = 500 \text{ nm}$) and emission spectra (solid lines, $\lambda_{Exc} = 350 \text{ nm}$) at room temperature in deaerated dichloromethane (c = 10⁻⁵ M); b) normalized excitation spectra (dashed lines, $\lambda_{Em} = 520 \text{ nm}$ for **Pt1** and $\lambda_{Em} = 500 \text{ nm}$ for **Pt2**) and emission spectra (solid lines, $\lambda_{Exc} = 350 \text{ nm}$) in glassy matrices of DCM/MeOH (V:V = 1:1, c = 10⁻⁵ M) at 77 K.

Photoluminescence spectra were recorded in dilute fluid solutions ($c = 10^{-5}$ M) of deaerated dichloromethane at room temperature and in frozen glassy matrices corresponding to a 1:1 (V:V) mixture of dichloromethane/methanol at 77 K and are shown in Fig. 4 along with the corresponding excitation spectra. The emission spectrum of Pt1 in fluid dichloromethane at room temperature shows a clear vibrational progression peaking at 506 nm and 537 nm. Pt2 shows a less pronounced vibrational progression peaking at 497 nm and 515 nm. Both emission spectra show an emission shoulder at ca. 475 nm - 480 nm, which is more pronounced in the case of Pt2. The excited state lifetimes of both complexes in solution are longer in the absence of oxygen (see Table 1). Together with the increased quantum yields of 0.17 and 0.25 for deaerated solutions, respectively, if compared to $\Phi_L < 0.02$ (*i.e.* below the detection limit for both complexes) in the presence of oxygen, the triplet state nature of the emissive states can be confirmed. The ligand centred nature of these states is indicated by the absence of significant blue-shifts and the pronounced vibrational progressions in the emission spectra at 77 K, if compared to those at room temperature. DFT-calculated isosurface plots of the HOMO and the LUMO at the optimized T₁ geometry are shown in **Fig. 5.** According to our TD-DFT calculations the T_1 states of both complexes can be mainly described as HOMO \rightarrow LUMO excitations accounting for 70% (Pt1) and 76% (Pt2) of all single electron contributions, respectively. As the MOs depicted in Fig. 5 clearly illustrate, the excited triplet states T_1 of Pt1 and Pt2 can be

described as having ³MP-ILCT character. A more detailed numerical analysis of the contributions of the different subsystems performed using the TheoDORE software^[52] confirms that **Pt1** has a somewhat more pronounced *ligand-to-ligand charge-transfer* (LLCT) character and reduced *metal-to-ligand charge-transfer* (MLCT) contributions (**Fig. 6**). The partitioning of the complexes used for this analysis is shown in **Fig. 7**.



Figure 5: Selected molecular orbital isosurface plots with an isovalue of 0.03 at the optimized T_1 geometry in dichloromethane. Shown are the MOs involved in the most significant monoelectronic excitations contributing to the description of the emissive T_1 state (percentages of the contributions are given for each complex).



Figure 6: Numerical analysis of subsystem contributions to the T_1 excited state for **Pt1** (black) and **Pt2** (red) using TheoDORE.^[52]



Figure 7: Partitioning of **Pt1** (left) and **Pt2** (right) into subsystems for the numerical analysis shown in **Fig. 6**.

In glassy matrices at 77 K, the emission spectrum of **Pt2** appears with a clearly structured vibrational progression and is blue-shifted if compared with measurements at room temperature, which can be attributed to a reduced charge-transfer character in frozen matrices. The emission spectrum of **Pt1** at 77 K also shows a significant blue-shift with respect to room temperature, if referring to the bluest local emission maximum at 494 nm. Nonetheless, the emission spectrum at 77 K of **Pt1** has a less defined vibrational progression than **Pt2**, probably due to the phenyl moieties at the pyrazoles: In fact, since the phenyl rings have a significant contribution to the HOMO, HOMO-1, and HOMO-5 and can adopt different conformations around the connecting σ-bonds, various degrees of conjugation are available for **Pt1** at 77 K that globally lead to a featureless vibrational progression and a red-shift for **Pt1**. The observed red shift of **Pt1** in comparison to **Pt2** can also be seen in the calculated vibrationally resolved emission spectra using the PBE0 functional (**Fig. 8**, right). However, this shift is absent when

the long-range corrected CAM-B3LYP functional is employed (**Fig. 8**, left), hinting at the fact that it is overestimated by PBEO due to the increased charge-transfer character of the T_1 state in **Pt1**. Interestingly, no trace of excimeric emission pointing towards Pt-Pt interactions were detectable, despite their low solubility.



Figure 8: Normalized calculated vibrationally resolved emission spectra of **Pt1** and **Pt2** in dichloromethane at 300 K obtained with the PBE0 and CAM-B3LYP functionals, respectively, together with the corresponding experimental spectra.

Conclusions

In agreement with previously reported azole-functionalized structures, the investigated complexes Pt1 – Pt3 show rather low solubilities. However, two out of three new platinum(II) complexes (Pt1 and Pt2) were successfully characterized by EM-MS and ¹H-NMR and their photophysical properties were investigated, while a purification and characterization of Pt3 has not been achieved so far. DFT calculations along with experimental absorption spectra indicate a ligand-centred nature of the transitions for both complexes, which is confirmed by the absence of significant hypsochromic shifts when going from room temperature to frozen matrices as well as by observed enhanced structural vibrational progression in the excitation- and emission-spectra monitored at 77 K. Furthermore, DFTinvestigations show that the excited S₁ and T₁ states can be mainly described as monoelectronic HOMO \rightarrow LUMO excitations with ¹MP-ILCT and ³MP-ILCT character, respectively, where the chargetransfer character arises from the diazole-related HOMOs with contribution from the metal and the pyridine-based LUMOs. The platinum(II) complexes Pt1 and Pt2 show green luminescence at 506 nm and 497 nm and quantum yields at room temperature rising from 17 % to 25 % upon replacement of phenyl moieties by adamantly groups. Despite their rather low solubilities, no excimeric emission pointing towards intermetallic interactions were detected, which can be attributed to the bulk of the peripheral substituents.

Acknowledgments

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Experimental

Experimental procedures

Commercially available reagents were used without further purification. Silica gel 60 (0.063 – 0.200 mm) for column chromatography from Merck (mentioned as *silica*) and aluminium oxide 90 standardized for column chromatography adsorption analysis acc. to Brockmann from Merck (mentioned as *alox*) were used for column chromatography if not otherwise stated.

MS-ESI-EM were determined at the *Organisch-Chemisches Institut - WWU Münster*, using a LTQ Orbitap LTQ XL (Thermo-Fisher Scientific, Bremen) with nanospray-injection. Relative intensities are given for single isotopic patterns each.

NMR-spectra were obtained from the *Organisch-Chemisches Institut – WWU Münster*, using with an Agilent DD2 500/ Agilent DD2 600 or a Bruker Avance II 300/ Bruker Avance II 400. All measurements were obtained at room temperature if not otherwise mentioned.

Absorption spectra were measured on a Varian Cary 5000 double-beam UV-Vis-NIR spectrometer and baseline-corrected. Steady-state excitation and emission spectra were recorded on a FluoTime300 spectrometer from PicoQuant equipped with a 300 W ozone-free Xe lamp (250-900 nm), a 10 W Xe flash-lamp (250-900 nm, pulse width < 10 μ s) with repetition rates of 0.1 – 300 Hz, an excitation monochromator (Czerny-Turner 2.7 nm/mm dispersion, 1200 grooves/mm, blazed at 300 nm), diode lasers (pulse width < 80 ps) operated by a computer-controlled laser driver PDL-820 (repetition rate up to 80 MHz, burst mode for slow and weak decays), two emission monochromators (Czerny-Turner, selectable gratings blazed at 500 nm with 2.7 nm/mm dispersion and 1200 grooves/mm, or blazed at 1250 nm with 5.4 nm/mm dispersion and 600 grooves/mm), Glan-Thompson polarizers for excitation (Xe-lamps) and emission, a Peltier-thermostatized sample holder from Quantum Northwest (-40 °C – 105 °C), and two detectors, namely a PMA Hybrid 40 (transit time spread FWHM < 120 ps, 300 – 720 nm) and a R5509-42 NIR-photomultiplier tube (transit time spread FWHM 1.5 ns, 300-1400 nm)

with external cooling (-80 °C) from Hamamatsu. Steady-state and fluorescence lifetimes were recorded in TCSPC mode by a PicoHarp 300 (minimum base resolution 4 ps). Emission and excitation spectra were corrected for source intensity (lamp and grating) by standard correction curves. 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) and visual inspection of the weighted residuals and their autocorrelation. Luminescence quantum yields were measured with a Hamamatsu Photonics absolute PL quantum yield measurement system (C9920-02) equipped with a L9799-01 CW Xenon light source (150 W), monochromator, C7473 photonic multi-channel analyzer, integrating sphere (± 0.02 for Φ_L is estimated) and employing U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan). All solvents used were of spectrometric grade.

DFT calculations

All density functional theory (DFT) calculations of gas phase complexes were carried out using the quantum chemistry package Gaussian 09 Rev. D.01^[44] employing the hybrid functional PBE0^[45] and the SDD basis set, which applies an effective core potential for the Pt atoms^[46] and the D95 basis set for H, C, N and O atoms^[47].

Absorption spectra of the gas phase monomers were obtained from time-dependent density functional linear response theory (TDDFT) calculations of the 40 lowest excited singlet states. A Lorentzian broadening with a half width at half maximum (HWHM) of 10 nm was used for each transition.

Vibrational Franck-Condon spectra were calculated according the method of *Barone et al.*^[48,49] with Kohn-Sham DFT-based geometry optimizations in the S₀ and T₁ states followed by frequency analysis calculations. The energies were corrected by zero-point vibrational energies and thermal free energy contributions. In order to calculate the overlap integrals for the vibronic spectra, the transitions are divided into classes C_n where n is the number of the excited normal modes in the final electronic state. The maximum number of quanta per mode was set to 100, the maximum number of quanta for combinations of two modes to 65. The number of integrals calculated was limited to 1.5×108 . A maximum of 20 classes were computed. The line spectrum was broadened by Gaussian functions with a half-width at half-maximum of 135 cm⁻¹. The solvent dichloromethane (DCM) was taken into account by the polarizable continuum model (PCM) in an integral equation formalism framework^[50] with atomic radii from the universal force field model (UFF)^[51]. The character of the emissive T₁ state in terms of single orbital excitations was determined by TDDFT calculations at the T₁ geometry optimized with unrestricted Kohn-Sham DFT. A subsequent numerical analysis of the contributions of different subsystems to the T₁ excitation was performed using the TheoDORE software.^[52] As a first step this

requires partitioning the molecule into different fragments (see Fig. 7 for our choice). The numbers given in Fig. 6 are charge transfer numbers obtained by integrating the square modulus of the oneelectron density matrix over two different fragments using a population analysis scheme.

Preparation of 1

The reaction procedure reported by *Hatanaka et al.*^[53] was varied, using 2-acetyl-6-bromopyridine (8.00 g, 40.0 mmol, 1 eq), ethylene glycol (3.36 mL, 60.0 mmol, 1.5 eq) and *p*-TsOH·H₂O (0.38 g, 2.00 mmol, 0.05 eq) in benzene (50 mL). The crude product was purified *via* column chromatography on silica, eluting with a mixture of n-hexane/ethyl acetate (2:1, V:V) to obtain the desired product as a colourless oil, which was recrystallized from n-hexane/ethyl acetate to obtain a white solid (8.59 g, 35.2 mmol, 88 %).

MS-ESI-EM (MeOH/CHCl₃, $M = C_9H_{10}N_1O_2Br_1$):

m/z (%) calcd.: [M+H]⁺ = 243.9968 (100), 244.9999 (10), 245.9948 (98), 246.9979 (10); [M+Na]⁺ = 265.9787 (100), 266.9819 (10), 267.9767 (98), 268.9799 (10); [2M+H]⁺ = 486.9863 (51), 487.9894 (10), 488.9843 (100), 489.9874 (20), 490.9826 (51); [2M+Na]⁺ = 508.9682 (51), 509.9714 (10), 510.9663 (100), 511.9694 (20), 512.9645 (51), 513.9675 (10), 514.9700 (1).

m/z (%) found: [M+H]⁺ = 243.9967 (100), 245.0002 (9), 245.9946 (99), 246.9979 (9); [M+Na]⁺ = 265.9786 (100), 266.9820 (10), 267.9765 (99), 268.9798 (10); [2M+H]⁺ = 486.9859 (42), 487.9920 (1), 488.9842 (100), 489.9633 (4), 490.9813 (24); [2M+Na]⁺ = 508.9682 (49), 509.9717 (10), 510.9660 (100), 511.9692 (19), 512.9638 (49), 513.9672 (9), 514.9692 (1).

¹**H-NMR** (400 MHz, methylene chloride- d_2): δ (ppm) = 7.56 (td, J = 7.6, 3.5 Hz, 1H), 7.50 (dd, J = 7.3, 2.7 Hz, 1H), 7.41 (dd, J = 7.6, 2.5 Hz, 1H), 4.27 – 3.61 (m, 4H), 1.66 (d, J = 3.5 Hz, 3H).

¹³**C-NMR** (101 MHz, methylene chloride-*d*₂): δ (ppm) = 163.01, 142.17, 139.52, 127.87, 118.93, 108.43, 65.65, 25.31.

Preparation of 2

Under argon atmosphere, **1** (7.32 g, 30.0 mmol, 2 eq), 4-hexylaniline (2.66 g, 15.0 mmol, 1 eq), 1,1'-ferrocenediyl-*bis*(diphenylphosphine) (dppf, 1.39 g, 2.50 mmol, 0.08 eq), $Pd_2(dba)_3$ (0.92 g, 1.00 mmol, 0.03 eq) and NaO^tBu (3.75 g, 39.0 mmol, 2.5 eq) were dissolved in toluene (50 mL) and refluxed at 100 °C for 25 h. After reaching room temperature, the reaction mixture was neutralized with 1 N HCl (aq.) and extracted with dichloromethane (3x30 mL). The combined organic phases were dried over Na_2SO_4 and the solvents removed under reduced pressure. After purification *via* column

chromatography on silica, eluting with a mixture of n-hexane/ethyl acetate (2:1, V:V) the product was obtained as an orange oil (4.31 g, 8.55 mmol, 57 %).

MS-ESI-EM (MeOH, $M = C_{30}H_{37}N_3O_4$):

m/z (%) calcd.: $[M+H]^+ = 504.2857$ (100), 505.2889 (34), 506.2918 (6); $[M+Li]^+ = 509.2930$ (8), 510.2939 (100), 511.2971 (34), 512.3000 (6); $[M+Na]^+ = 526.2676$ (100), 527.2708 (34), 528.2737 (6); $[2M+Na]^+ = 1029.5460$ (100), 1030.5492 (68), 1031.5523 (25), 1032.5552 (6).

m/z (%) found: [M+H]⁺ = 504.2856 (100), 505.2890 (32), 506.2923 (5); [M+Li]⁺ = 509.2929 (8), 510.2937 (100), 511.2972 (32), 512.3005 (6); [M+Na]⁺ = 526.2672 (100), 527.2706 (33), 528.2739 (6); [2M+Na]⁺ = 1029.5465 (100), 1030.5498 (70), 1031.5532 (24), 1032.5563 (6).

¹**H-NMR** (300 MHz, methylene chloride- d_2): δ (ppm) = 7.53 (td, 7.9, 0.8 Hz, 2H), 7.19 (dt, J = 8.5, 2.1 Hz, 2H), 7.13 (dd, J = 7.5, 0.8 Hz, 2H), 7.07 (dt, J = 8.4, 2.4 Hz, 2H), 6.93 (dd, J = 8.3, 0.8 Hz, 2H), 4.04 – 3.81 (m, 8H), 2.63 (t, 2H), 1.70 – 1.58 (m, 2H), 1.54 (s, 6H), 1.42 – 1.27 (m, 6H), 0.96 – 0.82 (m, 3H).

¹³C-NMR (75 MHz, methylene chloride-*d*₂): δ (ppm) = 159.80, 157.92, 142.89, 141.01, 137.96, 129.76, 127.95, 116.17, 113.61, 108.97, 65.56, 36.00, 32.30, 32.02, 29.55, 24.95, 23.20, 14.43.

Preparation of 3

2 (4.28 g, 8.50 mmol, 1 eq) was heated to 80 °C for 12 h in 1 M HCl (aq., 25 mL). After reaching room temperature, the mixture was neutralized with aqueous 1 M NaHCO₃ and extracted with dichloromethane (3x30 mL). The combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. After purification *via* column chromatography on silica, eluting with a mixture of n-hexane/ethyl acetate (2:1, V:V) the product was obtained as a pale-brownish solid (2.75 g, 6.63 mmol, 78 %).

MS-ESI-EM (MeOH, $M = C_{26}H_{29}N_3O_2$):

m/z (%) calcd.: [M+H]⁺ = 416.2333 (100), 417.2364 (30), 418.2394 (5); [M+Na]⁺ = 438.2152 (100), 439.2184 (30 %), 440.2213 (5).

m/z (%) found: [M+H]⁺ = 416.2328 (100), 417.2364 (27), 418.2400 (4); [M+Na]⁺ = 438.2146 (100), 439.2181 (27), 440.2216 (4).

¹**H-NMR** (400 MHz, methylene chloride- d_2): δ (ppm) = 7.71 (td, J = 7.9, 7.8, 0.8 Hz, 2H), 7.62 (dd, J = 7.4, 0.9 Hz, 2H), 7.32 (dd, J = 8.3, 0.9 Hz, 2H), 7.28 (dt, J = 8.4, 2.1 Hz, 2H), 7.18 (dt, J = 8.4, 2.5,

1.9 Hz, 2H), 2.67 (t, J = 7.4 Hz, 2H), 2.37 (s, 6H), 1.75 – 1.56 (m, 2H), 1.48 – 1.20 (m, 6H), 0.96 – 0.81 (m, 3H).

¹³**C-NMR** (101 MHz, methylene chloride-*d*₂): δ (ppm) = 200.29, 157.19, 152.27, 142.22, 141.92, 138.45, 130.25, 128.76, 120.17, 115.79, 54.00, 36.02, 32.29, 31.98, 29.40, 25.87, 23.20, 14.43, 1.34.

Preparation of L1

Under argon atmosphere, **3** (1.00 g, 2.41 mmol, 1 eq) was dissolved in dry toluene (20 mL), at 0 °C LiHMDS (5.06 mL, 1.0 M solution in THF, 5.06 mmol, 2.1 eq) was added and the solution stirred for 15 min at 0 °C. At 0 °C, 4-hexylbenzoyl chloride (1.14 g, 5.06 mmol, 2.1 eq) was added and the reaction mixture was stirred for 2 h to reach room temperature. Acetic acid (glacial, 100 %) was added first, until pH = 4 - 5 was reached, followed by addition of ethanol (20 mL) to form a suspension. Afterwards hydrazine-monohydrate (4.72 mL, 96.3 mmol, 40 eq) was added and the mixture was heated to 110 °C for 1 h. After reaching room temperature, water (40 mL) was added and the mixture was extracted with dichloromethane (3x30 mL). The combined organic phases were dried over Na₂SO₄ and the solvents were removed under reduced pressure. The crude product was purified *via* column chromatography on *silica*, eluting with a mixture of cyclohexane/ethyl acetate (2:1, V:V) to obtain the desired product as a white solid (0.32 g, 0.41 mmol, 17 %).

MS-ESI-MS (MeOH/CHCl₃, $M = C_{52}H_{61}N_7$):

m/z (%) calcd.: [M+H]⁺ = 784.5061 (100), 785.5092 (60), 786.5124 (17), 787.5155 (3); [M+Na]⁺ = 806.4881 (100), 807.4912 (60), 808.4943 (17), 809.4974 (3); [2M+Na]⁺ = 1589.9869 (84), 1590.9900 (100), 1591.9931 (59), 1592.9963 (23), 1593.9994 (7), 1595.0025 (2).

m/z (%) found: [M+H]⁺ = 784.5068 (100), 785.5100 (57), 786.5134 (16), 787.5167 (3); [M+Na]⁺ = 806.4886 (100), 807.4918 (59), 808.4952 (17), 809.4985 (2); [2M+Na]⁺ = 1589.9884 (84), 1590.9917 (100), 1591.9954 (57), 1592.9987 (22), 1594.0012 (7), 1595.0293 (1).

¹**H-NMR** (400 MHz, methylene chloride- d_2): δ (ppm) = 10.86 (s, 2H), 7.71 (d, J = 7.7 Hz, 4H), 7.62 (t, J = 7.9 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.27 - 7.19 (m, 8H), 6.99 (d, J = 8.3 Hz, 2H), 6.95 (s, 2H), 2.69 - 2.61 (m, 6H), 1.81 - 1.51 (m, 6H), 1.49 - 1.24 (m, 18H), 0.99 - 0.83 (m, 9H).

¹**H-NMR** (500 MHz, chloroform-*d*): δ (ppm) = 7.72 (d, J = 7.9 Hz, 4H), 7.59 (t, J = 8.0 Hz, 2H), 7.29 (d, J = 7.5 Hz, 2H), 7.25 – 7.18 (m, 8H), 6.98 (d, J = 8.3 Hz, 2H), 6.92 (s, 2H), 2.67 (t, J = 7.7 Hz, 2H), 2.63 (t, J = 7.7 Hz, 4H), 1.78 – 1.52 (m, 6H), 1.40 – 1.21 (m, 18H), 0.96 – 0.83 (m, 9H).

¹³C-NMR (126 MHz, chloroform-*d*): δ (ppm) = 157.15, 142.97, 141.73, 141.54, 138.31, 129.84, 128.87, 128.38, 125.63, 115.46, 113.79, 99.78, 77.17, 35.89, 35.77, 31.88, 31.87, 31.53, 31.46, 29.33, 29.13, 22.77, 22.75, 14.25.

Preparation of L2

Following the same procedure as for **L1**, using **3** (0.50 g, 1.20 mmol, 1 eq), dry toluene (10 mL), LiHMDS (2.52 mL, 1.0 M solution in THF, 2.52 mmol, 2.1 eq), 1-adamantanecarbonyl chloride (0.50 g, 2.52 mmol, 2.1 eq), acetic acid (glacial, 100 %), ethanol (10 mL) and hydrazine-monohydrate (2.34 mL, 48 mmol, 40 eq). The crude product was purified *via* column chromatography on silica, eluting with a mixture of n-hexane/ethyl acetate/triethylamine (1:3:1, V:V:V) to obtain the desired product as a pale green solid (0.38 g, 0.51 mmol, 42 %).

MS-ESI-EM (MeOH/CHCl₃, $M = C_{48}H_{57}N_7$):

m/z (%) calcd.: [M+H]⁺ = 732.4748 (100), 733.4779 (55), 734.4810 (15), 735.4841 (3); [M+Na]⁺ = 754.4568 (100), 755.4599 (55), 756.46230 (15), 757.4660 (3); [2M+H]⁺ = 1463.9424 (91), 1464.9455 (100), 1465.9486 (55), 1466.9516 (20); [2M+Na]⁺ = 1485.9243 (91), 1486.9274 (100), 1487.9305 (55), 1488.9336 (20), 1489.9367 (5).

m/z (%) found: [M+H]⁺ = 732.4753 (100), 733.4785 (54), 734.4821 (13), 735.4855 (2); [M+Na]⁺ = 754.4573 (100), 755.4606 (53), 756.4641 (14), 757.4676 (2); [2M+H]⁺ = 1463.9449 (90), 1464.9477 (100), 1465.9513 (56), 1466.9541 (17); [2M+Na]⁺ = 1485.9263 (92), 1486.9291 (100), 1487.9330 (54), 1488.9363 (19), 1489.9390 (5).

¹**H-NMR** (300 MHz, methylene chloride-*d*₂): δ (ppm) = 7.58 (td, J = 7.8, 0.7 Hz, 2H), 7.31 (d, J = 7.3 Hz, 2H), 7.24 (dt, J = 8.4, 2.1 Hz, 2H), 7.17 (dt, J = 8.4, 2.1 Hz, 2H), 6.92 (dd, J = 8.3, 0.8 Hz, 2H), 6.47 (s, 2H), 2.66 (t, J = 8.1, 7.5 Hz, 2H), 2.04 (m, 6H), 1.94 (m, 12H), 1.85 – 1.71 (m, 12H), 1.66 (m, 2H), 1.43 – 1.28 (m, 6H), 0.94 – 0.84 (m, 3H).

¹³C-NMR (75 MHz, methylene chloride-*d*₂): δ (ppm) = 138.56, 130.05, 128.47, 115.58, 113.99, 99.19,
43.07, 37.26, 34.21, 32.31, 32.02, 29.68, 29.26, 23.20.

Preparation of L3

Following the same procedure as for **L1**, using **3** (1.73 g, 4.15 mmol, 1 eq), dry toluene (30 mL), LiHMDS (8.72 mL, 1.0 M solution in THF, 8.72 mmol, 2.1 eq), 3,5-dimethoxybenzoyl chloride (1.75 g, 8.72 mmol, 2.1 eq), acetic acid (glacial, 100 %), ethanol (20 mL) and hydrazine-monohydrate (8.13 mL, 166 mmol, 40.0 eq). The crude product was purified *via* column chromatography on *silica*, eluting with

a mixture of dichloromethane/acetone/cyclohexane (0:0:100 \rightarrow 4:3:7, V:V:V) to obtain the desired product as a white solid (0.34 g, 0.47 mmol, 11 %).

MS-ESI-EM (MeOH/CHCl₃, $M = C_{44}H_{45}N_7O_4$):

m/z (%) calcd.: [M+H]⁺ = 736.3606 (100), 737.3636 (51), 738.3666 (13), 739.3695 (2); [M+Na]⁺ = 758.3425 (100), 759.3456 (51), 760.3485 (13), 761.3514 (2); [2M+H]⁺ = 1471.7139 (98), 1472.7170 (100), 1473.7200 (52), 1474.7229 (18); [2M+Na]⁺ = 1493.6958 (98), 1494.6989 (100), 1495.7019 (52), 1496.7049 (18), 1497.7078 (5).

m/z (%) found: [M+H]⁺ = 736.3609 (100), 737.3642 (49), 738.3675 (12), 739.3707 (2); [M+Na]⁺ = 758.3431 (100), 759.3465 (48), 760.3496 (12), 761.3527 (2); [2M+H]⁺ = 1471.7165 (100), 1472.7196 (99), 1473.7227 (49), 1474.7259 (14); [2M+Na]⁺ = 1493.6986 (100), 1494.7017 (99), 1495.7049 (50), 1496.7075 (17), 1497.7109 (3).

¹**H-NMR** (300 MHz, methylene-chloride- d_2): δ (ppm) = 10.87 (s, 1H), 7.63 (t, J = 8.0 Hz, 2H), 7.32 (d, J = 7.5 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.02 – 6.94 (m, 8H), 6.43 (t, J = 2.3 Hz, 2H), 3.82 (s, 12H), 2.66 (t, J = 7.6 Hz, 2H), 1.67 (p, J = 7.4 Hz, 2H), 1.41 – 1.28 (m, 6H), 0.95 – 0.81 (m, 3H).

¹**H-NMR** (600 MHz, methylene chloride-*d*₂): δ (ppm) = 7.63 (t, J = 7.9 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 2.3 Hz, 4H), 6.97 (s, 2H), 6.44 (t, J = 2.3 Hz, 2H), 3.83 (s, 12H), 2.67 (t, J = 7.9 Hz, 2H), 1.72 – 1.63 (m, 2H), 1.42 – 1.32 (m, 6H), 1.04 – 0.75 (m, 3H).

¹³**C-NMR** (151 MHz, methylene chloride-*d*₂): δ (ppm) = 161.74, 157.83, 142.16, 142.14, 138.95, 130.24, 128.56, 116.28, 114.34, 104.05, 100.67, 100.48, 55.95, 36.12, 32.32, 31.95, 29.70, 27.50, 23.21, 14.45.

Preparation of platinum(II) complex Pt1

L1 (0.14 g, 0.18 mmol, 1 eq) and $Pt(dmso)_2Cl_2$ (0.08 g, 0.18 mmol, 1 eq) were dissolved in 2-methoxyethanol (5 mL) and stirred at 80 °C for 1 h. After reaching room temperature, water (5 mL) was added to give a yellow precipitate, which was filtered and washed with water (5 mL). The crude product was purified *via* column chromatography on neutral *alox*, eluting with chloroform to obtain the desired product as yellow solid (0.10 g, 0.10 mmol, 56 %).

MS-ESI-EM (MeOH/CHCl₃, $M = C_{52}H_{59}N_7Pt$):

m/z (%) calcd.: [M+H]⁺ = 974.4515 (1), 976.4532 (62), 977.4556 (100), 978.4570 (96), 979.4595 (41), 980.4601 (24), 981.4622 (10), 982.4650 (3); [M+Na]⁺ = 998.4351 (62), 999.4376 (100), 1000.4390 (96),

1001.4415 (41), 1002.4421 (24); [2M+H]⁺ = 1951.8994 (18), 1952.9016 (52), 1953.9034 (91), 1954.9054 (100), 1955.9071 (84), 1956.9089 (57), 1957.9104 (35), 1958.9123 (18), 1959.9142 (8), 1960.9160 (3); [2M+Na]⁺ = 1973.8813 (18), 1974.8835 (52), 1975.8854 (91), 1976.8873 (100), 1977.8891 (84), 1978.8908 (57), 1979.8924 (35), 1980.8943 (18).

m/z (%) found: [M+H]⁺ = 974.4570 (1) 976.4575 (62), 977.4599 (100), 978.4607 (94), 979.4639 (39), 980.4647 (22), 981.4670 (9), 982.4690 (2); [M+Na]⁺ = 998.4393 (69), 999.4423 (100), 1000.4439 (96), 1001.4456 (37), 1002.4444 (12); [2M+H]⁺ = 1951.9070 (16), 1952.9099 (49), 1953.9114 (85), 1954.9134 (100), 1955.9157 (81), 1956.9164 (54), 1957.9180 (35), 1958.9198 (19), 1959.9199 (11), 1960.9207 (6); [2M+Na]⁺ = 1973.8923 (25), 1974.8927 (54), 1975.8943 (90), 1976.8957 (100), 1977.8976 (76), 1978.8982 (54), 1979.9010 (29), 1980.9049 (9).

¹**H-NMR** (300 MHz, methylene chloride-*d*₂): δ (ppm) = 7.93 (d, J = 7.7 Hz, 2H), 7.88 (d, J = 8.1 Hz, 4H), 7.43 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 7.9 Hz, 4H), 7.20 (t, J = 8.1 Hz, 2H), 6.99 (d, J = 7.4 Hz, 2H), 6.61 (s, 2H), 5.74 (d, J = 8.7 Hz, 2H), 2.81 – 2.57 (m, 6H), 1.74 – 1.62 (m, 6H), 1.54 – 1.30 (m, 18H), 1.03 – 0.89 (m, 12H).

¹**H-NMR** (599 MHz, chloroform-*d*): δ (ppm) = 7.93 (s, 2H), 7.86 (d, J = 7.5 Hz, 4H), 7.37 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 7.6 Hz, 4H), 7.13 (t, J = 7.8 Hz, 2H), 6.95 (d, J = 7.0 Hz, 2H), 6.57 (s, 2H), 5.67 (d, J = 8.7 Hz, 2H), 2.71 – 2.62 (m, 6H), 1.76 – 1.61 (m, 6H), 1.45 – 1.34 (m, 18H), 0.99 – 0.95 (m, 3H), 0.95 – 0.92 (m, 6H).

¹³C-NMR (151 MHz, chloroform-*d*): δ (ppm) = 146.82, 144.76, 136.89, 131.26, 128.37, 125.48, 36.06, 31.98, 31.96, 31.72, 31.65, 29.49, 29.42, 22.85, 22.84, 14.30, 14.29, 1.16.

Preparation of platinum(II) complex Pt2

L2 (0.24 g, 0.33 mmol, 1 eq) and $Pt(dmso)_2Cl_2$ (0.14 g, 0.33 mmol, 1 eq) were dissolved in 2-methoxyethanol (10 mL) and stirred at 80 °C for 1 h. After reaching room temperature, water was added for precipitation. The precipitate was washed with ethanol and acetone to give the product as yellow solid (0.21 g, 0.22 mmol, 67 %).

MS-ESI-MS (MeOH/CHCl₃, $M = C_{48}H_{55}N_7Pt$):

m/z (%) calcd.: [M+H]⁺ = 922.4202 (2), 924.4219 (64), 925.4243 (100), 926.4256 (94), 927.4281 (38), 928.4286 (23), 929.4308 (9), 930.4336 (2); [2M+H]⁺ = 1847.8367 (19), 1848.8390 (55), 1849.8407 (93), 1850.8427 (100), 1851.8443 (82), 1852.8461 (54), 1853.8476 (33), 1854.8495 (17), 1855.8513 (7).

m/z (%) found: [M+H]⁺ = 922.4246 (2), 924.4258 (63 , 925.4280 (100), 926.4287 (94), 927.4316 (37), 928.4324 (22), 929.4348 (8), 930.4377 (2); [2M+H]⁺ = 1847.8437 (18), 1848.8459 (54), 1849.8576 (91), 1850.8501 (100), 1851.8514 (81), 1852.8540 (52), 1853.8552 (31), 1854.8570 (15), 1855.8599 (6).

¹**H-NMR** (600 MHz, dimethylsulfoxide-*d*₆, 90 °C): δ (ppm) = 8.27 (t, J = 8.4 Hz, 2H), 8.13 (s, 2H), 7.67 (d, J = 7.8 Hz, 2H), 7.60 (d, J = 7.8 Hz, 2H), 7.29 (s, 2H), 6.76 (s, 2H), 2.82 (t, J = 8.0 Hz, 2H), 2.23 (s, 12H), 2.14 (s, 6H), 1.89 – 1.80 (m, 12H), 1.80 – 1.70 (m, 2H), 1.48 – 1.42 (m, 2H), 1.41 – 1.33 (m, 4H), 0.95 – 0.89 (m, 3H).

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Dear Ladies and Gentlemen,

we kindly acknowledge the exhaustive and in-depth review report from our colleagues. We have addressed all their questions and issues and modified the manuscript accordingly (all changes have been highlighted in yellow). A revised version of the main manuscript and of the supporting information file has been uploaded accordingly, along with a response letter addressing all the questions and suggestions from the Referees.

We are strongly convinced that our manuscript has improved in quality and readability and are looking forward to seeing our paper published in this exciting special issue!

With kindest regards from Münster,

Prof. Cristian A. Strassert



