### Supramolecular Chemistry

## Chiral Amplification by Self-Assembly of Neutral Luminescent Platinum(II) Complexes

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Abstract: Two novel enantiomerically pure chiral ligands and the corresponding neutral Pt<sup>II</sup> complexes have been synthetized and characterized. The self-assembly properties of the complexes have been investigated using different morphological and photophysical techniques. The two enantiomeric complexes, 4a and 4b, show high tendency to self-assemble into chiral supramolecular aggregates with right (P) and left-handed (M) helical configurations, respectively, as proven by SEM and absorption circular dichroism. The formation of such organized structures is driven by the formation of metallophilic and  $\pi$ - $\pi$  interactions between spatially close Pt complexes with an enhancement of the chiro-optical properties in the solid state.

The synthesis of long-range-ordered chiral structures with sizes spanning from the molecular level to nano- and microscale and up to the macroscopic world are still a great challenge. Indeed, chirality extended to tenth of units is synthetically not easily accessible because the structures are too small to be made individually by top-down methods.<sup>[1]</sup> Supramolecular chemistry and self-assembly are powerful tools for the creation of large architectures and they can be an alternative strategy to overcome such a problem. Nature makes large use of noncovalently bound systems possessing specific functions, and DNA helices and  $\alpha$ -helical proteins represent significant examples. Furthermore, the helical morphology of such biomolecules expresses the chiral information encoded in their chemical components.<sup>[2]</sup> Currently, there is a growing interest towards the preparation of synthetic chiral functional structures for application in asymmetric catalysis, molecular recognition, chiro-optical switches, optoelectronics, and sensing, amongst all.

Several planar, aromatic systems undergo self-assembly thanks to their favorable electronic and geometrical features. Amongst them,  $\mathsf{Pt}^{\scriptscriptstyle \parallel}$  complexes are a special class of molecules that can combine the physico-chemical properties of a heavy metal center together with the square-planar geometry that eventually yield self-assembled structures with enhanced properties.

During the last decades, luminescent Pt<sup>II</sup> complexes bearing large  $\pi$ -conjugated C- and N-based chelating ligands have drawn a lot of attention due to their fascinating photophysical and electrochemical properties.<sup>[3]</sup> Some of these complexes have been investigated for their high tendency towards stacking through weak noncovalent metal–metal and/or  $\pi$ - $\pi$  ligand interactions.  $^{\scriptscriptstyle [4]}$  It has been shown that luminescent  $\mathsf{Pt}^{\scriptscriptstyle II}$  complexes are capable to form supramolecular architectures as liquid crystals,<sup>[5]</sup> nanowires,<sup>[6]</sup> and metallogelators<sup>[7]</sup> with (electro)optical<sup>[8]</sup> and sensing<sup>[9]</sup> properties.

To date, some examples of platinum complexes showing chiro-optical properties in solution have already been reported using cyclometallated platinum(II) complexes,<sup>[10]</sup> alkynylplatinum(II) bipyridyl complexes,<sup>[11]</sup> and cycloplatinated helicenes.<sup>[12]</sup>

Our group has recently reported<sup>[13a]</sup> on self-assembled longrange-ordered fibers by using platinum complexes bearing N^N^N azole-based ligands that showed linearly polarized light emission with a very high photoluminescence quantum yield (PLQY) of up to 75%. We have also shown that it is possible to follow complex self-assembly processes in real time by taking advantage of different emission colors of the assemblies.[13b]

Herein, we report the synthesis of two enantiomeric pure Pt<sup>II</sup> complexes containing an ancillary pyridine functionalized with an asymmetric carbon atom to introduce chirality. The complexes do not display any sizeable spectroscopic chiral feature in solution, but upon self-assembly chiral fiber-type structures are formed. The fibers have been characterized using different spectroscopic techniques, such as electronic absorption, steady-state and time-resolved luminescence, absorption circular dichroism (CD), and fluorescent microscopy. Additionally the morphology of the assemblies was investigated by electron scanning microscopy (SEM).

The synthetic strategy employed for the preparation of two chiral pyridine derivatives and their respective platinum complexes is shown in Scheme 1.

Mandelic acid has been selected to introduce a single asymmetric carbon on the ancillary ligands, while the insertion of moieties able to engage in hydrogen bonds (amide and hydroxyl groups) and  $\pi$ - $\pi$  stacking (benzyl ring) promotes selfassembly. We expect that the establishment of the weak interactions provides a driving force to induce chiral supramolecular self-assembly of the platinum complexes. Also, platinum complexes bearing the chromophoric terdendate ligand, 2,6bis(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)pyridine  $(pyC_5-CF_3-$ 

1

Chem. Eur. J. 2017, 23, 1-6 Wiley Online Library

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**Scheme 1.** Synthesis of the chiral pyridine derivatives. a) NHS, DCC, 1,4-dioxane, room temperature, N<sub>2</sub>, overnight. b) 4-Picolylamine, 1,4-dioxane, 50 °C, N<sub>2</sub>, overnight. c) PtCl<sub>2</sub>DMSO<sub>2</sub>, TEA, MeOH, N<sub>2</sub>, 8 hours, reflux.

tzH<sub>2</sub>) have been already proven to possess a high tendency to form highly emissive assemblies,<sup>[13]</sup> and the occurrence of Pt…Pt and  $\pi$ - $\pi$  interactions can be assessed using emission spectroscopy.

The synthetic procedure starts form the selective activation of the carboxylic group of commercially available **1** a, b by using *N*-hydroxysuccinimide (NHS) and *N*,*N'*-dicyclohexylcarbodiimide (DCC) as the coupling agent in 1,4-dioxane under mild conditions. Subsequently, the amide coupling is carried out by adding 4-picolylamine to the activated NHS ester, yielding the pure enantiomer of the ancillary ligand **3** a, b as a white powder upon filtration and washing. Finally, the target Pt complexes **4** a, b have been obtained as enantiomerically pure derivatives in fairly good yields (60–77%) following the complexation procedure reported elsewhere.<sup>[13]</sup>

The absorption spectra of both complexes 4a and 4b in THF at  $5.1 \times 10^{-5}$  M are displayed in Figure 1.

As expected, upon irradiation with unpolarized light, samples of the two enantiomers show identical spectroscopic properties due to the fact that their different chirality has no effect on the absorption and the emission spectra.

The two complexes **4a**, **b** in THF at low concentration and room temperature display intense bands in the UV region of the absorption spectrum with  $\lambda_{max,abs} = 254$  nm ( $\varepsilon = 28451 \text{ m}^{-1} \text{ cm}^{-1}$ ), 300 nm ( $\varepsilon = 18706 \text{ m}^{-1} \text{ cm}^{-1}$ ), and 332 nm

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Figure 1. Absorption and emission spectra ( $\lambda_{exc}$  = 300 nm) of 4a (black line) and 4b (red line) in THF at a concentration of 5.1 × 10<sup>-5</sup> м.

( $\varepsilon$  = 3725 m<sup>-1</sup> cm<sup>-1</sup>), attributed to singlet-manifold intraligand (<sup>1</sup>IL)  $\pi$ → $\pi^*$  transitions of the tridentate ligand and metal-perturbed charge transfer transitions. A broad, featureless and weaker band ( $\varepsilon$  = 784 m<sup>-1</sup> cm<sup>-1</sup>) is observed in the region between 340–440 nm that can be attributed to the HOMO→ LUMO transitions described as the admixture of spin-allowed metal-to-ligand charge transfer (<sup>1</sup>MLCT) and intraligand (<sup>1</sup>IL) transitions. Such attributions have been made on the basis of closely-related achiral complexes previously reported.<sup>[13–14]</sup> Photoexcitation in any of the absorption band of samples of **4a**, **b** in THF at room temperature gave a structured blue emission with maxima at 462, 490, and 527 nm that display a low intensity with a PLQY of only 0.2%. The low emission intensities were also accompanied by very short excited state lifetimes ( $\tau$  = 2.8 ns) for both complexes.

Information about the chirality of the investigated systems was gathered by recording circular dichroic (CD) absorption spectra. As expected, samples of the chiral ligands **3a**,**b** in MeOH at  $1.03 \times 10^{-3}$  M gave a clear signal with a small either negative or positive Cotton effect at  $\lambda = 235$  nm, with resulting spectra that are mirror images of each other (Figure 2a).

These findings demonstrate that the two ligands are prepared as enantiomeric derivatives, confirming that the chirality that was present in the starting compound mandelic acid has been preserved during the synthetic pathway to obtain the pyridine derivative. We can thus expect that the chirality is



**Figure 2.** Ellipticity spectra recorded for the investigated ligands and complexes in solution. a) CD spectra obtained for the ligands **3a** (black trace) and **3b** (red trace) in MeOH at a concentration of  $1.03 \times 10^{-3}$  M at room temperature. b) CD spectra for the complex **4a** in THF (concentration range:  $2.78 \times 10^{-6}$  –  $4.00 \times 10^{-4}$  M) showing absence of differential absorption between left and right circularly polarized light.

Chem. Eur. J. **2017**, 23, 1–6

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2

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also preserved during the formation of complex 4a, b. The CD spectra of 4a and 4b have been recorded in THF and no sizeable CD signal was detected at any concentration in the range  $2.78 \times 10^{-6}$ – $4.00 \times 10^{-4}$  M (Figure 2b). The absence of a CD signal in solution can be explained if one takes into account the origin of the transitions observed in the unpolarized absorption spectra of the two enantiomeric complexes (Figure 1). In the same spectral region of the recorded CD spectra, the UV/Vis transitions are mainly due to the <sup>1</sup>LC bands of the tridentate ligand, as well as the <sup>1</sup>MLCT and <sup>1</sup>ILCT bands involving both tridentate ligands and also the heavy metal center. On such moieties chiral information is indeed not present, while only little contribution of the ancillary ligand to the absorption spectra can be expected in the spectral region. As a result, the intensity of the CD signal, which can be only caused by the single asymmetric carbon of the mandelic acid moiety, is too weak if compared to the overall light absorption of the complex. The increase of the concentration is expected to increase the CD signal, however the saturation of the detector occurs before detecting any CD signal.

Upon drop-casting of a 1 mg mL<sup>-1</sup> THF solution of either **4a** or **4b** onto a quartz substrate, the compounds tend to self-aggregate into highly luminescent fibers by a solvent-assisted self-assembly processes (Figure 3 a).

Photoexcitation of such fibers yields an intense broad featureless emission that is strongly bathochromically shifted when compared with the complex in solution (THF). For both complexes and as shown in Figure 3 b, the luminescence spectra display a maximum centered at 560 nm with a PLQY as high as 57% and 37% for 4a and 4b, respectively. Also, different from the THF solution, samples of the self-organized fibers showed much longer excited-state lifetime with multi-exponential decays, in which the longest components are 582 and 631 ns for 4a and 4b, respectively. The multi-exponential decay can be attributed to the different environment experienced by the emitting complexes in the aggregated samples. Such a finding is typically observed for solid-state samples. We attribute the different PLQY to the absence of morphological homogeneity of the drop-casted samples. Indeed, a small peak at 462 nm can be observed in both the emission spectra of the complexes 4a and 4b, which is characteristic of the emission of the noninteracting complexes (Figure 1), suggesting that the formation of the assemblies is not quantitative. The bathochromic shift in the emission profile and the higher emission quantum yields are strong indications that the nature of the emitting excited state of the assemblies is different from the luminescent excited state of the complexes in solution. The square planar geometry leads, indeed, to the formation of Pt...Pt interactions through the  $d_z^2$  orbitals of the metals that raise the energy of the HOMO orbitals. Upon assembly, the nature of the lowest electronic transitions is changed to a triplet metal-metal-to-ligand charge transfer (<sup>3</sup>MMLCT). The formation of the new excited state is also clearly evident in the excitation spectra recorded at  $\lambda_{em} = 560$  nm, which shows a strong bathochromic shift with respect to the absorption spectra in solution. This shift is due to the formation of a new band with a <sup>1</sup>MMLCT character upon establishment of Pt-Pt interactions.

Noteworthy, when the absorption CD spectra were recorded on samples of the self-assembled fibers made by either 4a or 4b, a strong signal was detected as shown in Figure 3c. For the two enantiomers, the signals appear to be mirror images of each other, even though the intensity was not the same due to the fact that the amount of deposited fibers might be different. Hence, unlike the THF solutions of 4a and 4b, in the aggregates, CD signals can be clearly observed with a mirror effect between the two enantiomer spectra and maxima at 260, 290, 322, 337, 370, and 472 nm. While the CD signal of the ancillary chiral ligands (Figure 2a) display a single peak and an onset at around 270 nm, the CD signal of the assembled fibers possess several bands with an onset at 580 nm corresponding to the <sup>3</sup>MMLCT band. Such findings suggest that the asymmetric carbon located on the ancillary pyridine induces the formation of a long-range-ordered chiral supramolecular architecture supported by the establishment of Pt-Pt and  $\pi - \pi$  interactions.

Unfortunately, we were not able to obtain single crystals of the assemblies to have a full structural characterization. To explore the morphological features of these fibers, SEM analysis was performed on the self-assembled structures and the images are depicted in Figure 4.

The SEM analyses were recorded on samples prepared from the same solution used for the photophysical characterizations,



**Figure 3.** a) Fluorescence microscopy images of the fibers obtained from **4b** upon irradiation at the excitation band of 400–440 nm and imaged with a longpass emission filter (filter onset 455 nm). Scale bar = 20  $\mu$ m. b) Emission and excitation spectra obtained for the self-organized fibers of **4a** (black trace) and **4b** (red trace) prepared by drop-casting onto a quartz substrate using a 1 mg mL<sup>-1</sup> THF solution;  $\lambda_{exc}$  and  $\lambda_{em}$  were 560 and 400 nm for emission and excitation spectra, respectively. c) CD spectra obtained for samples of fibers prepared by using complex **4a** (black trace) and **4b** (red trace).

3

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**Figure 4.** a, b) SEM images of fibers prepared using complex 4a showing *P* configuration. Scale bar is 4 and 1  $\mu$ m for (a) and (b), respectively. c, d) SEM images of fibers prepared using complex **4b** showing *M* configuration. Scale bar is 4  $\mu$ m and 500 nm for (c) and (d), respectively. All samples were prepared by drop-casting of a THF solution at 1 mg mL<sup>-1</sup> onto a glass slide that was subsequently sputtered with Au/Ag.

that is a 1 mg mL<sup>-1</sup> solution in THF (using a glass substrate). As show on the images of the fibers for both complexes **4a** (Figure 4a,b) and **4b** (Figure 4c,d), the samples gave interconnected fibers with a well-defined helicity as consequence of the supramolecular chiral organization of the complexes in the assemblies.

In particular, complexes **4a** and **4b** seems to aggregate in a clockwise and counterclockwise arrangement, respectively, yielding self-assembled aggregates with right-handed (P) and left-handed (M) helical configurations, respectively. Furthermore, in both cases, the fibrous nanostructures seem to be the results of a self-assembly of thinner nanostructures such as nanofibrils. This observation supports the formation of chiral supramolecular self-assembled structures onto a substrate based on the enantiomerically pure complexes prepared.

In conclusion, the synthesis and the characterizations of two enantiomerically pure blue emitting Pt<sup>II</sup> complexes, **4a** and **4b**, has been presented. The compounds show a high tendency towards self-assembly into chiral supramolecular aggregates with right- (P) and left-handed (M) helical configurations, respectively, as proven by SEM and CD. While both complexes **4a** and **4b** did not show any detectable CD signals in solution at any concentration investigated, a large enhancement of the CD signal was observed upon formation of self-assembled long-range-organized fibers in the solid state.

#### **Experimental Section**

All chemicals were obtained from Sigma-Aldrich except for pyC5- $\mathsf{CF}_3\text{-}\mathsf{tzH}_{2^{\prime}}$  which was synthesized as described previously.  $^{[13]}$  Electrospray ionization mass spectrometry (ESI-MS) was recorded on a MicroTOF (Bruker) mass spectrometer equipped with an electrospray source by the mass spectrometry service of the Institut de Chemie at the University of Strasbourg. Elemental analyses were recorded by the analytical service of physical measurements and optical spectroscopy at the University of Strasbourg. Absorption spectra were measured on a Shimadzu UV-3600 spectrophotometer double-beam UV-VIS-NIR spectrometer and baseline corrected. Steady-state emission spectra were recorded on a Horiba Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer. Time-resolved measurements were performed on a PicoQuant FluoTime 300 (PicoQuant GmbH, Germany). Circular dichroic experiments were performed on Jasco J-810. Photoluminescence quantum yield measurements (PLQY) were recorded at a fixed excitation wavelength ( $\lambda_{exc} =$ 400 nm) using a Hamamatsu Photonics absolute PLQY measurement Quantaurus. Fluorescence microscopy was performed with an Olympus BX51 microscope using a 20x objective and an Olympus U-MWBV BP 400–440 nm with dichroic 455 nm and LP 475 nm as excitation and emission filter cubes, respectively; images were recorded with a Olympus XC-10 color camera. SEM characterization was performed employing a FEI scanning electron microscope Quanta FEG 250 at an acceleration voltage of 10 kV. Samples were prepared by drop-casting of a THF solution onto a glass slide, and subsequent plasma-induced deposition of a 5 nm thick layer of Au/Ag.

S-hydroxy-N-(4-pyridinylmethyl)-benzeneacetamide (3 a): S(+)mandelic acid (1 equiv, 1.011 g, 6.64 mmol) and NHS (1 equiv., 757 mg, 6.58 mmol) were dissolved in 1,4-dioxane (20 mL) under nitrogen. DCC (1.358 g, 6.58 mmol) was added to the mixture at room temperature and the mixture was stirred for 22 hours and then filtered. The filtrate was added to a two-neck round-bottom flask, then 4-(aminomethyl)-pyridine (1 equiv, 714 mg, 6.60 mmol) was added and the solution was stirred for 1.5 hours under nitrogen at 50 °C. Afterwards, the solvent was evaporated and the crude product was purified by column chromatography over silica gel (SiO<sub>2</sub>, ethyl acetate/methanol: 97/3 then 95/5) to give the S-hydroxy-N-(4-pyridinylmethyl)-benzeneacetamide as a white solid (704 mg, 2.90 mmol) in 44% yield. <sup>1</sup>H NMR (400 MHz, [D<sub>4</sub>]MeOD):  $\delta = 8.41$  (d, J(H,H) = 6.2 Hz, 2H), 7.50 (d, J(H,H) = 6.8 Hz, 2H), 7.35 (m, 3H), 7.27 (d, J(H,H) = 6.2 Hz, 2H), 5.11 (s, 1H), 4.47 ppm (s, 2H).  $^{13}\text{C}$  NMR (100 MHz, [D<sub>4</sub>]MeOD)  $\delta\!=\!$  149.98, 129.42, 129.17, 127.63, 123.75, 75.59, 42.51 ppm. HRMS (ESI-TOF): m/z calcd: 243.1128 [*M*+H]<sup>+</sup>; found: 243.1121.

*R*-hydroxy-*N*-(4-pyridinylmethyl)-benzeneacetamide (3 b): *R*(–)-mandelic acid (1 equiv, 1.003 g, 6.59 mmol) and NHS (1 equiv, 757 mg, 6.58 mmol) were dissolved in 1,4-dioxane (50 mL) under nitrogen. DCC (1.359 g, 6.59 mmol) was added to the mixture at room temperature. The mixture was stirred for overnight and then filtered. The filtrate was added to a two-neck round-bottom flask, then 4-(aminomethyl)-pyridine (1 equiv, 722 mg, 6.68 mmol) was added and the solution was stirred overnight under nitrogen at 50 °C. The solution was dried and the crude solid was recrystallized from ethyl acetate to give *R*-hydroxy-*N*-(4-pyridinylmethyl)-benzeneacetamide as a white solid (450 mg, 1.86 mmol) in 28% yield. <sup>1</sup>H NMR (400 MHz,  $[D_4]$ MeOD)  $\delta$  = 8.41 (d, *J*(H,H) = 6.2 Hz, 2 H), 7.50 (d, *J*(H,H) = 6.7 Hz, 2 H), 7.35 (m, 3 H), 7.27 (2 H), 5.11 (s, 1 H), 4.47 ppm (s, 2 H). HRMS (ESI-TOF): *m/z* calcd: 243.1128  $[M+H]^+$ ; found: 243.1105.

**Preparation of platinum complex 4a:**  $pyC_5-CF_3-tzH_2$  (205 mg, 587 µmol), PtCl<sub>2</sub>(DMSO)<sub>2</sub> (244 mg, 578 µmol), and 20 mL methanol were added to a 50 mL two-neck round-bottom flask under nitrogen. Upon addition of 160 µL triethylamine with a syringe, the resulting mixture became bright yellow. Then *S*-hydroxy-*N*-(4-pyridi-nylmethyl)-benzeneacetamide **3a** (141 mg, 582 µmol) was added and the mixture was heated to 66 °C. All the products were solubi-

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lized in methanol after which a yellow solid precipitated at the bottom of the flask. The mixture was heated for 6 hours and the reaction monitored by TLC (silica, ethyl acetate/cyclohexane: 3/1). The mixture was filtrated at 0 °C, the light-yellow emissive solid washed in boiling methanol, then again filtrated, and finally washed several times with methanol. The yellow solid complex was synthetized with a yield of 60%. <sup>1</sup>H NMR (400 MHz, [D<sub>8</sub>]THF)  $\delta$ =9.56 (br d, J(H,H)=6.7 Hz, 2H), 8.28 (m, 1H), 8.20 (t, J(H,H)=8.12 Hz, 1H), 7.89 (d, J(H,H)=7.9 Hz, 2H), 7.53 (m, 4H), 7.31 (m, 3H), 5.53 (d, J(H,H)=3.9 Hz, 1H), 5.13 (d, J(H,H)=3.8 Hz, H), 4.54 ppm (m, 2H). <sup>19</sup>F NMR (376 MHz, [D<sub>8</sub>]THF)  $\delta$ =-67.00 ppm. HRMS (ESI-TOF) *m/z* calcd: 785.110 [*M*+H]<sup>+</sup>; found: 785.113. Elemental analysis calcd (%) for C<sub>25</sub>H<sub>17</sub>O<sub>2</sub>N<sub>9</sub>F<sub>6</sub>Pt: C 38.27, H 2.18, N 16.07; found: C 38.17, H 2.18, N 15.84.

Preparation of platinum complex 4b: pyC<sub>5</sub>-CF<sub>3</sub>-tzH<sub>2</sub> (201 mg, 576 µmol), PtCl<sub>2</sub>(DMSO)<sub>2</sub> (246 mg, 583 µmol), and 20 mL methanol were added to a 50 mL two-neck round-bottom flask under nitrogen. Upon addition of 160 µL triethylamine with a syringe, the resulting mixture became bright yellow Then R-hydroxy-N-(4-pyridinylmethyl)-benzeneacetamide 3b (142 mg, 586 µmol) was added and the mixture heated to  $66\,^\circ\text{C}$  for 6 hours. The mixture was filtrated and washed several times with methanol to give a yellow solid (347 mg, 442 µmol, yield 77%). 1H NMR (400 MHz, [D<sub>2</sub>]THF)  $\delta = 9.58$  (br d, J(H,H) = 6.7 Hz, 2 H), 8.23 (t, J(H,H) = 8.12 Hz, 2 H), 7.93 (d, J(H,H) = 7.9 Hz, 2 H), 7.54 (t, J(H,H) = 7.4 Hz, 4 H), 7.34-7.24 (m, 3 H), 5.51 (d, J(H,H) = 3.9 Hz, 1 H), 5.12 (d, J(H,H) = 3.9 Hz, 1 H), 4.62–4.47 ppm (m, 2 H).  $^{19}\text{F}$  NMR (376 MHz, [D\_8]THF)  $\delta =$ -65.14 ppm. HRMS (ESI-TOF) *m/z* calcd: 807.0951 [*M*+Na]<sup>+</sup>; found: 807.0855. Elemental analysis: calcd (%) for C25H17O2N9F6Pt: C 38.27, H 2.18, N 16.07; found: C 38.20, H 2.29, N 16.10.

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# COMMUNICATION

#### Supramolecular Chemistry

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Chiral Amplification by Self-Assembly of Neutral Luminescent Platinum(II) Complexes



United luminescence! Neutral Pt<sup>II</sup> complexes with two novel enantiomerically pure chiral ligands are presented. The platinum complexes self-assemble into

supramolecular fibers, thereby showing an enhancement in luminescence and chirality.