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¹ Investigating the Impact of Packing and Environmental Factors on ² the Luminescence of Pt(N^N^N) Chromophores

3 Guillermo Romo-Islas, Sergi Burguera, Antonio Frontera,* and Laura Rodríguez*

Cite This: https://doi.org/10.1021/acs.inorgchem.3c04562 **Read Online** ACCESS III Metrics & More Article Recommendations Supporting Information 4 ABSTRACT: Four Pt(II)(N^N^N) compounds featuring DMSO 5 coordination at the fourth position were synthesized. Ligands 6 varied in terms of pyridyl central ring (hydrogen/chlorine enhanced 7 substituent) and lateral rings (triazoles with CF₃ substitution or 8 tetrazoles). Coordination to pyridine yielded tetra-nitrogen +PV 9 coordinated Pt(II) complexes or Pt-functionalized polymers 10 using commercial 4-pyridyl polyvinyl (PV) or dimethylaminopyrluminescence 11 idine. Luminescence behaviors exhibited remarkable environmental 12 dependence. While some of the molecular compounds (tetrazole 13 derivatives) in solid state displayed quenched luminescence, all the

15 versely, monomer emission was evident on poly(methyl methacrylate) or polystyrene matrices. DFT calculations were used to 16 analyze the aggregation of the complexes both at the molecular level and coordinated to the PV polymer and their influence on the 17 HOMO-LUMO gaps.

18 INTRODUCTION

¹⁹ The research on metal-containing polymers and, in particular, ²⁰ metallopolymers, refer to a fascinating category of functional ²¹ soft materials, in the field of polymer and materials science. ²² These systems are composed of polymeric chains, metal ²³ centers, and/or metal-related segments¹⁻⁶ with specific roles ²⁴ suitable to provide a new dimension in several fields such as ²⁵ emissive materials, photovoltaics, electrochromic devices, ²⁶ sensors, nanowires, memory devices, catalysts, or memory ²⁷ and data storage.⁷⁻¹² The presence of metal centers into the ²⁸ metallopolymers is particularly relevant to attain phosphor-²⁹ escent materials for a variety of photonic applications.¹³⁻¹⁶

14 polymers exhibited ³MMLCT emission around 600 nm. Con-

The design and synthesis of coordination polymers, where 30 31 the metal centers coordinated to specific ligands in a polymeric 32 chain (being the metal part of the polymeric structure), has 33 been extensively explored.^{1-4,11} Nevertheless, the introduction 34 of metallic chromophores as side pending chains within an 35 organic polymer is less explored and even less, the particular 36 use of metal centers suitable to establish metal…metal 37 interactions, playing particular roles in the 2D and 3D 38 structure of metallopolymers or metal coordinating polymers 39 and also in the resulting emissive properties. Regarding this, 40 poly(4-vinylpyridine), PV, is a very good option due to the 41 presence of pyridyl pending groups, suitable for coordination 42 to a large number of metals and for this reason, it has been 43 used as support of metal-containing polymers, metal nano-⁴⁴ particles, or metal films with several applications such as ⁴⁵ (photo)sensing or catalysis.^{16–18} Nevertheless, the coordina-46 tion of specific metals well-known to establish metallophilic 47 contacts is scarcely explored. $^{17-20}$ The use of these metals is of

great importance regarding the development of luminescent 48 materials since the resulting photophysical properties are 49 strongly affected by the interplay of different noncovalent 50 interactions such as M···M but also hydrogen bonding, $\pi - \pi$ 51 stacking or halogen bonding, among others.^{21–25} Platinum(II), 52 with d^8 configuration, is one of the most studied metals 53 suitable for metallophilic contacts and with relevant emissive 54 properties. The involvement of several intra- and intermo- 55 lecular contacts has resulted in the modulation of the intrinsic 56 luminescence that can be tuned on energies (emission 57 wavelength), intensities (quantum yields), or lifetimes (from 58 a few ns to hundreds of microseconds). The establishment of 59 Pt…Pt interactions induces the formation of aggregates and 60 ³MMLCT phosphorescence emissions or excimeric transi-₆₁ tions.²⁶⁻³⁰ As expected, the establishment of this type of weak ₆₂ interactions is much more favorable if the Pt(II) moieties are 63 located as pendant arms.³¹⁻³⁴ For this reason, the develop- 64 ment and understanding of how supramolecular weak 65 interactions can affect both the packing and the resulting 66 applications as photonic materials is of great relevance and 67 deserves its investigation. In this sense, DFT calculations are 68 convenient to analyze the ability of molecules to aggregate and 69

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70 in the particular case of Pt-complexes, the formation of 71 metallophilic interactions.

Taking all of this into consideration, in this work we have 73 developed new Pt(II) systems containing different tridentate 74 N^N^N ligands as chromophoric units. These Pt(N^N^N) 75 moieties have been coordinated to a pyridyl group included as 76 pendant side in two different polymers (giving rise to the 77 formation of luminescent platinum(II) metallopolymers) and 78 to pyridyl ligands as model compounds. The chemical 79 environment of the Pt(II) systems that differ on specific 80 chemical modifications on the ligands (both on steric and 81 electronic point of view) has been analyzed experimentally and 82 theoretically to understand their role on the resulting packing 83 and photophysical properties.

84 **RESULTS AND DISCUSSION**

f1

Synthesis and Characterization. The development of the Pt(II) functionalized polymers requires the previous synthesis of the $Pt(II)(N^N^N)$ precursors (Figure 1),



Figure 1. [Pt(DMSO)L] complexes used for the synthesis of the Pt(II)-functionalized polymers.

⁸⁸ containing a labile ligand at the fourth coordination position ⁸⁹ (DMSO). These compounds were obtained based on the ⁹⁰ previous synthetic procedure where the corresponding ⁹¹ N^N^N H₂L ligands $(H_2L^1-H_2L^4)$ reacted with the ⁹² PtCl₂(DMSO)₂ complex.²⁶

As it is displayed in Figure 1, four different types of N^N^N 93 94 H₂L ligands have been used in this work that differ on the $_{95}$ lateral rings being the CF₃-substituted triazoles, previously $_{96}$ reported in the literature, $_{26,35}^{26,35}$ (Figure 1 left) and tetrazoles 97 (Figure 1 right). At the same time, the compounds differ on 98 the *p*-substituted group of the central pyridyl ring that can be a 99 H atom $(H_2L^1 \text{ and } H_2L^3)$ or Cl $(H_2L^2 \text{ and } H_2L^4)$. The 100 tetrazole ligands H_2L^3 and H_2L^4 were synthesized by a 101 modification of the procedure described in the literature.^{36,37} 102 That is, the corresponding dicyanopyridine and NaN_3 (2.5 103 equiv) reacted in DMF at 110 °C and using L-proline (0.3 104 equiv) as a catalyst. After 2 h of stirring, the reaction mixture 105 was then allowed to cool down to room temperature and was 106 poured into ice (15 mL) under stirring and then acidified with 107 HCl(c). The mixture was stirred vigorously to obtain the 108 desired product as a white (H_2L^3) or brownish H_2L^4) 109 precipitate in the reaction media (Scheme 1). The ¹H NMR 110 spectra of the ligands show a *ca*. 0.5 ppm downfield shift of the 111 central pyridyl protons with respect to the 2,6-dicyanopyridine 112 precursors. The well-defined band in the IR spectra centered 113 between 3580 and 3415 cm⁻¹ corresponding to the (N-H) 114 vibration and the molecular peak recorded in the mass spectra 115 were final evidence of the correct formation of the desired 116 products.





The four [Pt(DMSO)L] compounds were reacted with two 117 different commercially available pyridyl-functionalized poly- 118 mers 4-(dimethylamine)pyridine, dimethylaminopyridine 119 (DMAP)-containing polymer (an average of 3.0 mmol pyridyl 120 units per gram), and poly(4-vinylpyridine), PV (average MW 121 ~ 60 000) where the labile DMSO ligand leaves the Pt(II) $_{122}$ environment in the presence of the pyridyl group of the 123 polymer by the establishment of the new Pt-py bonds (Scheme 124 s2 2). There are clear differences between the two of them: while 125 s2 the PV polymer is completely functionalized by pending 126 pyridyl groups, the DMAP polymer is a $\sim 3.0 \text{ mmol/g DMAP}$ 127 loading, matrix cross-linked with 2% DVB. That is, the number 128 of coordination sites on the DMAP polymer is much lower 129 than that in the PV. This should affect the resulting 130 luminescent properties of the resulting functionalized poly- 131 mers. 132

The reactions were carried out in acetonitrile under reflux 133 for 18 h. An excess of the platinum complex was required to 134 complete the reaction in the DMAP derivatives, with lower 135 degree of pyridyl pending functionalization. The polymer was 136 insoluble in this medium but a color change in the solid 137 suspended in the reaction mixture was observed in all cases 138 after this time, being direct evidence of the formation of a new 139 insoluble product. The purification of the resulting solids was 140 carried out by filtration and washing with DMSO/EtOH, in 141 order to remove the possible traces of noncoordinated Pt(II) 142 precursors, giving the desired Pt(II)-functionalized polymers in 143 moderate-high yields (*ca.* 65-87%).

To better understand both the packing and the properties of 145 the Pt(N^N^N) functionalized-polymers, we decided to 146 synthesize the analogous Pt(N^N^N)-pyridyl compounds 147 containing 4-dimethylamino pyridine and 4-methylaminopy- 148 dine in the fourth coordination position, previously occupied 149 by the pyridyl unit of the polymers. For this goal, the 150 [Pt(DMSO)L] compounds were reacted with the correspond- 151 ing pyridyl ligand in a 1:1 stoichiometry in acetonitrile under 152 reflux for 18 h (Scheme 3).^{38,39} The purification by 153 s3 recrystallization with dichloromethane/hexane gave the desired 154 compounds moderate-high yields (*ca.* 42–84%). 155

The correct formation of the desired systems has been 156 clearly evidenced by ¹H NMR and mass spectrometry (for the 157 molecular compounds $1-4A_{J}B$). IR spectroscopy and powder 158 X-ray diffraction were carried out for all the systems since the 159 insolubility of the polymers precludes their characterization by 160 the previous techniques.

The ¹H NMR spectra of the final products exhibit the ¹⁶² presence of the corresponding protons of the pyridyl groups ¹⁶³ that are 0.12–0.89 ppm upfield shifted with respect to the free ¹⁶⁴ pyridine precursor. The signals corresponding to the $-CF_3$ ¹⁶⁵ moieties are also detected in the ¹⁹F NMR spectra of ¹⁶⁶ corresponding compounds and their IR spectra with a well- ¹⁶⁷ defined band between 1183 and 1061 cm⁻¹ corresponding to ¹⁶⁸ the ν (C–F). The final evidence of the correct formation of the ¹⁶⁹ compounds has been detected in the high-resolution mass ¹⁷⁰ spectra with the identification of the $[M + H^+]$ or $[M + Na^+]$ ¹⁷¹

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Scheme 2. Synthesis of the Pt(N^N^N)-Functionalized Polymers







172 molecular peaks. The IR spectra of the Pt(II) compounds 173 coordinated to the polymers all exhibit a similar behavior (see 174 Supporting Information). All the functionalized polymers 175 display shifts about 53-31 cm⁻¹ of the -N=N bond from 176 the N^N^N ligands compared to these vibrations in the $_{177}$ [Pt(DMSO)L] precursors, together with the presence of the 178 - CF₃ vibration bands (for the triazole functionalized 179 polymers) that are not detected in the free DMAP or 4-pyridy $_{180}$ polyvinyl polymers. The -C=N vibration of the pyridine is 181 observed in all cases better defined (less broad) in the 182 functionalized-polymers compared to the polymer precursors, due to the coordination to the Pt(II) moieties.⁴⁰⁻⁴² X-ray 183 diffraction analyses of the powders were carried out for both 184 185 the functionalized polymers and their precursors, the 186 uncoordinated DMAP and PVP polymers, and the molecular 187 compounds 1–4A,B.

The diffraction spectra of the initial polymers, DMAP and 189 PVP, exhibit a broad band ranging from 15 to 25°, which can 190 be attributed to the low crystallinity of the material, consistent 191 with prior research findings.^{18,43,44} Improved organization, 192 indicating higher crystallinity, is evident in the functionalized 193 polymers, particularly when compared to the powders of the 194 isolated molecules 1–4A,B (see Figure 2). The highest level of 195 organization is observed in systems derived from N^N^N 196 ligands L2 and L3, primarily influenced by the presence of 197 Pt(II) metal moieties, aligning with established literature.⁴⁵

 f_2



Figure 2. DRX spectra of 2A, 2-DMAP, and 2-PV showing the better crystallinity of the functionalized polymers.

Photophysical Characterization. All compounds and 198 Pt(N^N^N)-functionalized polymers were characterized from 199 photophysical point of view. None of the compounds were 200 t1

²⁰¹ significantly luminescent in solution, and thus, all the data ²⁰² presented herein are based on the solid state and it is ²⁰³ summarized in Table 1. The commercial DMAP and PV ²⁰⁴ polymers were also not luminescent.

Table 1. Photophysical Data of Pt(N^N^N)-Functionalized Polymers and Analogous Pt(N^N^N) Complexes

complay	λ_{max} Em	đ	σ (με)	$k_{r}(\times 10^{5})$	$k_{nr} (\times 10^5 c^{-1})$	k k
complex	(IIII)	Ψ	ι (μ s)	8)	5)	$\kappa_{\rm nr}/\kappa_{\rm r}$
1- DMAP	585	0.02	$\begin{aligned} \tau_1 &= 0.1 \ (42.19) \\ \tau_2 &= 0.5 \ (57.81) \end{aligned}$	0.6	31.4	52
1-PV	594	0.07	$\begin{aligned} \tau_1 &= 0.1 \ (67.39) \\ \tau_2 &= 0.6 \ (32.61) \end{aligned}$	2.4	34.9	15
2- DMAP	595	0.01	$\begin{aligned} \tau_1 &= 0.2 \ (45.01) \\ \tau_2 &= 0.9 \ (54.99) \end{aligned}$	0.2	17.2	86
2-PV	583	0.01	$\tau_1 = 0.1 (31.57) \tau_2 \\= 1.4 (68.43)$	0.1	9.8	98
3- DMAP	558	0.03	$\begin{array}{l} \tau_1 = 0.1 \ (49.28) \\ \tau_2 = 0.6 \ (50.72) \end{array}$	0.9	27.4	30
3-PV	568	0.03	$\begin{aligned} \tau_1 &= 0.1 \; (37.56) \\ \tau_2 &= 0.6 \; (64.44) \end{aligned}$	0.8	23.3	29
4- DMAP	572	0.01	$\begin{array}{l} \tau_1 = 0.1 \ (36.30) \\ \tau_2 = 0.9 \ (63.70) \end{array}$	0.1	16.1	161
4-PV	583	0.01	$\begin{aligned} \tau_1 &= 0.1 \; (36.33) \\ \tau_2 &= 0.9 \; (63.67) \end{aligned}$	0.2	16.0	80
1A	494, 585	0.01	$\begin{array}{l} \tau_1 = 0.1 \ (21.87) \\ \tau_2 = 0.7 \ (78.13) \end{array}$	0.2	14.3	72
1B	573	0.02	$\begin{aligned} \tau_1 &= 0.1 \ (45.52) \\ \tau_2 &= 0.4 \ (54.48) \end{aligned}$	0.5	35.2	70
2A	587	0.02	$\begin{array}{l} \tau_1 = 0.1 \ (35.99) \\ \tau_2 = 0.4 \ (64.01) \end{array}$	0.5	25.8	52
2B	596	0.01	$\begin{array}{l} \tau_1 = 0.1 \ (42.79) \\ \tau_2 = 0.2 \ (57.21) \end{array}$	0.9	65.8	73

The emission spectra of all the systems were recorded at room temperature upon excitation the samples at 450 nm. A provide a to 207 broad emission band between 500 and 600 nm is recorded in 208 all cases that is attributed to ³MMLCT transition based on

previous reports with similar $Pt(N^N^N)$ com- 209 pounds.^{26,31,46-50} This means that some kind of aggregation/ 210 intermolecular packing should be expected in all cases. An ³IL 211 contribution is also observed only in the case of **1A** with the 212 presence of a vibronic resolution band at higher energies⁵¹ 213 overlapped with the previous one, due to the possibility of 214 several metal environments or different numbers of M···M 215 interactions.²⁰ 216

Additionally, some differences can be observed in the 217 photophysical properties of the triazoles and tetrazoles 218 derivatives. First of all, tetrazole derivatives (compounds 3 219 and $4A_{,B}$) are not emissive in their molecular form but their 220 analogous functionalized polymers are. This can be due to the 221 different HOMO-LUMO transition, as predicted by TD-DFT 222 calculations for 3A and 4A (see below) and to a probable more 223 efficient packing in the solid state that can cause aggregation 224 caused quenching (ACQ). The emission of the Pt-function- 225 alized systems containing the triazole L^1 and L^2 ligands is ca. 226 20 nm red-shifted compared to those containing the tetrazole 227 L^3 and L^4 ligands. On the other hand, a *ca*. 10 nm emission 228 red-shift is observed for compounds containing X=Cl 229 compared to their analogous with X=H (Figure 3). 230 f3 Additionally, the Pt-functionalized systems derived from the 231 PV polymer also display an emission red-shift with respect to 232 the DMAP functionalized polymers. This can be due to the 233 very well distribution and closer proximity of the Pt(N^N^N) 234 moieties in the former polymer that would make a more 235 favored aggregates' emission and corresponding red-shift (see 236 below DFT studies). 237

Finally, we can observe a more efficient emission (higher $_{238}$ quantum yield) for the compounds with X=H compared to $_{239}$ their corresponding containing X=Cl (being 1-PV the most $_{240}$ efficient one) that present more favored nonradiative $_{241}$ deactivation pathways in the polymers (larger $k_{\rm nr}/k_{\rm r}$ values, $_{242}$ Table 1).



Figure 3. Emission spectra of the Pt(N^N^N) complexes and respective functionalized polymers in the solid state, being A) for L¹-derivatives; B) L²-derivatives; C) L³- and L⁴-derivatives. $\lambda_{exc} = 450$ nm.



Figure 4. Emission spectra of the emissive $Pt(N^N^N)$ complexes within PMMA and PS matrices and comparison with the corresponding spectra of the compound in the solid state, being A) for **1A**; B) for **1B**; C) for **1C**; C) for **1D**. $\lambda_{exc} = 380$ nm.

Table 2. Photophysical Data of Compounds 1-2A, D Dispersed in PhilviA and P	Table	2.	Photo	physica	ıl Data	of	Com	pounds	1-2A,B	b Dis	persed	in	PMMA	and	P
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compound	$\lambda_{\rm max}$ Em (nm) PMMA	ϕ PMMA	$ au$ (μ s) PMMA	$\lambda_{\rm max}$ Em (nm) PS	ϕ PS	$ au$ (μ s) PS
1A	461, 488	0.20	$\tau_1 = 1.0 (50.66) \tau_2 = 4.4 (49.34)$	464, 493	0.33	$\tau_1 = 0.9 \ (65.03) \ \tau_2 = 3.6 \ (34.97)$
1B	462, 491	0.04	$\tau_1 = 0.1 \ (45.52) \ \tau_2 = 0.4 \ (54.48)$	466, 494	0.12	$\tau_1 = 0.1 \ (45.52) \ \tau_2 = 0.4 \ (54.48)$
2A	463, 490	0.08	$\tau_1 = 0.9 \ (41.42) \ \tau_2 = 3.8 \ (58.58)$	465, 494	0.11	$\tau_1 = 0.1 \ (47.93) \ \tau_2 = 0.6 \ (52.07)$
2B	464, 493	0.06	$\tau_1 = 1.0 (49.84) \tau_2 = 5.2 (50.16)$	467, 495	0.12	$\tau_1 = 0.9 (55.23) \tau_2 = 4.3 (44.77)$

The recorded photophysical data let us suspect that the 244 packing is a key point on the resulting emissive properties of 245 our $Pt(N^N)$ complexes. According to this, largest packing 246 (solid state) produces ACQ effect while a better alignment of 247 248 the molecules (as further studied below), thanks to their 249 coordination to a polymer, improves their resulting emission. 250 An intermediate situation would be doping organic matrices, such as poly(methyl methacrylate) (PMMA) or polystyrene 251 252 (PS). Based on our previous experience, the dispersion of 253 luminophores within this type of matrices may improve their emission properties regarding emission quantum yields and 254 lifetimes.^{23,52-54} The recorded emission spectra indicate that 255 256 the intermolecular packing, responsible for the resulting MMLCT emission is observed to be not favored in these 257 258 media while the ³IL monomer is the emissive species instead 259 (Figure 4 and Table 2). Vibronically structured bands are 260 herein displayed due to a well distribution of the molecules within the thin film media, and they present, as expected, 261 262 higher emission quantum yields and larger emission lifetimes.² The recorded emission lifetimes show biexponential decays 263 probably ascribed to the different environments of the 2.64 265 molecules within the films.

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DFT Analysis of the Aggregation. The planarity and large aromatic surfaces present in the complexes may favor the formation of aggregates in solution and solid state. We have 268 studied this theoretically by comparing the relative ability of 269 these complexes to form self-assembled dimers and how the 270 formation of these dimers affects the HOMO–LUMO levels 271 and consequently their luminescent properties. In addition, the 272 presence of metallophilic Pt…Pt interactions in the dimers has 273 been also analyzed and correlated with the experimental 274 findings. 275

As starting point, the molecular electrostatic potential 276 (MEP) surfaces of all compounds have been computed to 277 study the most electron rich and poor regions of the molecules 278 and the π -acidity/basicity of the π -clouds. The MEP surfaces of 279 compounds **1A,B** and **2A,B** are given in Figure 5 and those of 280 fs **3A,B** and **4A,B** in Figure 6. It can be observed that the MEP 281 f6 minima and maxima are located at the molecular plane, being 282 the maximum values at the NMe₂ group in the A-series and 283 between the methyl group and the adjacent aromatic H atom 284 in the B-series. The values range between 28 and 38 kcal/mol. 285 The MEP minima are located at the N atoms of the triazole 286 (Figure 5) or tetrazole (Figure 6) derivatives, being the MEP 287 values more negative for the latter (-39 to -43 kcal/mol). 288

In all compounds, the MEP values at the aromatic rings are $_{289}$ relatively small, thus favoring the π -stacking interactions (small $_{290}$ electrostatic repulsion). Moreover, the MEP values at the Pt- $_{291}$



Figure 5. MEP surfaces of compounds 1A (a), 1B (b), 2A (c), and 2B (d) at the PBE0-D4/def2-TZVP level of theory. The values at the minimum, maximum, and selected points are given in kcal/mol. Density isovalue 0.001 au.



Figure 6. MEP surfaces of compounds 3A (a), 3B (b), 4A (c), and 4B (d) at the PBE0-D4/def2-TZVP level of theory. The values at the minimum, maximum, and selected points are given in kcal/mol. Density isovalue 0.001 au.

292 atoms are very small, also favoring the dispersion-dominated 293 metallophilic interactions.

For all compounds reported herein, the π -stacked dimers provide by using three different arrangements, which are parallel, antiparallel, and 90° rotated. The geometries for two exemplifying dimers are given in Figure 7 (1A and 4B and the rest in Figures S79 and S80). In general, the dimers of 298 the A series present longer metallophilic distances in line with 299 the more negative MEP values at the Pt(II)-atom. The triazole 300 dimers of **2A** and **2B** (Cl-substituted pyridine in tridentate 301 ligand) present shorter (or equivalent in some cases) distances 302 compared to **1A** and **1B** dimers (unsubstituted pyridine in 303 tridentate ligand) that aligns with the more efficient emission 304 of the latter. A similar result is also observed for the tetrazole 305 dimers, where the Cl-substituted ones. The metallophillic 307 distance variation within the dimers is more significant in the 308 triazole series, where the 90° rotated is shorter, that can be 309 related to the steric hindrance caused by the $-CF_3$ groups that 310 is minimized in the 90° rotated dimers.

The energetic features of the dimers of all compounds are 312 gathered in Table S1, in the gas phase and acetonitrile and 313 water solutions and briefly commented herein. In the gas 314 phase, the 90° rotated dimers are more favored that the other 315 two, however the differences become much smaller in the 316 presence of solvent, thus suggesting that the aggregation of the 317 complexes in solution leads to a mixture of all possible 318 conformations. Although the energy differences are small in 319 solution, some trends can be extracted from the inspection of 320 the results. First, the aggregation is more favored in water than 321 in acetonitrile in all cases. Second, the triazole derivatives have 322 more tendency to aggregate than the tetrazole ones, in spite of 323 having the CF₃ group likely due to additional van der Waals 324 $(C-F\cdots F-C)$ or $CH\cdots F$ contacts. The Cl substituent does not 325 have a noticeable influence on the interaction energies. The 326 energies have also been computed using unrestricted 327 calculations (UKS), providing similar tendencies but stronger 328 binding energies see Table S2. 329

The influence of aggregation on the HOMO-LUMO gaps 330 has also been investigated. Table S3 gathers the gaps for the 331 monomers and the dimers in all three orientations. In all cases, 332 the aggregation caused a reduction of the HOMO-LUMO 333 gap, ranging from 0.1 to 0.6 eV, depending on the orientation 334 and solvation. It is important to note that TD-DFT 335 calculations demonstrate (see theoretical methods for further 336 details) that the $S_0 \rightarrow S_1$ excitation corresponds to a HOMO 337 \rightarrow LUMO transition (~97%) in the monomers. A similar 338 behavior is observed in the dimers, where the HOMO \rightarrow 339 LUMO is also dominant (~85%). The HOMO-LUMO plots 340 of 1A are given in Figure 8 as a representative example and the 341 f8 rest in the Supporting Information (Figure S81). In 1A, the π - 342 system of the tridentate ligand and the metal center are 343 important contributors to the HOMO, while in the LUMOs, 344 the contribution of the metal is negligible. Therefore, this 345 transition can be considered as a mixture of MLCT and 346 intraligand CT. This explains the influence of the dimer 347 formation on the HOMO and LUMO energies (see Table S3). 348 The HOMO and LUMO plots are similar in the parallel dimer 349 of 1A (Figure 8c,d) compared to the monomer. It is interesting 350 to highlight that for compounds 3A and 4A, the HOMO is 351 located in the pyridine ligand instead of the tridentate ligand 352 (Figure S81), as observed in 1A and 2A. This can be related to 353 the lack of luminescence recorded for the tetrazole 354 compounds. 355

Furthermore, Figure 9 presents the natural transition orbitals 356 f9 (NTOs) for the dimer of 1A, accounting for 96% of the 357 transition. NTOs provide a more simplified and chemically 358 meaningful representation of orbital transitions in an excited 359 state compared to canonical MOs. The spatial distribution 360

f7



Figure 7. Perspective views of the PBE0-D4/def2-TZVP optimized geometries of the dimers 1A parallel (a), antiparallel (b), and 90° rotated (c) and 4B parallel (d), antiparallel (e), and 90° rotated (f). The Pt…Pt interactions are given in Å. Pt are represented as gray spheres and the rest of the molecule in "tube" format.



Figure 8. HOMO and LUMO plots of 1A (a,b) and the parallel dimer of 1B (c,d).

361 depicted in the NTOs strongly suggests a metal-to-ligand 362 charge transfer. Specifically, the occupied NTO (hole) is 363 primarily associated with the d_22 atomic orbitals of Pt(II), 364 while the unoccupied orbital embraces the π -system of the 365 aromatic ring. This pronounced charge transfer could 366 potentially enhance intersystem crossing to triplet states, 367 consistent with the observed red-shift and the ³MMLCT 368 emission in our experiments. It is noteworthy to mention that 369 emission assignments for Pt(II) compounds are well-under-370 stood, having been rigorously investigated both experimentally 371 and theoretically, as evidenced by several studies in the 372 literature.^{51,55–57}

Two functionalized PV polymers (1-PV and 3-PV) have modeled in order to rationalize the influence of the substrate immobilization on the luminescence properties. For rot the optimization, a tetrameric part was fully optimized at the RI-BP86-D4/def2-TZVP level of theory and then this unit was



Figure 9. Natural transition orbitals (NTOs) for the dimer of compound 1A illustrating the nature of the singlet excited state. The transition energy (eV) and the oscillator strength are also indicated. Shown are only occupied (hole) and unoccupied (electron) NTO pair that contributes more than 97% to the S_1 excited state.

used to generate the oligomer (12 units) shown in Figure 10 378 f10 for 1-PV and Figure S82 for 3-PV. For the calculations, we 379 have considered that all the pyridine residues of the polymer 380 are coordinated to Pt(N^N^N), although the real system most 381 likely has vacant positions. The examination of the geometry 382 suggests that the well-aligned parallel dimers are formed in the 383 polymer, in line with the improved emission of the polymers. It 384 seems that the formation of larger π - π aggregates within the 385 polymer is difficult, since the Pt…Pt distance between two 386 consecutive dimers is around 6.7 Å. Therefore, the effect of the 387 coordination to the PV seems to be generation of a large 388

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Figure 10. (a) Representation of the oligomer 1-PV. (b) Detail of the tetramer showing the formation of parallel π -stacked dimers. Distances in Å.

389 number of well-defined parallel dimers. Furthermore, the initial 390 coordination of a pyridyl group in the polymer with 391 Pt(N^NN) most likely assists, through π -stacking inter-392 actions, the functionalization of adjacent pyridyl moieties 393 (specifically those in the 1, 5 relative position relative to the 394 aliphatic chain). This mechanism could enhance the formation 395 of dimeric assemblies within the polymer, even under the less-396 than-optimal functionalization observed in our experiments. 397 Interestingly, the data in Table S3 show that the parallel dimers 398 cause the largest reduction of HOMO–LUMO gaps in most 399 cases. The results for the 3-PV polymer are very similar in 400 terms of Pt…Pt distances and the formation of well-defined 401 parallel π -stacked dimers.

402 CONCLUSIONS

403 The structural modifications on the chemical structure of a 404 series of (N^N^N)Pt(II) complexes have evidenced their key 405 role on the possible establishment of intermolecular weak 406 interactions and how these interactions can affect the resulting 407 luminescence. Thus, we can modulate the emission wave-408 lengths, efficiencies (quantum yields), and lifetimes of the 409 compounds depending on the environment and the corre-410 sponding intermolecular contacts between them in a well-411 aligned distribution (³MMLCT emission in the functionalized 412 polymers), with the organic matrix (³IL emission from the 413 monomer in PMMA or PS).

These results open a wide range of new possibilities on the research based on supramolecular chemistry and luminescent has materials, taking into consideration that many other parametres can be modified giving rise to an easy tune of the luminescence of this type of metallopolymers and materials.

419 The DFT study reveals the facility of these compounds to 420 form aggregates via π -stacking and metallophilic interactions. 421 Several possible orientations have been analyzed indicating 422 that parallel and antipararallel orientations have similar binding 423 energies and influence on HOMO–LUMO gaps. Models of 1-424 PV and 3-PV polymers have been computed confirming the 425 formation of well-defined parallel dimers that likely favor the 426 ³MMLCT emission.

427 **EXPERIMENTAL SECTION**

428 **General Information.** Solvents have been purchased from 429 commercial sources and dried by distillation under a nitrogen 430 atmosphere. Reagents 2,6-pyridinedicarbonitrile, 4-chloropyridine-431 2,6-carbonitrile, *N*,*N*-diisopropylethylamine (DIPEA), 1-proline, poly-432 (4-vinylpyridine) cross-linked (poly(4-VP), CAS: 9017-40-7), 4-433 (dimethylamino)pyridine polymer-bound (DMAP) with ~3.0 mmol/ 434 g "DMAP" loading, matrix cross-linked with 2% DVB (CAS: 8294226-5), hydrazine hydrate, and trifluoroacetic acid have been purchased 435 from commercial sources and used without further purification. The 436 precursor $[PtCl_2(DMSO)_2]$ was prepared following the procedure 437 described in the literature.⁵⁸

Physical Measurements. ¹H NMR (δ (TMS) = 0.0 ppm), ¹⁹F 439 NMR (δ (CFCl₃) = 0.0 ppm), and ³¹P{¹H} NMR (δ (85% H₃PO₄) = 440 0.0 ppm) spectra have been obtained on Bruker 400 and Bruker 500 441 (Universitat de Barcelona) instruments. Electrospray mass spectra (+) 442 have been recorded on a Fisons VG Quatro spectrometer (Universitat 443 de Barcelona). Infrared spectra have been recorded on an FT-IR 520 444 Nicolet spectrophotometer. The emission spectra of the compounds 445 in solution have been obtained in a fluorescence quartz cuvette of 5 446 mm or 10 mm path length, using a Horiba-Jobin-Yvon SPEX Nanolog 447 spectrofluorimeter (Universitat de Barcelona). Emission quantum 448 yields were determined with a Hamamatsu Quantaurus QY absolute 449 photoluminescence quantum yield spectrometer C11347 with an 450 absorbance in the range of 0.043-0.139. Luminescence lifetimes were 451 measured on a JYF-DELTAPRO-NL equipment upon excitation of 452 the samples with a 390 nm NanoLED and collecting the decays 453 through a cutoff filter at the corresponding emission maxima. X-ray 454 powder diffraction has been recorded on the PANalytical X'Pert PRO 455 MPD θ/θ powder diffractometer of 240 mm of radius, in a 456 configuration of convergent beam with a focalizing mirror and a 457 transmission geometry with flat samples sandwiched between low 458 absorbing films. With a Cu K α radiation (λ = 1.5418 Å). Work power: 459 45 kV - 40 mA. Incident beam slits defining a beam height of 0.4 460 mm. Incident and diffracted beam 0.02 radians Soller slits. PIXcel 461 detector: Active length = 3.347° . $2\theta/\theta$ scan from 2 to 60° 2θ with a 462 step size of 0.0263° 2θ and a measuring time of 300 s per step 463 (Universitat de Barcelona). 464

Preparation of Matrices Doped with the Pt(II) Complexes. 465 PMMA and PS were used as the matrix polymers. The films were 466 made using a drop-casting technique with a combination of dopant 467 and host (PMMA or PS). The polymer solutions were prepared as 468 follows: PMMA, MW 120000 in 30% solution in dichloromethane 469 and PS, MW 45000, in 35% solution in dichloromethane. The same 470 volume of a sample solution with a concentration of 20 gen L was 471 added to a polymer solution. To prevent any thermal and the 472 films were drop-cast onto a quartz substrate at ambient temperature. 473

Theoretical Calculations. The geometries of the complexes and 474 dimeric assemblies were fully optimized without symmetry constrains 475 at the RI-PBE0-D4(COSMO)/def2-TZVP//RI-BP86-D4/def2- 476 TZVP level of theory⁵⁹⁻ ⁻⁶² by means of the Turbomole 7.7 program.⁶³ 477 Moreover, this combination of functional and basis set has been 478 recently used by us to explain the aggregation of Pt-²⁶ and Au- 479 complexes.⁴⁹ The basis set includes relativistic effects for Pt in the 480 definition of the ECPs.⁶² The binding energies were computed by 481 subtracting the sum of the energies of the monomers to the energy of 482 the dimer. Solvent effects were taken into consideration using the 483 COSMO-RS method⁶⁴ as implemented in the Turbomole program.⁶³ 484 The TD-DFT calculations were computed using 30 excited states at 485 the RI-PBE0-D4/def2-TZVP level of theory⁶⁵ using ORCA 5.0 486 program.^{oc} 487

Synthesis and Characterization. Synthesis of H_2L^3 . 0.5 g of 2,6-489 pyridinedicarbonitrile (3.87 mmol) was dissolved in 5 mL of DMF in 490 a sealed Schlenk tube. 0.629 g of sodium azide (9.67 mmol) and 0.105 491 g of L-proline have been then added, and the solution was stirred for 3 492 h at 110 °C. After this, the solution was cooled to room temperature. 493 The mixture reaction was poured into an ice–water solution (20 mL) 494 with stirring. The mixture was acidulated with HCl 0.5 M under 495 stirring. The mixture was filtered and washed with water. After 496 filtration, a white solid (0.75 g, 90% yield) was obtained. ¹H NMR 497 (400 MHz, DMSO- d_6) $\delta = 8.34$ (s, 3H, *Hpy*) ppm. IR (cm⁻¹): $\nu =$ 498 3415 (N–H), 3003 (C-Har), 2923 (C–H), 1557 (C=N), 1453 499 (C=C), 1093 (C–N).

Synthesis of H_2L^4 . A similar procedure used for H_2L^3 was followed so1 in the synthesis of H_2L^4 but using 4-chloropyridine-2,6-carbonitrile so2 instead of 2,6-pyridinedicarbonitrile. After filtration, a brown solid was so3 obtained (0.601 g, 79% yield). ¹H NMR (400 MHz, DMSO- d_6) $\delta =$ so4 7.98 (s, 2H, *HPy*) ppm. IR (cm⁻¹): $\nu = 3415$ (N–H), 3003 (C-Har), so5 2923 (C–H), 1557 (C=N), 1453 (C=C), 1093 (C–N).

Synthesis of [Pt(DMSO)L³]. 0.20 g of H_2L_3 (0.92 mmol) have been tor dissolved in 1 mL of DMF in a Schenk flask equipped with reflux and to 406 μ L of DIPEA (2.32 mmol) have been added to the solution and so stirred for 15 min. Then, 0.339 g of [Pt(DMSO)₂Cl₂] (0.51 mmol) to was added to the mixture and heated at 75 °C for 24 h. The reaction was cooled to room temperature, and an excess of diethyl ether was to precipitate the product. After filtration, a red solid was to obtained (0.388 g, 86% yield). ¹H NMR (400 MHz, DMSO- d_6) δ = the 8.22 (t, J = 8.6 Hz, 1H, H4-py), 8.12 (d, J = 7.6 Hz, 2H, H3,5-py), to 2.70 (s, 6H, CH₃) ppm. IR (cm⁻¹): ν = 3081 (C-Har), 2945 (C-H), to 1619 (C=N), 1457 (C=C), 1118 (S=O), 823 (Pt-N).

517 Synthesis of [Pt(DMSO)L⁴]. A similar procedure used for 518 [Pt(DMSO)L³] was followed in the synthesis of [Pt(DMSO)L⁴] 519 but using H_2L^4 instead of H_2L^3 . A brown solid was obtained after 520 filtration (0.3378 g, 70% yield) 1H NMR (400 MHz, DMSO- d_6) $\delta =$ 521 8.51 (s, 3H, Hpy), 2.69 (s, 6H, CH₃) ppm. IR (cm⁻¹): $\nu =$ 3019 (C-522 Har), 2993 (C-H), 1667 (C=N), 1496 (C=C), 1385 (CH₃), 1023 523 (S=O), 916 (C-N), 746 (CCl).

524 Synthesis of $[Pt(L^1)(4-DMAP)]$, 1-DMAP. Twenty mg (0.032 525 mmol) of $[Pt(DMSO)L^1]$ and 5.3 mg (0.016 mmol of pyridyl 526 groups) of 4-(dimethylamine)pyridine polymer bounded have been 527 suspended in 5 mL of dry acetonitrile under a nitrogen atmosphere 528 and reflux. The reaction was stirred overnight at 65 °C. All the 529 volatiles have been then evaporated under vacuum, and the crude 530 product was washed with DMSO and EtOH. After filtration, a pale-531 yellow solid was obtained (12.2 mg, 79% yield). IR (cm⁻¹): ν = 3461 532 (N–H), 3083 (C-Har), 2923 (C–H), 2853 (N–CH₃), 1650 (C= 533 C), 1490(–C=N), 1384 (–CH₃), 1160 (–CF₃), 520 (Pt–N). Anal. 534 Calcd (For (C₂₁₃H₁₇₈F₃₀N₄₅Pt₅) unit): C: 52.07%, H: 3.65%, N: 535 12.83%, Pt: 19.85%; Found: C: 52.21%, H: 3.57%, N: 12.40%, Pt: 536 19.74%.

537 Synthesis of $[Pt(L^1)(4-Vynylpyridine)]$, 1-PV. A similar procedure 538 used for 1-DMAP was followed in the synthesis of 1-PV but using 3.5 539 mg (0.032 mmol) of poly(4-vinylpyridine) instead of 4-540 (dimethylamine)pyridine polymer-bounded. A yellow solid was 541 obtained after filtration (16.7 mg, 80% yield). IR (cm⁻¹): ν = 3421 542 (N–H), 3092 (C–H_{ar}), 2923 (C–H), 2851 (–CH₂), 1650 (C=C), 543 1481 (–C=N), 1152 (–CF₃), 555 (Pt–N). Anal. Calcd (For 544 (C₁₈H₁₀F₆N₈Pt) unit): C: 33.39%, H: 1.56%, N: 17.31%, Pt: 30.13%; 545 Found: C: 33.45%, H: 1.60%, N: 17.58%, Pt: 30.18%.

Synthesis of $[Pt(L^2)(4-DMAP)]$, 2-DMAP. A similar procedure used for 1-DMAP was followed in the synthesis of DMAP (5.1 mg, 0.015 stammol of DMAP) but using $[Pt(DMSO)L^2]$ instead of [Pt(DMSO)stammol of DMAP) but using [Pt(DMSO)- but using [Pt(DMS

Synthesis of $[Pt(L^2)(4-Vynylpyridine)]$, 2-PV. A similar procedure soused for 1-PV was followed in the synthesis of 2-PV (3.3 mg, 0.030 mmol of PV) but using $[Pt(DMSO)L^2]$ instead of $[Pt(DMSO)L^1]$. A brown solid was obtained after filtration (14.3 mg, 69% yield). IR 558 (cm⁻¹): ν = 3421 (N–H), 3092 (CH_{ar}), 2985 (C–H), 2705 (–CH₂), 559 1618 (C=C), 1476 (–C=N), 1156 (–CF₃), 559 (Pt–N). Anal. 560 Calcd (For (C₁₈H₉ClF₆N₈Pt) unit): C: 31.71%, H: 1.33%, N: 16.43%, 561 Pt: 28.61%; Found: C: 31.65%, H: 1.39%, N: 16.62%, Pt: 28.81%. 562

Synthesis of $[Pt(L^3)(4-DMAP)]$, 3-DMAP. A similar procedure used 563 for 1-DMAP was followed in the synthesis of 3-DMAP (6.8 mg, 0.02 564 mmol of DMAP) but using $[Pt(DMSO)L^3]$ instead of [Pt(DMSO)- 565 L^1]. A yellow solid was obtained after filtration (12.2 mg, 72% yield). 566 IR (cm⁻¹): ν = 3412 (N–H), 3083 (C-Har), 2918 (C–H), 2843 567 (NCH₃), 1628 (C–C), 1459 (–C–N). Anal. Calcd (For 568 (C₁₉₃H₁₇₈N₅₅Pt₅) unit): C: 54.63%, H: 4.23%, N: 18.16%, Pt: 569 22.99%; Found: C: 54.60%, H: 4.19%, N: 18.12%, Pt: 22.94%. 570

Synthesis of $[Pt(L^3)(4-Vynylpyridine)]$, 3-PV. A similar procedure 571 used for 1-PV was followed in the synthesis of 3-PV (4.4 mg, 0.041 572 mmol of PV) but using $[Pt(DMSO)L^3]$ instead of $[Pt(DMSO)L^1]$. 573 An orange solid was obtained after filtration (19.6 mg, 93% yield). IR 574 (cm⁻¹): ν = 3412 (N–H), 3083 (C–H_{ar}), 2918 (C–H), 1628 (C= 575 C), 1459 (–C=N). Anal. Calcd (For (C₁₄H₁₀N₁₀Pt) unit): C: 576 32.75%, H: 1.96%, N: 27.28%, Pt: 38.00%; Found: C: 32.81%, H: 577 2.01%, N: 27.42%, Pt: 38.14%. 578

Synthesis of $[Pt(L^4)(4-DMAP)]$, 4-DMAP. A similar procedure used 579 for 1-DMAP was followed in the synthesis of 4-DMAP (6.4 mg, 0.02 580 mmol of DMAP) but using $[Pt(DMSO)L^4]$ instead of [Pt(DMSO)- 581 L^1]. A pale-brown solid was obtained after filtration (13.4 mg, 81% 582 yield). IR (cm⁻¹): ν = 3333 (N–H), 3053 (C-Har), 2921 (C–H), 583 2852 (N–CH₃), 1638 (C=C), 1459 (–C=N). Anal. Calcd (For 584 (C₁₉₃H₁₇₃Cl₅N₅₅Pt₅) unit): C: 52.50%, H: 3.95%, N: 17.45%, Pt: 585 22.09%; Found: C: 52.45%, H: 3.92%, N: 17.43%, Pt: 22.04%. 586

Synthesis of $[Pt(L^4)(4-vynylpyridine)]$, 4-PV. A similar procedure 587 used for 1-PV was followed in the synthesis of 4-PV (4.2 mg, 0.038 588 mmol of PV) but using $[Pt(DMSO)L^4]$ instead of $[Pt(DMSO)L^1]$. 589 An orange solid was obtained after filtration (18.5 mg, 88% yield). IR 590 (cm⁻¹): ν = 3425 (N–H), 2923 (C–H), 2754 (–CH₂), 1641 (C= 591 C), 1454 (–C=N), 555 (Pt–N). Anal. Calcd (For (C₁₄H₂ClN₁₀Pt) 592 unit): C: 30.69%, H: 1.66%, N: 25.57%, Pt: 35.61%; Found: C: 593 30.74%, H: 1.69%, N: 25.62%, Pt: 35.66%. 594

Synthesis of $[Pt(L^3)(4\text{-Dimethylaminopyridine})]$, 1A. A similar 595 procedure used for 1-DMAP was followed in the synthesis of 1A but 596 using 4-dimethylaminopyridine instead of 4-(dimethylamine)pyridine 597 polymer. A pale-yellow solid was obtained after filtration (18.2 mg, 598 84% yield). ¹H NMR (400 MHz, DMSO-d⁶) δ = 8.87–8.83 (m, 2H, 599 $H_{3,5\text{-Py}}$), 8.33–8.25 (m, 1H, $H_{4\text{-Py}}$), 7.98 (d, J = 8.0 Hz, 2H, 600 $H_{2,6\text{-PyNMe}}$), 6.99–6.87 (m, 2H, $H_{3,5\text{-PyNMe}}$), 3.13 (s, 6H, HN_{Me_2}). ¹⁹F 601 NMR (471 MHz, DMSO-d⁶) δ = -64.6 ppm. ESI (m/z): 666.2 [1A 602 + H⁺]⁺, 655.1 [1A - CH₃]⁺, 635.2 [1A - 2 CH₃]⁺. IR (cm⁻¹): ν = 603 3068 (C-H_ar), 2927 (C-H), 2358 (N-CH), 1633 (C-N), 1486 604 (-CH₃), 1145 (-CF₃), 811 (Pt-N).

Synthesis of [Pt(L)](4-Methylpyridine)], 1B. A similar procedure 606 used for 1-PV was followed in the synthesis of 1B but using 4 607 methylpyridine instead of poly(4-vinylpyridine) polymer. A pale 608 brown solid was obtained after filtration (8.7 mg, 43% yield). ¹H 609 NMR (500 MHz, CDCl₃) δ = 9.53–9.47 (m, 2H, H_{3,5-Py}), 8.06 (t, *J* = 610 7.9 Hz, 1H, H_{4-Py}), 7.87 (d, *J* = 7.9 Hz, 2H, H_{2,6-PyMe}), 7.49–7.43 (m, 611 2H, H_{3,5-PyMe}), 2.54 (s, 3H, H_{CH3}) ppm. ¹⁹F NMR (471 MHz, CDCl₃) 612 δ = -64.3 ppm. ESI (*m*/*z*): 659.11 [1B + Na⁺]⁺, 636.06 [1B + H⁺]⁺. 613 IR (cm⁻¹): ν = 3034 (C-H_a), 2948 (C-H), 2372 (N-CH), 1634 614 (C-N), 1482 (-CH₃), 1125 (-CF₃), 814 (Pt-N).

Synthesis of $[Pt(L^4)(4-Dimethylaminopyridine)]$, 2A. A similar 616 procedure used for 2-DMAP was followed in the synthesis of 2A but 617 using 4-dimethylaminopyridine instead of 4-(dimethylamine)pyridine 618 polymer. A pale-yellow solid was obtained after filtration (17.8 mg, 619 83% yield). ¹H 0 NMR (400 MHz, DMSO-d⁶) δ = 8.76–8.70 (m, 620 2H, H_{3, 5-Py}), 8.19 (d, *J* = 6.4 Hz, 1H, H_{2-PyNMe}), 8.02 (d, *J* = 1.2 Hz, 621 1H, H_{6-PyNMe}), 6.91 (d, *J* = 6.6 Hz, 1H, H_{3-PyNMe}), 6.77 (d, *J* = 6.8 Hz, 622 1H, H_{5-PyNMe}), 3.12 (d, *J* = 11.7 Hz, 6H, HN_{Me2}). ¹⁹F NMR (471 623 MHz, DMSO-d⁶) δ = -63.4 ppm. ESI (*m*/*z*): 693.1[**2A** + H⁺]⁺, 624 664.1 [**2A** - Cl + H⁺]⁺, 655.1 [**2A** - Cl - CH₃]⁺, 635.2 [**2A**-Cl-2 625 626 CH₃]⁺. IR (cm⁻¹): ν = 3085 (C–H_{ar}), 2939 (C–H), 2346 (N–CH), 627 1625 (C–N), 1444 (C–H), 1153 (–CF₃), 817 (Pt–N), 746 (C–Cl). 628 Synthesis of [*Pt*(*L*⁴)(4-Methylpyridine)], 2B. A similar procedure 629 used for 2-PV was followed in the synthesis of 2B but using 4-630 methylpyridine instead of poly(4-vinylpyridine) polymer. A pale-631 yellow solid was obtained after filtration (9.5 mg, 47% yield). ¹H 632 NMR (500 MHz, CDCl₃) δ = 9.51 (d, *J* = 6.1 Hz, 2H, H_{3,5-Py}), 7.90 (s, 633 2H, H_{2,6-PyMe}), 7.50–7.45 (m, 2H, H_{3,5-PyMe}), 2.55 (s, 3H, H_{CH₃}) ppm. 634 ¹⁹F NMR (471 MHz, CDCl₃) δ = -64.4 ppm. ESI (*m*/*z*): 636.06 [2B 635 – Cl + H⁺]⁺, 510.10 [2B– CF₃ – C₆H₇N + H⁺]⁺. IR (cm⁻¹): ν = 636 3088 (C–H_{ar}), 2948 (C–H), 2486 (N–CH), 1631 (C–N), 1444 637 (C–H), 1121 (–CF3), 814 (Pt–N), 748 (C–Cl).

Synthesis of $[Pt(L^5)(4-Methylpyridine)]$, 3A. A similar procedure 638 639 used for 3-DMAP was followed in the synthesis of 3A but using 4-640 dimethylaminopyridine instead of 4-(dimethylamine)pyridine poly-641 mer. A pale-orange solid was obtained after filtration (16.3 mg, 74% 642 yield). ¹H NMR (400 MHz, DMSO-d⁶) δ = 8.22 (d, J = 6.2 Hz, 2H, ₆₄₃ H_{2,6-PyNMe}), 6.99 (d, J = 6.5 Hz, 2H, H_{3,5-PyNMe}), 3.19 (s, 6H, HN_{Me₂}). 644 ESI (m/z): 532.1[3B + H⁺]⁺. IR (cm^{-1}) : $\nu = 3079 (C-H_{ar})$, 2937 645 (С-Н), 2366 (N-CH), 1646 (С-N), 1456 (С-Н), 813 (Pt-N). Synthesis of $[Pt(L^5)(4-Dimethylaminopyridine)]$, 3B. A similar 646 647 procedure used for 3-PV was followed in the synthesis of 3B but using 648 4-methylpyridine instead of poly(4-vinylpyridine) polymer. A pale-649 orange solid was obtained after filtration (15.9 mg, 77% yield). ¹H 650 NMR (400 MHz, DMSO-d⁶) δ= 8.77-8.64 (m, 2H, H_{2,6-PyMe}), 7.87-₆₅₁ 7.79 (m, 2H, $H_{3,5-PyMe}$), 2.58 (s, 3H, H_{CH_3}). ESI (m/z): 502.1 [3A + 652 H⁺]⁺, 477.1 [**3A** - N₂ + H⁺]⁺. IR (cm⁻¹): ν = 3077 (C-H_{ar}), 2927 653 (C-H), 2422 (N-CH), 1619 (C-N), 1384 (C-H), 819 (Pt-N). 654 Synthesis of [Pt(L^o)(4-Methylpyridine)], 4A. A similar procedure 655 used for 4-DMAP was followed in the synthesis of 4A but using 4-656 dimethylaminopyridine instead of 4-(dimethylamine)pyridine poly-657 mer. A pale-orange solid was obtained after filtration (17.3 mg, 79% 658 yield). ¹H NMR (400 MHz, DMSO-d⁶) δ = 8.19 (d, J = 7.0 Hz, 2H, 659 $H_{2,6-PyNMe}$), 6.94 (dd, J = 14.8, 6.8 Hz, 2H, $H_{3,5-PyNMe}$), 3.16 (s, 6H, H ₆₆₀ N_{Me_2}). ESI (*m*/*z*): 584.0 [4B + NH₄⁺]⁺, 568.0 [4B + H⁺]⁺. IR 661 (cm⁻¹): ν = 3085 (C-H_{ar}), 2954 (C-H), 2416 (N-CH), 1645 (C-662 N), 1442 (C-H), 809 (Pt-N), 620 (C-Cl).

663 Synthesis of $[Pt(L^6)$ (4-Dimethylaminopyridine)], 4B. A similar 664 procedure used for 4-PV was followed in the synthesis of 4B but using 665 4-methylpyridine instead of poly(4-vinylpyridine) polymer. A pale-666 orange solid was obtained after filtration (15.4 mg, 75% yield). ¹H 667 NMR (400 MHz, DMSO-d⁶) $\delta = 8.70$ (d, J = 6.0 Hz, 2H, H_{2,6-PyMe}), 668 7.75 (d, J = 5.7 Hz, 2H, H_{3,5-PyMe}), 2.53 (s, 3H, H_{CH3}). ESI (*m*/z): 669 555.0 [4A + NH₄⁺]⁺, 539.1 [4A + H⁺]⁺. IR (cm⁻¹): $\nu = 3060$ (C-670 H_{ar}), 2983 (C-H), 2424 (N-CH), 1641 (C-N), 1384 (C-H), 809 671 (Pt-N), 620 (C-Cl).

672 **ASSOCIATED CONTENT**

673 **Supporting Information**

674 The Supporting Information is available free of charge at 675 https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c04562.

676 Characterization data of the compounds, emission lifetime decays; optimized geometries calculated for 677 the dimers at different disposition; HOMO-LUMO 678 plots of the compounds, representation of the calculated 679 oligomer 3-PV; Interaction energies (Eint, kcal/mol) 680 computed for the dimers of compounds, binding 681 energies using the unrestricted UKS-PBE0-d4/def2-682 TZVP level of theory, and Cartesian coordinates of the 683 optimized geometries (PDF) 684

685 **AUTHOR INFORMATION**

686 Corresponding Authors

Antonio Frontera – Departament de Química, Universitat de
 les Illes Balears, Palma de Mallorca 07122, Spain;

o orcid.org/0000-0001-7840-2139; Email: toni.frontera@ 689 uib.es 690

Laura Rodríguez – Departament de Química Inorgànica i691Orgànica, Secció de Química Inorgànica., Institut de692Nanociència i Nanotecnologia (IN2UB). Universitat de693Barcelona, Barcelona E-08028, Spain; o orcid.org/0000-6940003-1289-1587; Email: laurarodriguezr@ub.edu695

Authors

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Guillermo Romo-Islas – Departament de Química Inorgànica	697
i Orgànica, Secció de Química Inorgànica., Institut de	698
Nanociència i Nanotecnologia (IN2UB). Universitat de	699
Barcelona, Barcelona E-08028, Spain; 💿 orcid.org/0000-	700
0002-2841-9546	701
Sergi Burguera – Departament de Química, Universitat de les	702
Illes Balears, Palma de Mallorca 07122, Spain 😑	703
Complete contact information is available at:	704
https://pubs.acs.org/10.1021/acs.inorgchem.3c04562	705

Notes

The authors declare no competing financial interest. 707

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