Supporting Information

Luminescence and Length Control in Nonchelated d^8-Metallosupramolecular Polymers through Metal-Metal Interactions

J. Matern, I. Maisuls, C. A. Strassert, G. Fernández*
# Table of Contents

**Supplementary Experiments/Figures**
- Preliminary Self-Assembly Studies ........................................................................ 3
- Morphology Studies .............................................................................................. 5
- Photophysical Properties ...................................................................................... 7
- Thermodynamic and kinetic Characterization ....................................................... 11
- Packing Mode Analysis ......................................................................................... 15
- Mechanistic Studies .............................................................................................. 17
- Theoretical Calculations ....................................................................................... 20
- Seed-mediated Living Supramolecular Polymerization .......................................... 23

**Experimental Section** ......................................................................................... 26
- Materials and Methods ......................................................................................... 26
- Synthesis and Characterization ............................................................................. 28

**References** ........................................................................................................... 30

**Author Contributions** ......................................................................................... 30
First insights into the self-assembly behavior of 1 were gained by UV/Vis absorption spectroscopy in a variety of solvents (a). In dichloromethane (DCM), chloroform (CHCl$_3$) and tetrahydrofuran (THF), 1 is characterized by a sharp absorption maximum at 333 nm that exhibits a shoulder between 310 - 320 nm. Based on previous reports, this shoulder band can be assigned to metal-perturbed intra-ligand transitions (IL), corresponding to stretchings of the phenyl rings and ethynylene units. The strong intensity of the transition at 333 nm and the absence of the same in the spectrum of the free ligand (c) suggests that this absorption component originates from a metal-to-ligand charge transfer (1MLCT), in accordance with literature reports. Considering the known tendency of bisamide groups to undergo inter- and intramolecular hydrogen bonding, a 1:1 mixture of CHCl$_3$ and dimethylformamide (DMF) as H-bonding acceptor (mixture that guarantees the prevalence of the extended monomer conformation) was also studied. The fact that the spectra in this solvent mixture are equal to those in pure CHCl$_3$, DCM and THF pinpoints that 1 is present in its monomeric form in all four media (→ "good" solvents). On the other hand, in the apolar solvents n-hexane (n-Hex) and methylcyclohexane (MCH), a concomitant blue-shift and depletion of the absorption maximum are observed. Moreover, a Tyndall effect can be recognized from the tailing of the spectrum beyond 600 nm. These characteristics indicate the formation of poorly solvated self-assembled structures that cause light scattering. Over time, these aggregates cluster to form macroscopic superstructures, which can be observed with the naked eye as cloudy precipitates (photo in (a)).

The emission spectra of 1 under identical conditions are depicted in (b). In solvents favoring a monomer state (DCM, CHCl$_3$, THF and CHCl$_3$:DMF 1:1), a weak, poorly defined emission band between 375 - 500 nm is observed. The similarity of the emission profile of the free ligand and the complex in its monomeric state (d) strongly suggests that the emission of the Pt$^{	ext{II}}$ complex originates from ligand-centered excited states. In comparison to the free ligand, the emission of 1 is shifted to lower energies as a result of metal complexation and the emission intensity of the complex is far less intense than that of the free ligand (intensity of the spectra in (d) was normalized for a better comparison). Hence, the emission is assigned to originate from mixed metal/ligand-centered ($^3$MLCT) excited states.

In the aggregation-inducing solvents n-Hex and MCH, a broad but pronounced emission centered at 593 nm occurs. Such broad and unstructured emission profiles with pronounced Stokes shifts are typically attributed to triplet metal-metal-to-ligand charge transfer ($^3$MMLCT) excited states, which are accessible as a consequence of extended metal-metal contacts.
Figure S2. UV/Vis absorption spectra of complex 1 in solvent mixtures of different MCH:CHCl₃ ratios (c = 20 µM, T = 298 K).

The complex is present in its monomeric form under ambient conditions in solutions containing CHCl₃ volume fractions exceeding 30 % v/v, whereas its aggregates precipitate at CHCl₃ contents lower than 20 % v/v. Hence, the self-assembly of 1 in solution was studied in mixtures of MCH containing 20 - 30 % v/v CHCl₃.
Morphology Studies

**Figure S3.** AFM images (a,b) of aggregates 1A and height-profile analyses (c-f) of the cross-sections indicated in the images.

**Figure S4.** SEM images of SP 1A at different levels of magnification (back-scattered electron detector). The dashed box in (a) marks the area that is magnified in (b).
Figure S5. AFM studies of aggregates 1B and thinfilms ATR FTIR spectra of SP 1A and SP 1B. a-g) AFM height images recorded at different levels of magnification and height profile analyses (c,d) of the cross-sections indicated in the images. The dashed boxes in (a) and (e) mark the areas that are magnified in (b),(f) and (g). h) ATR FTIR spectra of thinfilms of SP 1A and SP 1B in the spectral region of the methylene CH$_2$ stretchings.

The IR frequencies observed for the antisymmetric (2920 cm$^{-1}$) and symmetric stretching (2852 cm$^{-1}$) of the methylene units of the aliphatic chains are characteristic for the interdigitation of the side chains.$^{[2,7]}$
Photophysical Properties

Figure S6. Photophysical studies of monomer solutions of 1 at RT (c = 20 µM, CHCl₃). a) Emission and excitation spectra. b) Time-resolved photoluminescence decay profile (blue), instrument response function (IRF, red) and fit curve (black) with the corresponding residuals plot below (λₐm = 430 nm). c) Fitting parameters including pre-exponential factors and confidence limits.

The short photoluminescence lifetime can be attributed to quenching through the population of thermally accessible metal-centered states. This is on the one hand due to the weak ligand field of the chlorido ligands, and on the other hand due to the non-coplanar arrangement of the pyridine ligands with respect to the Pt-Cl-Npyridine plane, both lowering the energetic levels of the metal-centered states.[8]
Figure S7. Photophysical studies of solutions of SP 1A at RT (a-c) and at 77 K (d-f) in a glassy matrix (c = 20 µM, MCH:CHCl₃ 8:2). a,d) Emission and excitation spectra. b,e) Time-resolved photoluminescence decay profile (blue), instrument response function (IRF, red) and fit curve (black) with the corresponding residuals plot below (\(\lambda_{\text{em}} = 430\ \text{nm}\)). c,f) Fitting parameters including pre-exponential factors and confidence limits.

The extracted emission lifetimes of SP 1A are very close to those measured for the monomer in CHCl₃ (\(\tau_{\text{SP 1A}} = 1.87\ \text{ns}\) vs. \(\tau_{\text{Mono}} = 1.51\ \text{ns}\)). Furthermore, the excitation spectra show similar features (in both cases the excitation maximum is centered at \(\lambda_{\text{max}} \approx 365\ \text{nm}\)). Thus, the excited states in 1 are poorly affected by aggregation into SP 1A.

Note: The emission centered around 600 nm stems from minor traces of SP 1B in the solutions. Due to the high intensity of this emission band and the quenched emission of SP 1A, the small traces of 1B seem to dominate the spectra. However, due to the fact that 1B does not exhibit an emission at 430 nm (please see Figure S8), where excitation spectra, quantum yield and photoluminescence decay profiles were measured, the extracted data can be confidently assigned to SP 1A.
Figure S8. Photophysical studies of solutions of SP 1B at RT (a-c) and at 77 K (d-f) in a glassy matrix (c = 20 µM, MCH:CHCl₃ 8:2). a,d) Emission and excitation spectra. b,e) Time-resolved photoluminescence decay profile (blue) and fit curve (black) with the corresponding residuals plot below (λₜₐₘₚ = 600 nm). c,f) Fitting parameters including pre-exponential factors and confidence limits.

The amplification of the emission lifetimes at 77 K can be explained by a reduced $k_{nr}$ in frozen environments, where non-radiative decays caused by the interaction with the solvent are diminished. When the complexes are dissolved in dilute fluid solutions, different conformations are thermally accessible with comparable excited-state character, yet different deactivation rates and therefore multiexponential decays are observed. This effect is also noticed at 77 K, where different molecular microenvironments are sensed, yielding also multiexponential decays. This justifies the use of the amplitude-weighted average lifetimes.
Figure S9. Phosphorescence lifetime imaging (PLIM) studies of SP\textsuperscript{1A} (a) and SP\textsuperscript{1B} (b-f, $\lambda_{\text{exc}} = 375$ nm). a) Photoluminescence lifetime map image of SP\textsuperscript{1A}. b) Photoluminescence lifetime map image of SP\textsuperscript{1B}. c) Detector events plot image (photons that reach the detector) of SP\textsuperscript{1B}. d) Phase contrast microscopy image of SP\textsuperscript{1B}. e) Photoluminescence lifetime fitting parameters including pre-exponential factors and confidence limits of SP\textsuperscript{1B}. f) Emission spectrum extracted at an arbitrary point of the 1B structures in the PLIM lifetime map image of SP\textsuperscript{1B}.

As our microscope is coupled to a spectrometer via an optical fiber, the emission spectra and lifetimes at any given pixel of the images can be obtained (e,f). The extracted spectra and lifetimes are in good agreement with the results obtained for the solutions, thus excluding a bias through drying artifacts or surface effects in the imaging studies.
Thermodynamic and kinetic Characterization

Table S1. Thermodynamic parameters obtained with the nucleation-elongation model.[11]

|          | $\Delta G^{298}$ / kJ mol$^{-1}$ | $\sigma$ / - | $\Delta H^{nucl.}$ / kJ mol$^{-1}$ |
|----------|----------------------------------|-------------|-----------------------------------|
| 1A       | -32.9                            | 6.21$\times$10$^{-3}$ | -19.1                             |
| 1B       | -47.8                            | 2.93$\times$10$^{-3}$ | -16.2                             |

Figure S10. Cooling curves for the SP of 1A extracted at 333 nm and fit curves to the nucleation-elongation model (MCH:CHCl$_3$ 8:2, 1 Kmin$^{-1}$).
Figure S11. Cooling curves for the SP of 1B extracted at 333 nm and fit curves to the nucleation-elongation model (MCH:CHCl₃ 8:2, 800 rpm, 1 Kmin⁻¹). Notably, higher concentrations also favor the formation of SP 1B, which is why for SP 1A a concentration range from 5 - 20µM was fitted, whereas for SP 1B a concentration range from 10 - 25 µM was fitted.

Figure S12. VT-UV/Vis spectra recorded upon heating solutions of SP 1A at different concentrations (MCH:CHCl₃ 8:2, 1 Kmin⁻¹), showing the formation of SP 1B prior to disassembly into the monomers.
Figure S13. UV/Vis spectra recorded upon disassembly of SP 1A upon stepwise increasing the CHCl_3 volume fraction of the solutions, at different concentrations (starting point: MCH:CHCl_3 8:2, 800 rpm, T = 298 K).

In this set of experiments, formation of SP 1B prior to disassembly into the monomers does not occur. Although increasing concentrations should favor the formation of thermodynamic 1B, no 1A → 1B transformation is observed. This illustrates that a considerable activation barrier has to be overcome for the growth of SP 1B, which can only be surpassed by an influx of energy (or as shown later by seed-mediated growth).
Figure S14. SP interconversion experiments. a,b) Time-dependent emission spectra of the $1A \rightarrow 1B$ transformation upon stirring a solution of SP $1A$ ($c = 30 \mu M$, $T = 298$ K, 800 rpm). c,d) Plot of the emission intensity at the emission maximum against the time (c) and after shortly heating the solutions to 313 K and cooling back to 298 K (d, MCH:CHCl$_3$ 7:3, 800 rpm, $T = 298$ K).

For this experiment, SP $1A$ was obtained by fast cooling of hot solutions of $1$ at a rate of 5 K/min in a mixture of MCH:CHCl$_3$ 8:2. Subsequently, the required amount of $1$ in CHCl$_3$ was added to reach the final solvent composition of MCH:CHCl$_3$ 7:3 at an unchanged concentration. The solutions were shortly sonicated (~5 sec), transferred to a cuvette equipped with a small stirring bar and the measurement was started at 298 K (a,c). After the initial rapid growth, the solutions reach a phase where an almost linear growth is observed. In that phase, the solutions were heated to 313 K for 5 min and subsequently cooled back to 298 K and the measurement was continued (b,d).

In all cases, the transformation sets in practically instantly, thus supporting a consecutive mechanism, as this allows the formation of SP $1B$ directly from SP $1A$ without a previous disassembly step. In the case of a competitive mechanism, a lag time would be expected before the transformation starts, considering that at the given temperature and solvent composition there is no transformation at all if the solution is not stirred. Furthermore, the initially more pronounced rise of the emission intensity and the subsequent levelling could be correlated to an initially greater number of SP strands for which the energy barrier for the transformation to SP $1B$ was already surpassed in the initial sonication step. Once these strands have fully transformed to SP $1B$, the continuous mechanical stirring can only induce a gradual transformation for residual $1A$ SP strands. If then the solution is shortly heated, the thermal energy input again helps to overcome the activation barrier for a larger number of SP strands and shortly accelerates the transformation rate, until it again levels after some time. In the case of a competitive transformation, usually sigmoidal transition curves are observed as a result of the autocatalytic nature of the transformation of cooperatively formed SPs (which is the case for SP $1B$).
Packing Mode Analysis

**Figure S15.** UV/Vis spectra of the solutions used for the packing mode NMR studies in Figure 4a, showing that the spectral changes in the NMR experiment can be correlated to the self-assembly of 1B (c = 2 mM, T = 298 K).

**Figure S16.** a) VT-1H NMR spectra upon cooling a solution of 1 at a rate of 1 Kmin\(^{-1}\) (c = 2 mM, MCH-d\(_{14}\)-CDCl\(_3\) 3:7). b) Corresponding UV/Vis spectra recorded under equal conditions, showing that the spectral changes in the VT-NMR experiment can be correlated to the self-assembly of 1B.

Upon cooling the solution, the amide resonances (blue & cyan) are deshielding as a consequence of intermolecular H-bonding. The resonances of the central phenyl ring of the OPE unit (black) and the β-pyridine proton (orange) are shielding, indicative of aromatic interactions. Only the α-pyridine proton (red) is unchanged. This is due to the fact that this resonance is mainly affected by the interactions with the adjacent chloride ligand upon planarization of the pyridine ring with respect to the ML\(_4\) plane, which is a prerequisite for the spatial approximation of the complexes and thus the formation of aromatic interactions.
Only the amide proton resonances (blue & cyan) exhibit significant changes. This behavior is characteristic for the formation of intramolecular hydrogen bonds between the amide groups of the bisamide linker. The UV/Vis spectra recorded under equal conditions confirmed that the spectral changes in the VT-NMR experiment can be correlated to the open-closed monomer regime, as no signs of aggregate formation were observed.
Figure S18. Time-dependent UV/Vis studies showing the instant self-assembly into SP 1A. a) Absorption spectra recorded upon injection of aggregation-inducing MCH to a solution of 1 in CHCl₃ (final solvent composition MCH:CHCl₃ 8:2, c = 20 µM, T = 298 K). Inset: Corresponding secondary plot of the absorption at 333 nm against time. b) Absorption spectra recorded upon rapid cooling of a hot solution (368 K) of monomeric 1 to 298 K (MCH:CHCl₃ 8:2, c = 20 µM). Inset: Corresponding secondary plot of the absorption at 333 nm against time.
Only conformers in which all bisamide moieties form intramolecular H-bonds can significantly delay spontaneous SP driven by intermolecular H-bonding. Conformers of 1 in which one of the two bisamide units is present in its open conformation are susceptible to form intermolecular H-bonds at this site. Upon subsequent intermolecular association of the dimer, the yet pseudo-cyclic bisamides at the other end of the complex are prone to be dissociated in favor the exothermal formation of intermolecular H-bonds.
Figure S20. a,b) Comparison of the metastable dimer formed during the SP of the ligand alone (a) and possible dimers of 1 with similar interactions (b). c) Possible structure of a tetramer in which all H-bonding sites are saturated and locked in conformation, in analogy to the metastable dimer in (a).
Theoretical Calculations

The geometries of monomers, dimers and tetramers in a parallel and a slipped packing mode were optimized using the dispersion-corrected semiempirical PM6-D3H4X method, as implemented in the MOPAC package. All calculations were carried out in vacuum.

The stabilization energy per monomer ($\Delta E_{avg}$) was calculated as the difference in energies of an oligomer of $n$ molecular units ($\Delta H_n$) and $n$ corresponding monomers ($n \cdot \Delta H_\text{mono}$) divided by the term ($n-1$) (Equation S1).

$$\Delta E_{avg} = \frac{(\Delta H_n - n \cdot \Delta H_{\text{mono}})}{n-1}$$ (S1)

### Table S2: Heats of formation ($\Delta H_\text{f}$), stabilization energies per monomer ($\Delta E_{avg}$), C-N-Pt-Cl dihedral angles ($\theta$ (C-N-Pt-Cl)) and dihedral angles between the planes of the two pyridines coordinated to the metal ($\theta$(py-py)), intermolecular N-H-O=C H-bonding distances and intermolecular Pt-Pt distances obtained from semiempirical PM6 calculations in vacuum. Data for the parallel, kinetic aggregate:

|              | $\Delta H_f$/kJ mol$^{-1}$ | $\Delta E_{avg}$/kJ mol$^{-1}$ | $\theta$(C-N-Pt-Cl)/$^\circ$ | $\theta$(py-py)/$^\circ$ | N-H-O=C/Å | Pt-Pt/Å |
|--------------|-----------------------------|--------------------------------|------------------------------|--------------------------|------------|---------|
| Monomer      | -623.66892                  | -                              | 48.8                         | 0.5                      | -          | -       |
| Dimer        | -1532.90499                 | -285.56715                     | 52.6                         | 2.3                      | 1.94       | 3.83    |
| Trimer       | -2467.94472                 | -298.46898                     | 55.2                         | 2.4                      | 1.91       | 3.84    |
| Tetramer     | -3398.09028                 | -301.1382                      | 55.0                         | 2.4                      | 1.91       | 3.86    |

Note: $\theta = 0^\circ$ means that the Cl-Pt-Cl fragment is fully coplanar with the plane of the pyridine, a torsion of $\theta = 90^\circ$ means it is completely perpendicular to the ring.

### Table S3: Heats of formation ($\Delta H_\text{f}$), stabilization energies per monomer ($\Delta E_{avg}$), C-N-Pt-Cl dihedral angles ($\theta$ (C-N-Pt-Cl)) and dihedral angles between the planes of the two pyridines coordinated to the metal ($\theta$(py-py)), intermolecular N-H-O=C H-bonding distances and intermolecular Pt-Pt distances obtained from semiempirical PM6 calculations in vacuum. Data for the helical, thermodynamic aggregate:

|              | $\Delta H_f$/kJ mol$^{-1}$ | $\Delta E_{avg}$/kJ mol$^{-1}$ | $\theta$(C-N-Pt-Cl)/$^\circ$ | $\theta$(py-py)/$^\circ$ | N-H-O=C/Å | Pt-Pt/Å |
|--------------|-----------------------------|--------------------------------|------------------------------|--------------------------|------------|---------|
| Monomer      | -623.66892                  | -                              | 48.8                         | 0.5                      | -          | -       |
| Dimer        | -1537.80292                 | -290.46508                     | 49.7                         | 5.6                      | 1.94       | 3.90    |
| Trimer       | -2449.36241                 | -289.177825                    | 47.9                         | 9.1                      | 1.90       | 3.89    |
| Tetramer     | -3388.60535                 | -297.976567                    | 47.5                         | 9.1                      | 1.94       | 3.81    |

In a parallel arrangement, $\Delta E_{avg}$ ($\rightarrow 1A$) decreases during the initial association steps, whereas for the helical solution ($\rightarrow 1B$) $\Delta E_{avg}$ slightly increases up to the trimer. However, subsequently $\Delta E_{avg}$ decreases to a greater extent than for the parallel stacks ($\Delta E_{avg}$) from dimerization to trimerization (-8.80 kJ/mol (helical) vs. -2.57 kJ/mol (parallel)). Considering that the situation in a polymer consisting of a much larger number of molecules is not accurately described by the absolute data of these short oligomers, rather the developments should be considered. Thus, extrapolation of the trends in energy gain for the helical arrangement should yield a much greater stabilization in a polymer than for the parallel one. This agrees with the proposed disfavored nucleation of SP 1B, whereas 1A forms spontaneously. On the other hand, once nucleation of 1B has occurred, the elongation of SP 1B is energetically favored over elongation of SP 1A. Moreover, the dihedral angles between the planes of the two pyridines coordinated to the metal were analyzed. The data shows that in kinetic SP 1A, the pyridines and thus the OPE backbones are arranged in a more planar fashion, beneficial for aromatic interactions. On the other hand, in SP 1B, the dihedral angles between the pyridines are slightly increased. Thus, in order to establish attractive Pt-Pt interactions the pyridines and OPE backbones are slightly twisted (possibly at the expense of aromatic interactions), while at the same time enabling more efficient H-bonds in the ligands’ peripheries.
Figure S21. Geometry-optimized structures (dispersion-corrected semiempirical PM6 method) of 1-OMe in a parallel packing mode (SP 1A). a) Monomer, b) dimer top view, c) dimer side view, d) trimer top view, e) trimer side view, f) tetramer top view, g) tetramer side view.
Figure S22. Geometry-optimized structures (dispersion-corrected semiempirical PM6 method) of 1-OMe in a helical packing mode (SP 1B). a) Monomer, b) dimer top view, c) dimer side view, d) trimer top view, e) trimer side view, f) tetramer top view, g) tetramer side view.
Seed-mediated Living Supramolecular Polymerization

Seeds of thermodinamic 1B were prepared by sonication of elongated 1B SPs (~5 min). These seeds were then added to a solution of kinetic 1A. Initially the seed-mediated SP-convension studies were performed in MCH:CHCl₃ 8:2 (Figure S23). Although the transformation into 1B was successfully initiated in this solvent mixture, the time period necessary for the transformation was rather large (> 12 h). Therefore, the volume fraction of good solvent was raised to 30 % in the multi-cycle LSP, in order to increase the dynamics in the solution.[6,15]

Figure S23. Emission spectra of two subsequent cycles of seeded SP upon addition of one equivalent of kinetic 1A to a constant amount of seeds of 1B in a solvent mixture MCH:CHCl₃ 8:2 (c = 20 µM, T = 298 K, λexc = 333 nm).

Over a timespan of at least 10 h, no transformation to SP 1B was observed. Thus, despite the higher CHCl₃ volume fraction, a sufficiently strong kinetic trapping of SP 1A takes place, enabling LSP experiments in this solvent mixture.

Figure S24. Time-dependent UV/Vis absorption spectra of SP 1A in the solvent mixture MCH:CHCl₃ 7:3 (c = 20 µM, T = 298 K).

Figure S25. SEM images recorded after completion of each cycle of LSP (backscattered-electron detector). For the SEM measurements, samples were prepared by drop-casting the respective solution (MCH:CHCl₃ 7:3, c = 20 µM, T = 298 K) onto silicon wafer and subsequent evaporation of the solvent.
Figure S26. Detailed data of the PLIM measurements of SP 1B seeds used for LSP ($\lambda_{\text{exc}} = 375$ nm, $T = 298$ K). a) Phase contrast microscopy image. b) Detector events plot image (photons that reach the detector). c) Photoluminescence lifetime map image. d) Photoluminescence lifetime fitting parameters including pre-exponential factors and confidence limits (bottom).

Figure S27. Detailed data of the PLIM measurements during LSP cycles I - IV ($\lambda_{\text{exc}} = 375$ nm, $T = 298$ K). a-d) Phase contrast microscopy images. e-h) Micrographs depicting detection events (photons that reach the detector, which correlates with the photoluminescence intensity). i-l) Photoluminescence lifetime maps. m-p) Photoluminescence lifetime decay curves (top) and fitting parameters including pre-exponential factors and confidence limits (bottom).
Figure S28. Emission spectra extracted at given points of the SP 1B structures in the PLIM images of the LSP experiment ($\lambda_{exc} = 375$ nm, $T = 298$ K).
Experimental Section

Materials and Methods

General Procedures

All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon or nitrogen atmosphere.

For all spectroscopic measurements, spectroscopic grade solvents were used.

Column Chromatography

Preparative column chromatography was conducted in self-packed glass columns of different sizes with silica gel (Merck Silica 60, particle size 0.04 – 0.063 mm).

NMR measurements

\(^1\)H and \(^13\)C NMR spectra were recorded on a Bruker Avance II 300 (\(^1\)H: 300 MHz, \(^13\)C: 75 MHz), and a Bruker Avance II 400 (\(^1\)H: 400 MHz, \(^13\)C: 101 MHz). Additional 1D \(^1\)H spectra were recorded on an Agilent DD2 500 (\(^1\)H: 500 MHz, \(^13\)C: 126 MHz) and an Agilent DD2 600 (\(^1\)H: 600 MHz, \(^13\)C: 151 MHz) at a standard temperature of 298 K in deuterated solvents. The recorded spectra were referenced to the remaining resonance signals of the deuterated solvents. The coupling constant J of the measured spin multiplets is given in Hertz (Hz) and the chemical shift \(\delta\) is given in reference to the chemical shift of trimethylsilane (0 ppm). Multiplicities for proton signals are abbreviated as \(s\), \(d\), \(t\), \(q\), \(qu\) and \(m\) for singlet, doublet, triplet, quartet, quintet and multiplet, respectively.

Mass spectrometry (MS)

MALDI mass spectra were recorded on a Bruker Daltronic Ultraflex ToF/ToF or a Bruker Daltronics Autoflex Speed with a SmartBeam\textsuperscript{TM} NdYAF-Laser with a wavelength of 335 nm. ESI mass spectra were measured on a Bruker MicrOTOF system. The signals are described by their mass/charge ratio (m/z) in u.

UV/Vis absorption spectroscopy

UV/Vis absorption spectra were recorded on a JASCO V-770 or a JASCO V-750 with a spectral bandwidth of 1.0 nm and a scan rate of 1000 nm min\(^{-1}\) or on an Agilent Cary 4000 with a spectral bandwidth of 2 nm at a scan rate of 600 nm min\(^{-1}\). Glass cuvettes with an optical length of 1 cm, 1 mm and 0.1 mm and 0.01 mm were used. All measurements were conducted in commercially available solvents in spectroscopic grade.

Emission spectroscopy

Fluorescence emission- and excitation spectra were recorded on a JASCO Spectrofluorometer FP-8500 with an excitation and emission bandwidth of 5.0 nm at a scan rate of 1000 nm min\(^{-1}\) in quartz cuvettes with an optical length of 1 cm.

Additional steady-state excitation and emission spectra were recorded on a FluorTime300 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 µs) with repetition rates of 0.1 – 300 Hz, a double grating excitation monochromator (Czerny-Turner 2.7 nm/mm dispersion, 1200 grooves/mm), 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 double grating 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) with adjustable slit width between 0 mm and 10 mm, Glan-Thompson polarizers for excitation (Xe-lamps) and emission, a Peltier-thermostated sample holder (-40 °C – 105 °C), and two detectors, namely a PMA Hybrid 40 (transit time spread FWHM < 120 ps, 200 – 900 nm) and a H10330C-45-C3 NIR-photomultiplier tube from Hamamatsu. Signal-to-noise ratio (optical noise) typically better than 29000:1, as measured with double monochromators in the excitation and emission light path. Steady-state spectra and fluorescence lifetimes were recorded in TCSPC mode by a PicoHarp300 (minimum base resolution 4 ps) or in MCS mode by a TimeHarp300, where up to several ms can be detected. Emission and excitation spectra were corrected for source intensity (lamp and grating) by standard correction curves. For samples with lifetimes in ns order instrument response function calibration (IRF) was performed using a diluted Ludox\textsuperscript{®} solution. Lifetime analysis was performed using the commercial EasyTau 2 (PicoQuant\textsuperscript{®}) software. The quality of the fit was assessed by minimizing the reduced chi square function (\(\chi^2\)) and visual inspection of the weighted residuals and their autocorrelation.

Phosphorescence lifetime imaging

Microscopy samples were prepared by drop-casting a solution of the respective aggregates onto glass object holder and evaporating the solvent (\(T = 298 K\)).

Phosphorescence lifetime imaging microscopy (PLIM) was performed on a confocal fluorescence microscope (IX 73 from Olympus) with a complete confocal system with a laser combining unit (LCU), inverted microscope body and multichannel detection unit (MicroTime300, PicoQuant) equipped with diode lasers with adjustable output power and repetition rates up to 80 MHz inside a compact fibre couple unit with wavelengths between 375 and 900 nm. For beam diagnostics, a Charge-couple device (CCD) camera and a photodiode were available in the main optical unit (MOU) of the microscope. The MOU was equipped with two detectors, namely a Single Photon Avalanche Diode (SPAD) and a Hybrid-Photomultiplier Tube. Data acquisition was based on the method of Time-Correlated Single Photon Counting (TCSPC) in the unique Time-Tagged Time Resolved (TTTR) measurement mode, where simultaneous data acquisition of two channels were possible. Data were processed and analysed with SymphoTime64\textsuperscript{®} (PicoQuant) software.
In order to allow interface between the MicroTime200 array and the FluoTime 300 spectrometer, a fiber coupler was connected. In this way, the spectrometer can be used to record either steady-state or time-resolved luminescence spectra from a sample mounted in the microscope.

**Photoluminescence quantum yield measurements**

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 and employing U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan).

**FTIR spectroscopy**

All measurements were carried out using a JASCO-FT-IR-6800. Measurements in solution were performed using a CaF$_2$ transmission cell with a path length of 0.1 mm. Measurements in the solid-state (thin films) were performed using a JASCO ATR Pro-One single reflection ATR accessory.

**Atomic force microscopy (AFM)**

Microscopy samples were prepared by drop-casting a solution of the respective aggregates onto HOPG and evaporating the solvent ($T = 298$ K).

The AFM images were recorded on a Multimode®8 SPM System manufactured by Bruker AXS. The used cantilevers were AC200TS by Oxford Instruments with an average spring constant of 9 N m$^{-1}$, an average frequency of 150 kHz, an average length of 200 µm, an average width of 40 µm and an average tip radius of 7 nm. All samples were drop casted or spin-coated at a spin velocity between 2000 and 4000 rpm from freshly prepared solutions onto an HOPG surface.

**Scanning Electron Microscopy (SEM)**

Microscopy samples were prepared by drop-casting a solution of the respective aggregates onto silicon wafer and evaporating the solvent ($T = 298$ K).

SEM images were recorded on a Thermo Fisher Scientific Phenom ProX Desktop SEM. The individual images were recorded with an acceleration voltage between 5 to 15 kV. A backscattered-electron detector (BSD) or a secondary-electron detector (SED) were used. All samples were prepared by drop casting the sample onto Si-wafer surfaces which were then dried under ambient conditions. Length analysis was conducted using the external program ImageJ.

**Gel permeation chromatography (GPC)**

Gel permeation chromatography was performed on a Shimadzu prominence GPC system equipped with a Japan Analytical Industry Co., Ltd. JAIGEL-2HR (20 mm I.D. x 600 mm) with CHCl$_3$ as eluent. The solvent flow was set to be 4 mL/min. Detection was carried out via a Shimadzu prominence SPD-M20A diode array detector (DAD).
Synthesis and Characterization

The pyridine-based oligo(phenylene-ethynylene) (OPE) ligand \( \text{L} \) with a bisamide-appended peripheral solubilizing moiety was synthesized according to a previously published protocol (Scheme S1).\(^{16}\) Complex 1 was synthesized according to a standard complexation protocol from the corresponding ligand and bis(benzonitrile)dichloroplatinum(II) in chloroform at 70 °C.

**Scheme S1.** Synthesis of ligand \( \text{L} \) and complex 1.

**Complex 1**

3,4,5-tris(dodecyloxy)-N-[2-(4-pyridin-4-ylethynyl)benzamido]ethyl]benzamide \( \text{L} \) (40.8 mg, 43.4 µmol, 2.0 eq.) and bis(benzonitrile)dichloroplatinum(II) \( \text{Pt(NCPh)}_2\text{Cl}_2 \) (10.0 mg, 21.7 µmol, 1.0 eq.) were placed in a Schleck tube and 2 mL of chloroform were added. The reaction mixture was stirred at 70 °C for five days. Subsequently, the reaction solution was filtered through a 0.2 µm PTFE syringe filter and was directly subjected to purification by means of gel permeation chromatography (eluent CHCl\(_3\)). After evaporation of the solvent in vacuo, the product was obtained as a pale-yellow solid (39.0 mg, 18.5 µmol, 85.2 %).

**\(^{1}\)H NMR** (CDCl\(_3\), 600 MHz) \( \delta \) (ppm) = 8.89 (AA’XX’, 4H, H\(^1\)), 7.84 (m, 4H, H\(^4\)), 7.57 (m, 6H, H\(^3\)+NH\(^5\)), 7.34 (AA’XX’, 4H, H\(^2\)), 7.12 (m, 2H, NH\(^8\)), 7.00 (s, 4H, H\(^9\)), 3.99 (m, 12H, OCH\(_2\)), 3.69 (m, 8H, N-CH\(_2\)-CH\(_2\)-N), 1.79 (qui, \(^3\)J\(_{HH}\) = 7.3 Hz, 8H, C\(^1\)H\(_2\)), 1.73 (qui, \(^3\)J\(_{HH}\) = 7.3 Hz 4H, C\(^2\)H\(_2\)), 1.45 (m, 12H, C\(^3\)H\(_2\)), 1.30 (m, 96H, C\(^4\)H\(_2\)-C\(^{11}\)H\(_2\)), 0.87 (t, \(^3\)J\(_{HH}\) = 6.9 Hz, 18H, C\(^{12}\)H\(_3\)).

**\(^{13}\)C NMR** (CDCl\(_3\), 151 MHz) \( \delta \) (ppm) = 169.00, 167.40, 153.29, 153.11, 141.27, 134.79, 133.64, 132.25, 128.57, 127.29, 126.92, 124.43, 105.59, 96.97, 87.23, 73.52, 69.26, 61.46, 40.73, 31.92, 31.91, 30.31, 29.73, 29.72, 29.71, 29.69, 29.65, 29.63, 29.57, 29.40, 29.37, 29.35, 29.31, 29.26, 26.09, 26.06, 22.67, 14.10, 14.09.

**HR-MS** (ESI-Orbitrap, CHCl\(_3\)/MeOH): calculated for C\(_{120}\)H\(_{182}\)N\(_6\)O\(_{10}\)Cl\(_2\)Pt\(^2\)\(^{[M+2H]^{2+}}\): 1056.1556; found: 1056.1574.
Figure S29. $^1$H NMR (CDCl$_3$, 600 MHz) spectrum of complex 1.

Figure S30. $^{13}$C NMR (CDCl$_3$, 151 MHz) spectrum of complex 1.
Author Contributions

G.F. and J.M. conceived the project. J. M. performed the majority of the experiments and wrote the initial manuscript draft. I.M. conducted emission lifetime and quantum yield measurements, additional excitation & emission studies, as well as PLIM measurements. C.A.S. assisted in evaluation and interpretation of the photophysical studies. G.F. supervised the project and revised the manuscript, data and images. All authors were involved in the finalization of the manuscript.

References

[1] H.-Y. Chao, W. Lu, Y. Li, M. C. W. Chan, C.-M. Che, K.-K. Cheung, N. Zhu, J. Am. Chem. Soc. 2002, 124, 14696.
[2] N. Bäumer, K. K. Kartha, S. Buss, I. Maisuls, J. P. Palakkal, C. A. Strassert, G. Fernández, Chem. Soc. 2021, 12, 5236.
[3] a) M. Textor, W. Ludwig, Helv. Chim. Acta 1972, 55, 184; b) N. Bäumer, K. K. Kartha, N. K. Allampany, S. Yagai, R. Q. Albuquerque, G. Fernández, Angew. Chem. Int. Ed. 2019, 58, 15626.
[4] S. Ogi, V. Stepchenkof, J. Thein, F. Würthner, J. Am. Chem. Soc. 2016, 138, 670.
[5] a) M. H.-Y. Chan, M. Ng, S. Y.-L. Leung, W. H. Lam, V. W.-W. Yam, J. Am. Chem. Soc. 2017, 139, 8639; b) V. C.-H. Wong, C. Po, S. Y.-L. Leung, A. K.-W. Chan, S. Yang, B. Zhu, X. Cui, V. W.-W. Yam, J. Am. Chem. Soc. 2018, 140, 657; c) M. E. Robinson, A. Nazemi, D. J. Lunn, D. W. Hayward, C. E. Boot, M.-S. Hsiao, R. L. Hamiman, S. A. Davis, G. R. Whittle, R. M. Richardson, L. de Cola, I. Manners, ACS Nano 2017, 11, 9162; d) G. Moreno-Alcántar, A. Allprandi, R. Rouquette, L. Peske, K. Wurst, C. Pereg, P. Brüggheller, G. M. Pavan, L. de Cola, Angew. Chem. Int. Ed. 2021, 60, 5407; e) Q. Wan, W.-P. To, X. Chang, C.-M. Che, Chem 2020, 6, 945; f) Q. Wan, W.-P. To, C. Yang, C.-M. Che, Angew. Chem. Int. Ed. 2018, 57, 3089; g) Z. Li, Y. Han, Z. Gao, F. Wang, ACS Catal. 2017, 7, 4676; h) S. Chatahahali Gangadhararappa, I. Maisuls, I. P. Salto, S. Niemann, V. Bachtin, F. C. Herrmann, C. A. Strassert, J. Phys. Chem. C 2021, 125, 5739; i) I. Maisuls, C. Wang, M. E. Gutiérrez Suburu, S. Wilde, C.-G. Daniliuc, D. Brünink, N. L. Doltsinis, S. Ostendorp, G. Wilde, J. Kösters, U. Resch-Genger, C. A. Strassert, Chem. Sci. 2021, 12, 3270; j) C. A. Strassert, C.-H. Chien, M. D. Galvez Lopez, D. Koukoulos, D. Herpel, K. Meierholz, L. de Cola, Angew. Chem. Int. Ed. 2011, 50, 946; k) M. Mydlak, M. Mauro, F. Polo, M. Felcetti, J. Leonhardt, G. Diener, L. de Cola, C. A. Strassert, Chem. Mater. 2011, 23, 3659.
[6] A. Allprandi, M. Mauro, L. de Cola, Nat. Chem. 2015, 8, 10.
[7] a) B. H. Stuart, Infrared Spectroscopy: Fundamentals and Applications, John Wiley & Sons, Chichester 2004, p. 72; b) G. Fernández, F. García, F. Aparicio, E. Matesanz, L. Sánchez, Chem. Commun. 2009, 7155.
[8] a) P.-T. Chou, Y. Chi, M.-W. Chung, C.-C. Lin, Coord. Chem. Rev. 2011, 255, 2653; b) V. Balzani, S. Campagna, A. Barbieri (Eds.) Photochemistry and Photophysics of Coordination Compounds II, Springer, Berlin, Heidelberg 2007.
[9] N. Bäumer, K. K. Kartha, S. Buss, J. P. Palakkal, C. A. Strassert, G. Fernández, Org. Chem. Front. 2021, 8, 4138.
[10] A. Sillen, Y. Engelborghs, Photochem. Photobiol. 1998, 67, 475.
[11] a) H. M. M. ten Eikelder, A. J. Markvoort, T. F. A. de Greef, P. A. J. Hilbers, F. T. de Greef, E. W. Meijer, Nat. Commun. 2011, 2, 509.
[12] a) J. J. P. Stewart, J. Mol. Model. 2013, 19, 1; b) J. Rezác, K. E. Riley, P. Hobza, J. Chem. Theory Comput. 2012, 8, 4285.
[13] J. J. P. Stewart 2016, Stewart Computational Chemistry, MOPAC2016 Version 19.206L, Colorado Springs, CO, USA.
[14] L. N. J. de Windt, C. Kulkarni, H. M. M. ten Eikelder, A. J. Markvoort, E. W. Meijer, A. R. A. Palmons, Macromolecules 2019, 52, 7430.
[15] a) Y. Tidhar, H. Weissman, S. G. Wolf, A. Gulino, B. Rybtchinski, Chem. Eur. J. 2011, 17, 6068; b) I. Helmers, N. Bäumer, G. Fernández, Chem. Commun. 2020, 56, 13808.
[16] J. Matern, Z. Fernandez, N. Bäumer, G. Fernandez, Angew. Chem. Int. Ed. 2022, e202203783.

SUPPORTING INFORMATION