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Chiral-at-Metal Phosphorescent Square-Planar Pt(II)-Complexes from an Achiral Organometallic Ligand

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Supporting Information Placeholder

ABSTRACT: The synthesis and characterization of a new kind of *cis*- and *trans*-cyclometalated square-planar platinum(II) complexes is reported. Uncharged organometallic compounds carrying one or two of the C^N-donor ligand L^{CN} were prepared. Due to the heterobidentate coordination of the achiral chelate ligand, the formed [PtL^{CN}Cl(SEt₂)], *cis*- and *trans*-[PtL^{CN}₂] complexes are chiral with the metal serving as the stereo center. The enantiomers of complex *trans*-[PtL^{CN}₂] could be separated and their absolute configuration was determined by anomalous X-ray diffraction, in accordance with CD spectroscopic results and TD-DFT calculations. All compounds were fully characterized by NMR spectroscopy, mass spectrometry and X-ray structure determination. The photophysical properties of *trans*-[PtL^{CN}₂] have been investigated showing phosphorescence in solution and in the solid state with a moderate quantum yield. For the enantiomers, strong circular dichroism (CD) and circularly polarized luminescence (CPL) effects were observed, rendering this new structural motif suitable for application in chiroptical and luminescent materials.

Square-planar organometallic platinum complexes containing phenylpyridine ligands have been intensively studied during the last three decades due to their interesting photophysical properties.¹ Beginning with the first examples introduced by von Zelewsky, numerous derivatives of phenylpyridine Pt(II)-complexes have been synthesized in order to tune and improve their luminescence behavior (Scheme 1).² Such organometallic compounds are usually obtained by cyclometalation under CH-activation or by transmetalation from organolithium precursors.³

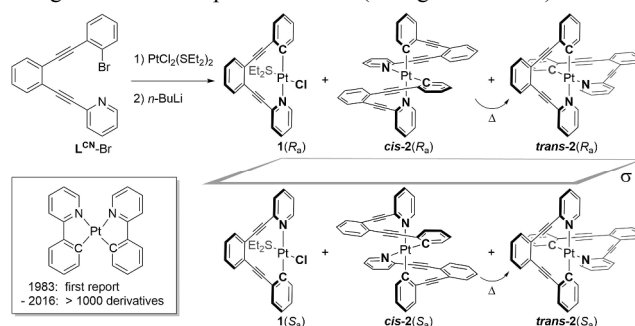
Among the various photophysical properties of such compounds that can be technologically exploited, circularly polarized luminescence (CPL) of chiral derivatives gained special interest in light of its potential use in optical probes and sensors,⁴ data storage⁵ and (3D)-OLED devices.⁶ Both, organic and inorganic compounds featuring CPL effects are therefore intensively studied.⁷ In octahedral complexes based on heterobidentate chelate ligands, chirality is often an intrinsic feature,⁸ and the separation and even enantioselective synthesis of stereoisomers gained a lot of interest, lately.⁹

In contrast to octahedral complexes, the chirality of square-planar complexes is often overlooked,¹⁰ and most of the known examples utilize chiral ligands to introduce chirality.^{7a,7c,11} There

are only a few reports of achiral ligands leading to chiral-at-metal square-planar complexes.¹²

Trans-spanning bispyridyl ligands have been reported for square-planar Cu(II), Pd(II) complexes as well as for linear Ag(I), Cu(I), Hg(II).¹³ Also heterobidentate *trans*-spanning ligands have been reported.¹⁴ To the best of our knowledge, only one chiral bidentate *trans*-chelated Pd(II) complex based on an enantiopure ligand has been published so far.¹⁵ Our approach combines the concepts of heterobidentate *trans*-spanning coordination by an achiral ligand with an organometallic C^N-donor environment to obtain the first example of a new type of chiral-at-metal cyclometalated complexes.¹⁶

The synthesis of the ligand consists of a series of Sonogashira cross-coupling reactions leading to the precursor 2-((2-bromophenyl)ethynyl)phenyl)ethynyl)pyridine L^{CN}-Br (Scheme 1). The reaction of the lithiated species with the Pt(II) source Pt(SEt₂)₂Cl₂ in THF delivered a racemic mixture of two chiral cyclometalated Pt(II) compounds in form of the monochelated [PtL^{CN}Cl(SEt₂)] complex **1** and the dichelated [PtL^{CN}₂] complex *trans*-**2** (Scheme 1).^{2a,17} The mixture of metal complexes **1** and *trans*-**2** was separated by flash column chromatography, followed by resolution into their enantiomers by chiral HPLC using a Daicel Chiralpak IC column (SI Figures S14-15).



Scheme 1. Synthesis of [PtL^{CN}Cl(SEt₂)] (**1**), *cis*- and *trans*-[PtL^{CN}₂] (*cis*-**2** and *trans*-**2**).

To further optimize the yield, the reaction conditions were varied. While the addition of diethylether increased the yield of *trans*-**2**, it also caused the formation of a significant amount of a side product, which could be isolated by a tedious washing protocol and turned out to be complex *cis*-[PtL^{CN}₂] (*cis*-**2**; Scheme 1).

As the kinetic product of the reaction, *cis-2* can be quantitatively transformed into the thermodynamic minimum *trans-2* by heating its chloroform solution at 40° C for 9h (SI Figure S1). In both copounds the carbon-bound ligands are in a *cis*-relationship and we assume this interconversion to occur via a de- and recomplexation of the pyridine arms. A DFT calculation further supported *trans-2* to be energetically favored over *cis-2* by about 28 kJ/mol (B3LYP-D3BJ/def2-SVP//def2-TZVP; PCM:THF). Furthermore, the observed transformation solved the problem of the difficult separation of *cis-2* and *trans-2* and allowed to increase the yield of *trans-2* from 16 to 25 %.

1, *cis-2* and *trans-2* were characterized by ¹H NMR spectroscopy and mass spectrometry (see the SI). In the ¹H NMR spectra, the protons in *ortho*-position to the nitrogen atom are assigned to a strongly downfield shifted signal compared to precursor **L**^{CN}-Br due to coordination to the Pt(II) center. The chemical shift difference observed for this proton, as compared between *cis-2* and *trans-2*, could be reproduced in sign and magnitude by a GIAO-NMR calculation (B3LYP-D3BJ/def2-TZVP; PCM:THF). On the other hand, the phenyl protons could be assigned to strongly highfield shifted signals, in agreement with the literature for similarly *cis*-coordinated complexes.¹⁸ Only in case of the *cis-2* complex, a ¹H-¹H NOESY NMR experiment showed a correlation between one proton of the pyridyl group and one proton of the phenyl group coordinated to the platinum (SI Figure S13) supporting the *cis*-coordination mode. In the high resolution electrospray ionization (ESI) mass spectrum, compound **1** and *cis-2* gave rise to a signal for the mono-cationic fragment [PtL^{CN}]⁺. Compound **1** further showed a peak for the species [PtL^{CN}(CH₃CN)(SEt₂)]⁺. In the field desorption (FD) mass spectrum, *trans-2* was observed as the one-electron-oxidized mono cationic species [PtL^{CN}₂]⁺.

Single crystals of **1**, racemic *cis-2* and *trans-2* as well as enantiopure *trans-2*(*S_a*) (chiral HPLC fraction 1) suitable for X-ray structure determination could be obtained by slow solvent evaporation from CHCl₃/hexane, CH₂Cl₂ and CH₂Cl₂/hexane mixtures, respectively.

[PtL^{CN}Cl(SEt₂)] **1** crystallized in the monoclinic space group *P2₁/n*. The asymmetric unit of **1** contains one enantiomer of the complex together with one CHCl₃ solvent molecule (Figure 1a). In structure **1**, the Pt atom is slightly disordered (~5%) around the equilibrium position between the C and N donor atoms, which seems to be connected to the disorder of the thioether. Unfortunately, this induces an unresolved C-N disorder for which the differences are too small to be unambiguously determined, but coupled to the Pt occupancy. Yet, a structure solution in *P2₁* yielded both enantiomers in the asymmetric unit, rendering the centrosymmetric solution valid. The Pt1-N1 (2.1392(15)Å) distance is slightly larger than the Pt1-C1 (1.9909(17)Å) bond which is in agreement with literature known phenylpyridine complexes.² The angle C1-Pt1-N1 (179.65(6)°) shows no significant distortion from the ideal 180° angle, where Cl1-Pt1-N1 (88.19(4)°) and Cl1-Pt1-C1 (91.46(5)°) are minimally distorted having the diethyl sulfide ligand slightly bent away from the pyridine with S1-Pt1-C11 = 85.77(5)° and S1-Pt1-N = 94.58(4)°.

A racemic mixture of *cis*-[PtL^{CN}₂] (*cis-2*) crystallized in the triclinic space group *P1̄* (Figure 1b). The ligand is strongly twisted compared to **1** and *trans-2*, and the observed correlation in the ¹H-¹H NOESY NMR experiment can be explained with the close H-H distance (2.553–2.903 Å) of the protons in *ortho*-position to the nitrogen and the carbon atoms binding to platinum. The angles N18_1-Pt1-C1 (177.4(1)°) and C2_1-Pt1-N18_2 (175.7(1)°) are significantly distorted compared to **1** indicating the tension on the ligand for this thermodynamically unfavored product.

A racemic mixture of [PtL^{CN}₂] *trans-2* crystallized in the monoclinic *P2₁/c* space group without any solvent molecules. Both enantiomers are present in the crystal structure (the *S_a* enantiomer of *trans-2* is shown in Figure 1c). The Pt1-N (2.1075(11)–2.1095(11) Å) and Pt1-C (1.9900(13)–1.9895(12) Å) bonds are of similar lengths to what was found in **1**. The angles N1-Pt1-C1 (178.92(4)°) and C22-Pt1-N2 (179.09(5)°) are close to the ideal square-planar coordination and show the perfect fit of the Pt(II) cation inside the chelating ligand environment. The packing diagram reveals that the distance for the closest Pt-Pt contact is 8.998(2) Å, much longer than for many other reported solid state structures of related square-planar systems due to the steric hindrance of the ligands that surround the Pt(II) center in *trans-2*.¹⁹ Therefore, close metal-metal interactions are not possible for this system, which would require much smaller distances between the Pt centers.²⁰

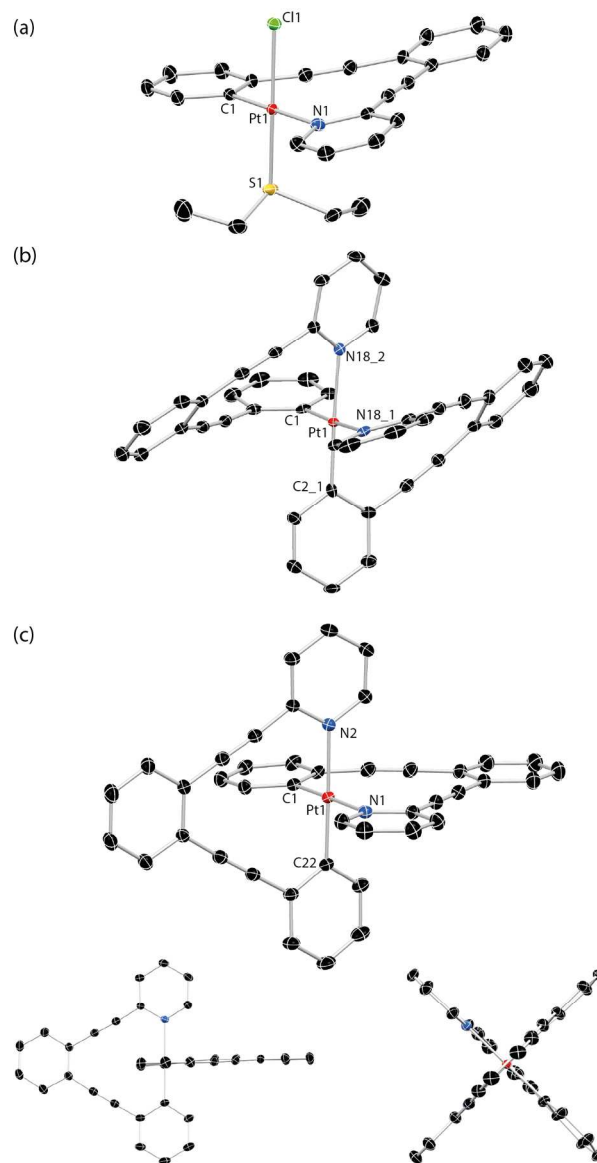


Figure 1. ORTEP drawings of (a) [PtL^{CN}Cl(SEt₂)] **1**, (b) *cis*-[PtL^{CN}₂] (*cis-2*) and (c) *trans*-[PtL^{CN}₂] (*trans-2*(*S_a*)). C: black, N: blue, Pt: red. H atoms and solvents are omitted for clarity.

The X-ray structure of enantiopure **trans-2**(S_a) (HPLC fraction 1) was solved in space group $P2_1$ with two identical enantiomers in the asymmetric unit. The absolute configuration of the molecules was confirmed using the enantiopure distinguishing parameter calculated with methods of Flack [$x = 0.164(8)$], Hoofit [$y = 0.138(7)$] and Parsons [$z = 0.166(8)$].²¹ This is remarkable as chirality and corresponding anomalous differences from resonant scattering originate only from the difference of one nitrogen atom compared to one carbon atom in the structure (see the SI for further information on the anomalous diffraction data).

UV-vis spectra were recorded for **trans-2**, showing two strong absorption maxima at 276 nm and 298 nm with an extinction coefficient of $\epsilon_{298\text{nm}} = 63500 \text{ M}^{-1} \text{ cm}^{-1}$ (Figure 2a). Figure S20 in the SI compares the measured and DFT-calculated electronic spectra, revealing that absorption features between 350 - 450 nm are well represented by the calculations after applying a 30 nm shift of the calculated spectrum to lower wavelengths. From the analysis reported in the SI, the absorption around 412 nm receives contributions from MLCT as well as LC transitions, and the one around 370 nm is dominated by a LC transition. Thus, these bands are similar to bands that have been often assigned to MLCT and LC transitions in similar $C^{\wedge}N$ -coordinated complexes.^{11,17} Overall, the wavelengths and extinction coefficients of the UV-vis spectral features of **trans-2** are comparable to those of other phenylpyridine Pt(II) complexes reported in the literature.²²

Emission spectra were recorded for **trans-2** in solution, with an excitation wavelength of 350 nm, and in the solid state, with excitation wavelengths of 350 and 400 nm, at room temperature (rt) and at 77 K, respectively (Figure 2a and c). Complex **trans-2** exhibits a structured emission spectrum in CH_2Cl_2 at rt with the emission maxima at 519, 553 and 580 nm. The solid state spectrum at 77 K is similar to that in solution showing slightly red-shifted bands at 536, 572, 602 nm. At room temperature, the solid state emission band is heavily broadened with a maximum at 533 nm, most likely due to close intermolecular π - π interactions as observed in the crystal structure of **trans-2** (there, the stacked π - π plane distance is about 3.4 Å).

Emission lifetimes were recorded for **trans-2** in CH_2Cl_2 under argon atmosphere (Figure 2b). The phosphorescence lifetime of **trans-2** at 298 K ($\tau_{298} = 10.9 \mu\text{s}$) and the quantum yield ($\Phi_{\text{PL}} = 0.07$) are in the range of similar reported cyclometalated Pt(II) complexes. The linear slope of the emission decay on the logarithmic scale indicates that the triplet state is the only significant radiative relaxation pathway.²³ Under air, the phosphorescence life time of **trans-2** was found to be significantly shortened due to the interaction of the triplet state with oxygen.

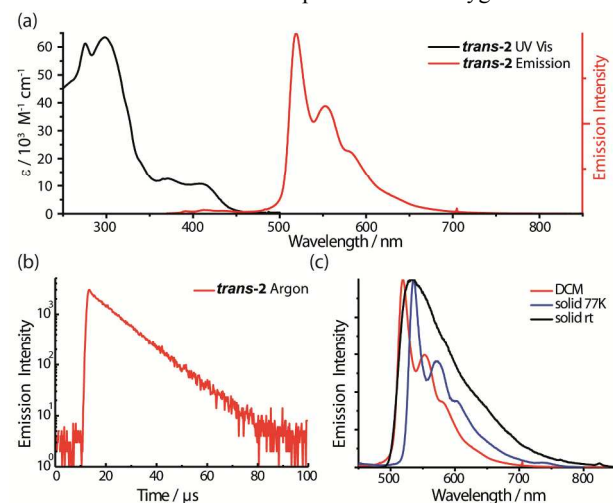


Figure 2. (a) Combined UV-vis and emission spectra (excitation wavelength = 350 nm) of **trans-2** in DCM at 293 K, (b) emission lifetime measurement under argon atmosphere of **trans-2**, (c) normalized emission spectra for solution and solid state samples at 77 K and 293 K.

Circular dichroism (CD) spectra have been recorded for both enantiomers of **trans-2** in CH_2Cl_2 after resolution of the racemate via chiral HPLC (Figure 3a; compare SI Figure S29 for the CD spectra of the enantiomers of **1**). The first fraction of **trans-2**, the S_a enantiomer, shows a positive Cotton effect at 421 nm and further strong peaks at 380, 319 and 259 nm. The second fraction of **trans-2**, the R_a enantiomer, reveals exactly the opposite CD spectrum indicating that the two fractions are a pair of enantiomers. Heating of **trans-2** (S_a) in CHCl_3 at 50 °C over 3 days showed no signs of racemization, proving **trans-2** to be conformational stable under these conditions. In contrast, the racemization of **1** was proceeding on an hour timescale, depending on the solvent ($k_{333}(\text{MeCN}) = 3 \times 10^{-4} \text{ s}^{-1}$; SI Figure S30). To support the absolute configuration based on the X-ray structure, the recorded CD spectra of both HPLC fractions of **trans-2** were compared with TD-DFT-computed CD spectra for the (R_a) enantiomer (see the SI).²⁴ Both methods were found to be in agreement and allow us to assign the absolute stereochemistry as given above. TD-DFT calculations also permitted us to analyze the orbitals involved in the transitions underneath the CD and absorption bands, shedding light on and confirming the descriptions introduced above (SI Figure S21).

Finally, we examined if the chiral-at-metal phosphorescent enantiomers of complex **trans-2** show the emission of circularly polarized light that might render them interesting for corresponding photophysical applications.

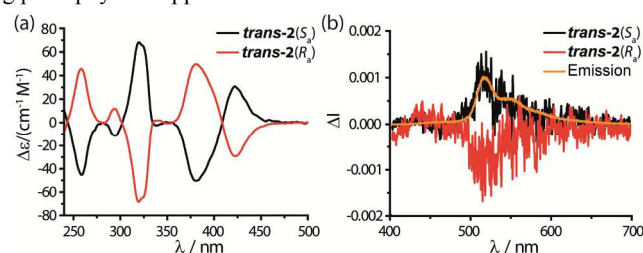


Figure 3. (a) CD and (b) CPL spectra (excitation wavelength = 370 nm, ΔI scale determined after normalization of the emission band) of both enantiomers of **trans-2**.

Therefore, CPL spectra of both enantiomers were recorded in CH_2Cl_2 using a home-built apparatus,²⁵ which had been previously employed also for organometallic complexes.²⁶ The spectra nicely show the opposite polarization of the emitted light for both enantiomers of **trans-2** upon excitation at 370 nm (Figure 3b). The emission dissymmetry factor g is about 10^{-3} .²⁷

In conclusion, we have presented a new $C^{\wedge}N$ -coordination motif for organometallic Pt(II) compounds sharing a structural relationship with the heavily studied family of flat square-planar phenylpyridine complexes. The luminescence properties of the new compounds were elucidated and compared to literature reported systems. Metal-centered chirality of the studied complexes is an immanent consequence of the *cis*- and *trans*-coordination by the achiral $C^{\wedge}N$ -donor ligand. The separation of the enantiomers of two derivatives was successfully conducted by chiral HPLC and circular dichroism as well as circularly polarized luminescence spectra were measured.

Keeping in mind that thousands of publications describe the properties and application of square-planar and octahedral phe-

1 nylpyridine and related organometallic systems, we expect the
2 unique coordination motif introduced herein to spur new devel-
3 opments in this technologically important field of research. Cur-
4 rently, we study the effect of structural and chemical modification
5 of the new ligand framework on the resulting complexes' photo-
6 physical properties with a focus on engineering the luminescent
7 lifetimes, quantum yields and CPL spectral characteristics. Fur-
8 thermore, features such as chemical reactivity,²⁸ redox behavior
9 and interaction with chiral biopolymers will be worth examining.

10 ASSOCIATED CONTENT

11 Supporting Information

12 Synthetic procedures, NMR, MS, X-ray and further spectroscopic
13 data, DFT calculation results. This material is available free of
14 charge via the Internet at <http://pubs.acs.org>.

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17 Notes

18 The authors declare no competing financial interests.

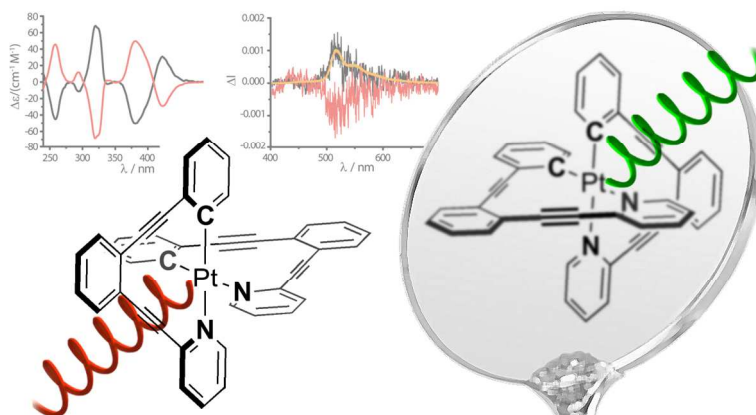
19 ACKNOWLEDGMENT

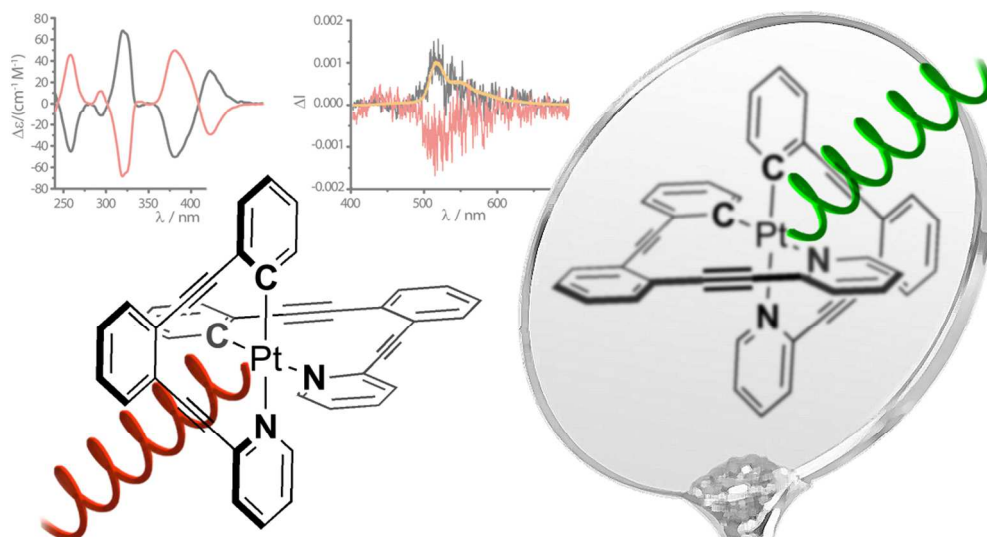
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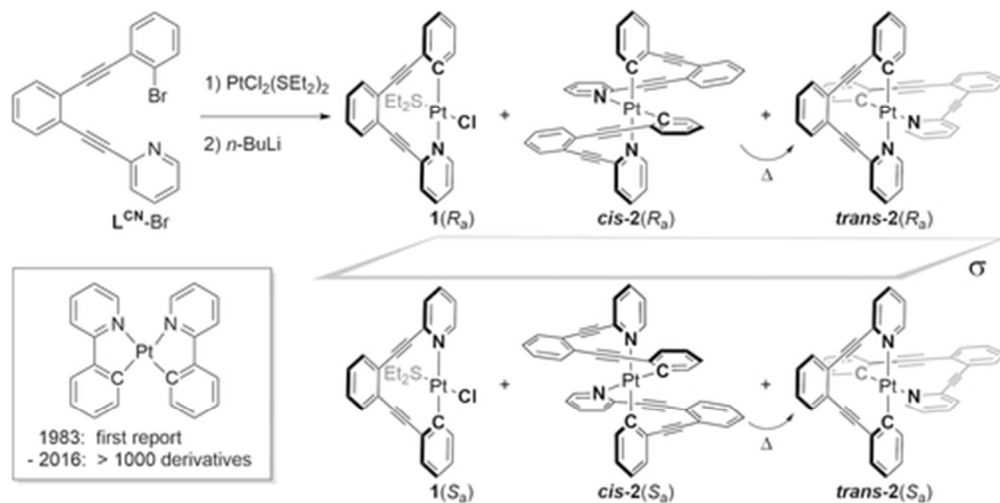
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TOC Figure:

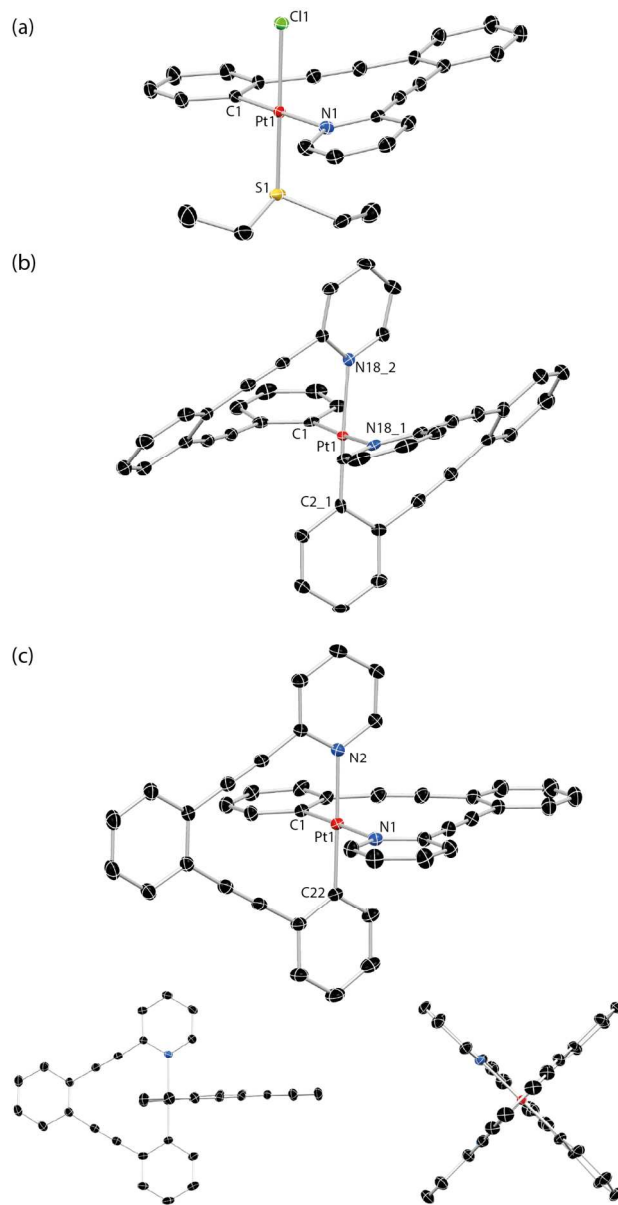




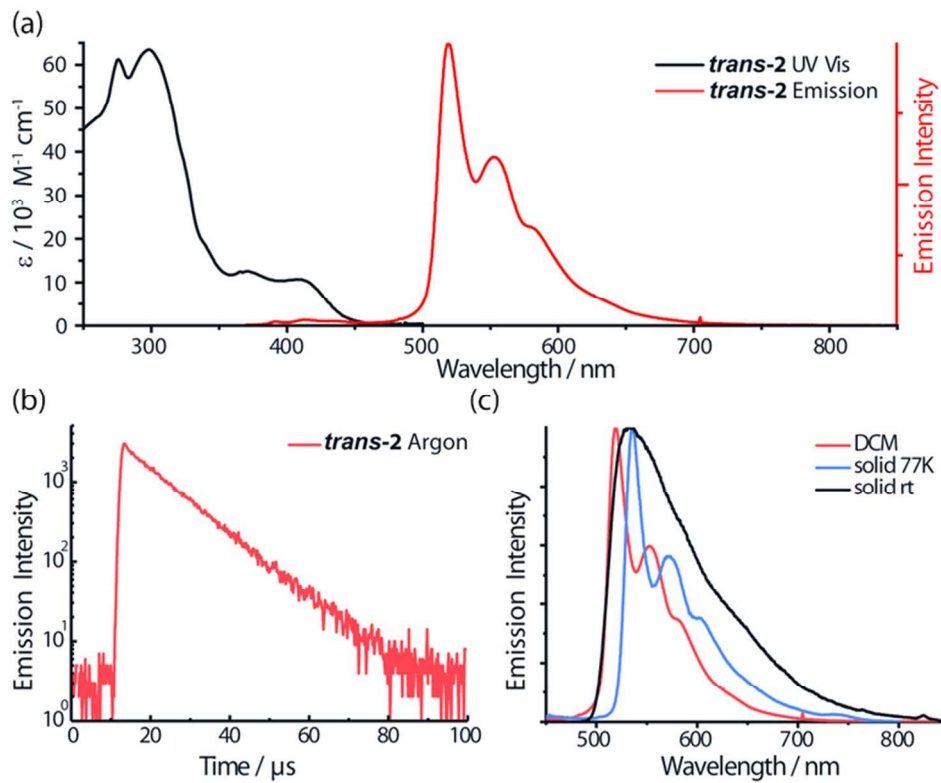
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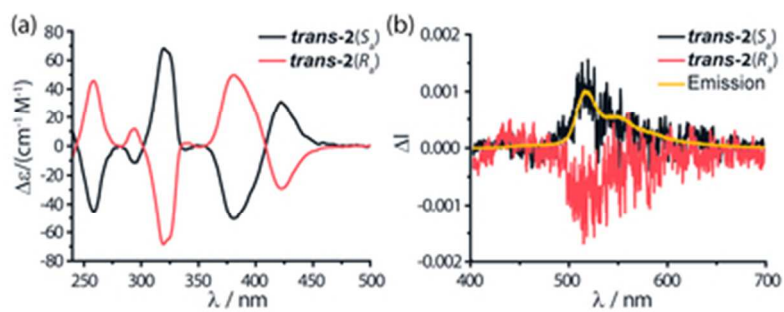
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