ChemPubSoc Europe

DOI: 10.1002/chem.201501179

CHEMISTRY A European Journal Full Paper

Nitrogen Heterocycles

Fluorescent Pyrene-Based Bis-azole Compounds: Synthesis and Photophysical Analysis

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Abstract: A rational synthetic procedure for the preparation of a series of pyrene-based neutral and dicationic bis-azole compounds is reported. The method allows the tailored design of pyrene-based azoles with different substituents at the nitrogen atoms of the heterocycles, for which the relative conformation of the resulting bis-azoles can be easily controlled. The bis-azoliums were used for the preparation of the related diplatinum complexes by reaction with $[\{Pt(ppy)(\mu\text{-}Cl)_2\}_2]$ (ppy = 2-phenylpyridinate). The X-ray molecular structure of one of the resulting compounds, a diplatinum(II) bis(N-heterocyclic carbene) complex, is described. Studies on the photophysical properties of all new species are described. The emission of the bis-azole-based compounds seems to be independent of their substitution patterns, which basically indicates that physical properties such as solubility, melting point, and viscosity can be fine-tuned while maintaining the luminescence properties. Finally, the energies associated with the HOMO and LUMO levels suggest that this family provides versatility to match the energy levels of a wide range of host materials, which is important for the preparation of organic light-emitting devices.

Introduction

In the last few years there has been increasing interest in the preparation of bis-azolium and tris-azolium salts as starting materials for the preparation of electronically active materials, mainly because these compounds feature high synthetic flexibility that allows fine-tuning of their physicochemical properties. Many of these poly-azoliums were used as synthons for the preparation of N-heterocyclic carbenes (NHCs),[1] which found applications in multimetallic catalysis[2] and in the preparation of structurally dynamic polymers,[3] molecular switches, and other materials with properties that are consistent with extensively delocalized electronic systems,[4] such as luminophores.[5] Materials with luminescence properties are of great interest in the preparation of organic light-emitting diodes (OLEDs) for use in flat-panel displays and solid-state light sources, for which three-color white OLEDs are needed to generate a good color-rendering index.[6] Two types of emitters can be used for OLED applications, namely, fluorescent emitters, which are typically neutral organic molecules,[7] and phosphorescent emitters based on organometallic species containing heavy atoms, such as iridium or platinum.[8] For current applications of OLEDs, the processability of their emitters is also of major interest. Designing high-yield reactions and easy-to-purify components to avoid losses of material and issues related with the presence of impurities is highly desirable.[9]

Among bis-azoliums, benzo bis-imidazoliums (BBIs) were the first materials to be studied as fluorescent emitters.[10] BBIs have a benzene backbone flanked by two facially opposed imidazolium moieties, and thus the charged moieties are embodied within the chromophore of the system, a property that makes them different from most common fluorescent organic salts. Replacing the benzene linker by a rigid polyaromatic spacer such as pyracene[4a,11] or pyrene[12] allows related compounds in which the two azolium units are connected by a highly delocalized system to be obtained. In principle, the presence of these polyaromatic spacers introduces low-lying LUMO levels that improve environmental stability.[13] This is also important for operating electronic devices under ambient conditions, which generally requires LUMO levels located below −4.0 eV to avoid H_2O reduction[14] and to minimize O_2 trapping.[15] Because pyrene is the chromophore of choice in fundamental and applied photochemical research[16] (it is sometimes called the photochemist's fruit fly),[16a] we recently envisaged that its incorporation as linker between two azolium units should afford interesting photophysical properties.[12] Our preliminary results showed that pyrene-based bis-azoliums showed emissions in the range of 370–420 nm and quantum yields ranging from 0.29–0.41. On the basis of these previous promising findings, in this work we prepared a series of pyrene-linked neutral and dicationic bis-azoles through systematic variation of *N*-substituents. The presence of four nitrogen atoms in the bis-azoles allows for multiple variations, for which we designed specific synthetic procedures to reach all possible desired conformations. The photophysical properties of the resulting products were evaluated, together with their related Pt^{II} coordination complexes, the luminescent properties of which are described. A family of pyrene-based compounds

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201501179.

was synthesized with a variety of photophysical properties that will potentially provide flexibility in their use for different OLED platforms.

Results and Discussion

Synthesis of the pyrene-based azole compounds

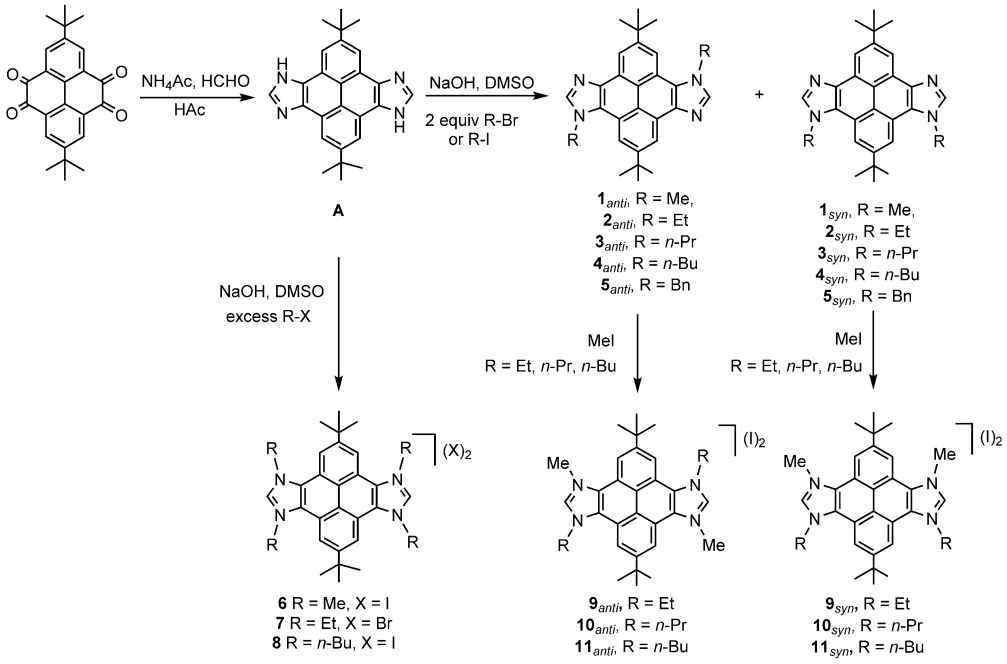
Di-*tert*-butyl pyrene bis-imidazole **A** was obtained by condensation of 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone, formaldehyde, and ammonium acetate in acetic acid (Scheme 1). The bis-alkylation of **A** was carried out by treatment with NaOH followed by the addition of two equivalents of the corresponding alkyl halide (alkyl = Me, Et, *n*Pr, *n*Bu, benzyl) to afford pyrene-based compounds **1**–**5**, which were obtained as mixtures of the *anti* and *syn* regioisomers in moderate to good overall yields. The separation of the two isomers was accomplished for compounds **1**–**4**, on the basis of their different solubilities in diethyl ether. However, all the attempts to separate the two isomers of compound **5** bearing an *N*-benzyl group were unsuccessful.

Because we recently obtained a series of pyrene-based bis-imidazolium salts (PBIs) with very good luminescence properties,[12] we decided to prepare new salts based on the same motif by employing the above-described neutral compounds. Our purpose was to perform a rational study on the influence of the substitution patterns of the salts on their photophysical properties. As separation of the *anti* and *syn* isomers was possible for compounds **1**–**4**, we were able to obtain a series of regioisomeric dialkyl dimethylpyrenebis(imidazolium) salts. As shown in Scheme 1, alkylation of compounds $\mathbf{2}_{anti}$, $\mathbf{3}_{anti}$, and $\mathbf{4}_{anti}$ with MeI afforded PBIs $\mathbf{9}_{anti}$, $\mathbf{10}_{anti}$, and $\mathbf{11}_{anti}$, respectively. Their regioisomeric counterparts, $\mathbf{9}_{syn}$, $\mathbf{10}_{syn}$ and $\mathbf{11}_{syn}$, were prepared in a similar manner starting from $\mathbf{2}_{syn}$, $\mathbf{3}_{syn}$, and $\mathbf{4}_{syn}$, respectively. All salts were isolated as yellowish solids in good to excellent yields. To obtain the related BF_4 salts, the iodide salts **9** and **11** were treated with $Et_3O{\cdot}BF_4$,[17] to produce **9**-BF_4 and **11**-BF_4, respectively (see Experimental Section for further details).

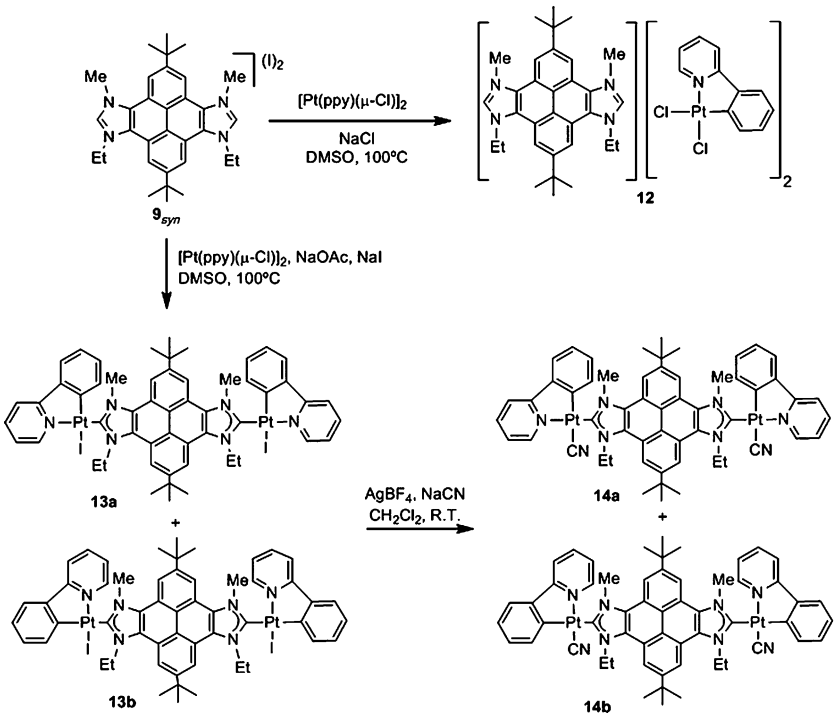
Additionally, homo-tetraalkylated bis-azolium compounds **6**–**8** were prepared by tetraalkylation of compound **A** with the appropriate alkyl halide (Scheme 1). These salts, albeit with different counterions, were prepared earlier by us by a different experimental procedure.[12] Our previously reported methodology, which involves the multifold amination of tetrabromopyrene and subsequent formylative cyclization with $HC(OR)_3$, provided the bis-imidazolium salts bearing *N*-alkyl groups originating from the trialkyl orthoformate. Hence, the scope of the procedure was limited by the availability of the trialkyl orthoformate reagents. The alternative synthetic route that we propose here circumvents this limitation because it allows the introduction of a wide range of alkyl substituents. Following this methodology, the homo-tetraalkylated salts **6**–**8** were isolated as yellowish solids in moderate to good yields. Overall, the synthesis of neutral compounds **1**–**5** and PBI salts **6**–**11** required a maximum of five chromatography-free steps starting from pyrene.

To further explore the capabilities of this family of pyrene-based bis-imidazoliums, we used them as precursors in the preparation of cyclometalated platinum complexes. Cyclometalated platinum complexes have shown potential in highly efficient OLEDs[9,18] and, in conjunction with NHC ligands, have provided Pt^{II} complexes with luminescent properties.[5a]

The reaction of $\mathbf{9}_{syn}$ with $[\{Pt(ppy)(\mu\text{-}Cl)_2\}_2]$ (ppy = 2-phenylpyridinate) in the presence of NaCl afforded dichloroplatinate(II) salt **12** (Scheme 2). The ^1H NMR spectrum of **12** shows



Scheme 1.



Scheme 2.

a signal at 9.91 ppm attributed to the acidic protons at the imidazolium rings, which suggests the integrity of the bis-azolium dication.

If the reaction between [{Pt(ppy)(μ-Cl)$_2$}$_2$] and $\mathbf{9}_{syn}$ is performed in the presence of NaOAc and NaI, a mixture of two isomers (**13a** and **13b**) is obtained (6:4 molar ratio), but this time the deprotonation of the bis-azolium gives rise to the formation of the corresponding bis-NHC complexes. The ^{1}H NMR spectrum sheds light on the nature of the resulting isomers. The resonance arising from the proton at C6 of the pyridyl moiety of the 2-phenylpyridine ligand ($\delta = 10.2$ ppm for **13a** and 8.93 ppm for **13b**) is a clear indication of the ligand distribution about the platinum center,[19] which in our case has the iodide ligand *cis* to the pyridyl group in **13a** and *trans* in **13b**. The ^{13}C NMR spectrum of the mixture of isomers showed the characteristic signals due to the metalated carbon atoms at 170.0 and 165.2 ppm for **13a** and **13b**, respectively. Slow diffusion of hexane into a concentrated solution of the crude solid in chloroform allowed the crystallization of isomer **13a**, the molecular structure of which was unambiguously confirmed by XRD (see below).

Iodide abstraction with a silver salt ($AgBF_4$) and subsequent reaction with NaCN afforded a mixture of two isomers that contain strong-field CN^- auxiliary ligands (**14a** and **14b**). The ^{1}H NMR spectrum of the mixture again suggests the presence of two isomers. The ^{1}H resonance due to the proton on C6 of the pyridyl moiety ($\delta = 9.56$ ppm for **14a** and 9.16 ppm for **14b**) indicates that the cyanide ligand is *cis* to pyridyl in **14a** and *trans* in **14b**. The ^{13}C NMR spectrum of the mixture of the two isomers showed the characteristic signals due to the metalated carbon atoms at 178.1 and 170.0 for **14a** and **14b**, respectively.

The molecular structure of complex **13a** was unambiguously confirmed by XRD. The molecule contains a pyrene-bis-imidazolylidene ligand bridging the two platinum centers (Figure 1). The relative orientation of the ligands about the two metal fragments in **13a** is *syn*, based on the orientation of the Pt–I bonds. The average Pt–$C_{carbene}$ distance is 1.988 Å, and the through-space Pt···Pt distance of 13.095 Å is slightly shorter than that found in Ir^{I},[12] Rh^{I},[12] and Ru^{II}[20] complexes supported by related pyrene-bis-imidazolylidene ligands reported earlier by us.

Photophysical properties

With a series of regioisomeric pyrene-based neutral compounds, their derived symmetrical and asymmetrical PBI salts, and three Pt^{II}-based complexes in hand, we turned our attention toward the photophysical characteristics of these materials. All photophysical studies were carried out in CH_3CN solution, except for those involving complexes **13a**,**b**, which were performed in CH_2Cl_2. The results are summarized in Table 1.

The nature of the different *N*-substituents had little effect on λ_{abs} and λ_{em} (cf. Table 1, entries 1–4 and 5–8) of neutral com-

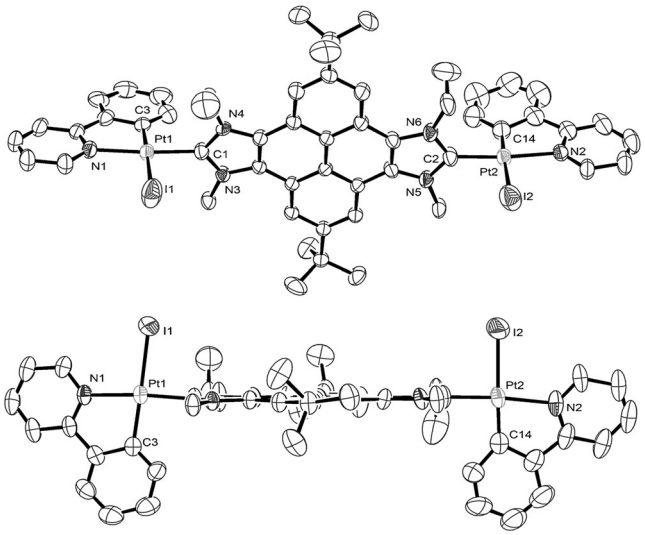


Figure 1. Two perspectives of the molecular structure of **13a**. Hydrogen atoms and solvents (hexane and chloroform) have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Pd1–C1 1.997(10), Pt1–N1 2.089(8), Pt1–I1 2.6905(11), Pt1–C3 2.026(11), Pt2–C2 1.979(11), Pt2–N2 2.122(9), Pt2–I2 2.6522(12), Pt2–C14 1.768(11); C1-Pt1-C3 93.6(5), C14-Pt2-C2, 92.4(5), N1-Pt1-I1 97.4(3), N2-Pt2-I2, 96.5(3).

Table 1. Photophysical and electrochemical parameters and frontier orbital energies for **1**–**14** in solution.

Entry	Compound	λ_{abs} [nm][a]	λ_{em} [nm][a]	Optical E_{gap} [eV]	ϕ_f[b]	HOMO [eV][c]	LUMO [eV]
1	$\mathbf{1}_{anti}$	263, 290, 361	379_{max}, 400, 422	3.35	0.47	−5.56	−2.21
2	$\mathbf{2}_{anti}$	264, 290, 361	379_{max}, 400, 421	3.35	0.40	−5.38	−2.03
3	$\mathbf{3}_{anti}$	264, 290, 361	379_{max}, 399, 422	3.35	0.40	−5.50	−2.15
4	$\mathbf{4}_{anti}$	264, 290, 361	379_{max}, 400, 422	3.35	0.46	−5.59	−2.24
5	$\mathbf{1}_{syn}$	264, 291, 360	380_{max}, 401, 423	3.33	0.47	−5.54	−2.21
6	$\mathbf{2}_{syn}$	264, 291, 362	380_{max}, 401, 423	3.33	0.50	−5.53	−2.20
7	$\mathbf{3}_{syn}$	263, 291, 360	379_{max}, 400, 422	3.33	0.46	−5.44	−2.11
8	$\mathbf{4}_{syn}$	264, 291, 360	381_{max}, 401, 423	3.33	0.46	−5.54	−2.21
9	**5**	263, 291, 359	379_{max}, 399, 421	3.33	0.50	−5.54	−2.21
10	**6**	263, 286, 360	371_{max}, 391, 413	3.37	0.14	−4.96	−1.59
11	**7**	263, 287, 340	372_{max}, 392, 413	3.40	0.37	−5.42	−2.02
12	**8**	264, 288, 360	372_{max}, 392, 414	3.37	0.19	−5.02	−1.65
13	$\mathbf{9}_{anti}$	263, 287, 340	371_{max}, 392, 413	3.37	0.35	−5.05	−1.68
14	$\mathbf{10}_{anti}$	263, 287, 360	372_{max}, 392, 413	3.40	0.26	−5.03	−1.63
15	$\mathbf{11}_{anti}$	263, 287, 340	372_{max}, 392, 413	3.37	0.27	−4.99	−1.62
16[d]	$\mathbf{9}_{syn}$	263, 287, 340	372_{max}, 392, 413	3.39	0.45	−5.09	−1.70
17	$\mathbf{10}_{syn}$	263, 287, 340	372_{max}, 392, 413	3.36	0.44	−5.13	−1.77
18[d]	$\mathbf{11}_{syn}$	263, 287, 340	372_{max}, 392, 413	3.39	0.27	−5.05	−1.66
19	$\mathbf{9}_{anti}$-$\mathbf{BF_4}$	263, 287, 340	372_{max}, 392, 413	3.35	0.55	−6.07	−2.72
20	$\mathbf{11}_{anti}$-$\mathbf{BF_4}$	263, 287, 340	372_{max}, 392, 413	3.35	0.45	−6.13	−2.78
21[d]	$\mathbf{9}_{syn}$-$\mathbf{BF_4}$	263, 287, 340	372_{max}, 392, 413	3.35	0.75	−6.06	−2.71
22[d]	$\mathbf{11}_{syn}$-$\mathbf{BF_4}$	264, 287, 340	372_{max}, 392, 414	3.35	0.43	−6.11	−2.76
23[d]	**12**	256, 288, 339	372_{max}, 391, 414	3.58	0.35	−4.77	−1.19
24	**13a,b**	241, 272, 336	372_{max}, 382, 392	3.44	–	−5.33	−1.89
25	**14a,b**	241, 272, 336	379_{max}, 401, 423	3.39	0.025	−4.77	−1.38

[a] Measurements were performed in CH_3CN or CH_2Cl_2 (**13a,b**) under ambient conditions. [b] Emission quantum yields Φ_f were determined relative to anthracene or $[Ru(bipy)_3]Cl_2 \cdot 6H_2O$ (**13a,b**) in deoxygenated solutions. [c] Calculated by comparison with Fc (4.88 eV) and calibrated by using Fc/Fc^+ ($E_{1/2} = 0.40$ V (CH_3CN) or 0.46 V (CH_2Cl_2) vs. SCE)[22] as internal standard. [d] These complexes may contain impurities in amounts of less than 10%.

pounds **1**–**5** (for more details, see Figures S1 and S2 of the Supporting Information). In fact, the emission spectra of **1**–**5** were almost superimposable (Figures S8 and S9 of the Supporting Information). In particular, solutions of compounds **1**–**5** in CH_3CN show a deep-blue band ($\lambda_{max} = 378$ nm) with vibronic spacings of 1455–1303 and 1322–1253 cm^{-1}, respectively. Hence, the optical bandgaps calculated for **1**–**5** are very similar, with values close to 3.35 eV. The fluorescence quantum yields Φ_f are high, in the region of 0.4 and 0.5.

The absorption spectra of PBIs **6**–**11** in CH_3CN are quite similar to those of their neutral precursors (see Figures S3–S5 in the Supporting Information). The emission spectra of these bis-imidazolium salts are also vibronically resolved at room temperature with peak maxima between 370 and 420 nm (see Figures S10–S12 in the Supporting Information). In general, the tetrafluoroborate PBIs with a *syn* configuration showed higher fluorescence quantum yields than their *anti* isomers, and $\mathbf{9}_{syn}$-BF_4 was the most efficient fluorophore among all compounds tested. All the similarities found suggest that the exciton that forms in all these molecules is localized largely on the pyrene linker, with minimum participation of the heterocyclic fragments. This result is interesting, because it indicates that we can produce materials with the emissive properties of pyrene while modifying physical properties such as solubility, melting point, and viscosity.

The absorption and emission spectra of $\mathbf{9}_{syn}$ and dichloroplatinate(II) salt **12** are superimposable, although the intensity of the emission decreases on the introduction of the platinum fragment, as reflected by the decrease of 0.1 in Φ_f (cf. Table 1, entries 16 and 23). For complexes **13a,b** and **14a,b**, carbene coordination significantly reduces Φ_f (cf. Table 1, entries 23, 24 and 25), which suggests that carbene coordination to the Pt^{II} center may increase the proportion of nonradiative decay processes.[19b] Complexes **13a,b** and **14a,b** exhibit vibronically resolved emission bands ($\lambda_{max} = 372$ nm for **13**, 379 nm for **14**). Whereas complexes **13a,b** show almost negligible emission in solution at room temperature, the introduction of strong-field cyanide ligands (**14a,b**) provided more intense emission bands in the region of 240–340 nm. The quantum yield of complexes **14a,b** was calculated to be 0.025.

The electrochemical properties of the compounds were studied by cyclic voltammetry.Representative cyclic voltammograms (CVs) are shown in Figures S15–S20 of the Supporting Information. The HOMO levels were extracted by comparison of the oxidative wave with an external ferrocene/ferrocenium (Fc/Fc^+) reference redox couple, by assuming an ionization potential of 4.88 eV versus vacuum [$E_{HOMO} = -(E_{ox} + 4.58$ eV)].[21] The LUMO levels were calculated from the HOMO levels and the optical bandgap E_{gap}.

The CVs of neutral compounds **1**–**5** showed irreversible oxidation waves with oxidative onset potentials in the range of 0.9–0.95 V. These values allowed us to estimate that the HOMO levels are about −5.5 eV. Taking the optical bandgaps into account, the calculated LUMO levels lie in the range of −2.0 and −2.2 eV. Interestingly, the emissions and the

HOMO and LUMO levels of **1**–**5** are in the range of those calculated for phenanthro[9,10-*d*]imidazole-based compounds successfully employed for constructing blue light-emitting materials.[7d] On the other hand, all PBIs showed reversible oxidation waves. The calculated HOMO levels for the iodide PBIs (between −5.4 and −5.0 eV) are considerably higher than those of the tetrafluoroborate PBIs (about −6.1 eV), which suggests that different host materials could be used for the production of light-emitting devices such as OLEDs. A significant difference is also observed in the LUMO levels, which are significantly lower for the tetrafluoroborate PBIs. Finally, platinum-containing complexes **12**–**14** show shallow HOMO and LUMO levels spanning from −4.8 to −5.3 eV and −1.2 to −1.9 eV, respectively. Overall, the wide range of HOMO and LUMO levels calculated for this family of pyrene-based compounds provides versatility in matching the energy levels with a wide range of host materials. For example, **1**–**5** could be used in combination with triarylamines, and those showing HOMO levels of about −6.0 eV (**9**-BF_4 and **11**-BF_4) with polycarbazoles, both of which are commonly used as host materials in the production of OLEDs.

Conclusion

We have reported an efficient method for the controlled synthesis of a series of pyrene-based bis-azoles and bis-azoliums. The new compounds can be obtained with a wide range of *N*-alkyl substituents and with two possible relative configurations, and therefore afford a systematic approach to a large variety of compounds with fine-tuned physicochemical properties. One of the bis-azolium salts reacted with $[\{Pt(ppy)(\mu\text{-}Cl)_2\}_2]$ to afford the related di-Pt^{II} complexes. The resulting products were either the dimetallic pyrene-based bis-NHC diplatinum(II) complex or the bis-azolium salt with two $[Pt(ppy)Cl_2]^-$ counteranions, depending on whether the reaction was carried out with or without the presence of an external base (NaOAc), respectively.

Studies on the photophysical properties of all new species revealed that the organic molecules showed emissions in the range of 379–423 and 370–420 nm for the neutral bis-azole and dicationic bis-azolium compounds, respectively. The quantum yields are in the range of $\Phi_f = 0.20$–0.55. In general, both the emissions and the quantum yields are only slightly sensitive to the nature of the bis-azoles and their substituents and thus indicate that the emissive properties are centered in the pyrene moiety, with little participation of the heterocycles. This is interesting because the presence of linear alkyl groups in the azole units is known to highly influence the thermotropic properties of the ionic liquid crystals derived therefrom.

Overall, the results presented here indicate that we can prepare materials with the emissive properties of pyrene while tuning physical properties directly related to their processability, such as solubility, thermal stability, or other requirements. Indeed, a wide variety of solvents can be used to process films to meet external requirements. For example, while the neutral compounds **1**–**5** are soluble in halogenated solvents, the PBI salts and Pt complexes are soluble in highly coordinating solvents such as DMSO and acetonitrile. In addition, the wide range of HOMO and LUMO levels suggest that this family provides versatility in matching the energy levels with a large variety of host materials having different physical properties.

Experimental Section

General considerations

2,7-Di-*tert*-butyl-pyrene,[23] 2,7-di-*tert*-butyl-pyrene-4,5,9,10-tetraone,[24] and the metal precursors $[\{Pt(ppy)(\mu\text{-}Cl)_2\}_2]$[25] and $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$[26] (bipy = 2,2′-bipyridine) were prepared according to literature methods. All other reagents were used as received from commercial suppliers. Compound **A** was prepared in a similar manner to that reported for related compounds.[27] NMR spectra were recorded on Varian Innova 300 and 500 MHz spectrometers by using $CDCl_3$, CD_3CN, [D_6]acetone, or [D_6]DMSO as solvent. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were carried out on a TruSpec Micro Series. UV/Vis absorption spectra were recorded on a Varian Cary 300 BIO spectrophotometer in CH_3CN or CH_2Cl_2 solution (**13a**,**b**) under ambient conditions. Emission spectra were recorded on a modular Horiba FluoroLog-3 spectrofluorometer in degassed CH_3CN or degassed CH_2Cl_2 (**13a**,**b**). Quantum yields were determined relative to recrystallized anthracene in degassed EtOH as standard ($\Phi_f = 0.27$),[28] with excitation at 316 and 340 nm (**13** and **14a**,**b**). The quantum yield of Pt^{II} complex **13a**,**b** was determined relative to $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ in degassed H_2O as standard ($\Phi_f = 0.042$),[29] with excitation at 340 nm. All solutions were prepared in air and deaerated by sparging with nitrogen for 15 min prior performing emission and quantum-yield measurements. The electrochemical studies were carried out by using an Autolab Potentiostat (Model PGSTAT101) with a three-electrode cell. The cell was equipped with platinum working and counter electrodes, as well as a silver wire reference electrode. In all experiments, a 0.1 M solution of $[NBu_4][PF_6]$ in dry CH_3CN or CH_2Cl_2 (**13a**,**b**) was used as the supporting electrolyte with analyte concentration of approximately 1 mM. Measurements were performed at a scan rate of 50 mV s^{-1}. All redox potentials were referenced to ferrocenium/ferrocene (Fc/Fc^+; $E_{1/2} = 0.40$ V (CH_3CN) or 0.46 V (CH_2Cl_2) vs. SCE)[22] as internal standard.

Synthesis and characterization of neutral compounds A and 1–5

Compound A: Formaldehyde (0.44 mL, 5.88 mmol) was added dropwise to a solution of 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone (1.0 g, 2.67 mmol) and NH_4Ac (8.41 g, 106.95 mmol) in glacial acetic acid (40 mL). The mixture was heated to reflux overnight, after which the reaction mixture was cooled to room temperature and subsequently treated with 400 mL of water and neutralized with concentrated aqueous ammonia (10 mL). The off-white solid thus formed was separated by filtration and washed successively with water and cold diethyl ether. Yield: 1.077 g (90%). ^{1}H NMR (500 MHz, [D_6]DMSO): $\delta = 8.69$ (s, 4H, CH_{pyr}), 8.40 (s, 2H, NCHN), 1.60 ppm (s, 18H, $C(CH_3)_3$); ^{13}C NMR (126 MHz, [D_6]DMSO): $\delta =$ 176.6 ($C_{q\,pyr}$), 172.4 (NCHN), 149.0 ($C_{q\,pyr}$), 139.5 ($C_{q\,pyr}$), 118.2 ($C_{q\,pyr}$), 114.9 (CH_{pyr}), 35.7 ($C(CH_3)_3$), 32.2 ppm ($C(CH_3)_3$); ESI-MS (20 V, *m/z*): 395.3 $[M+H]^+$; elemental analysis calcd for $C_{26}H_{32}N_4O_3$ (448.56): C 69.62, H 7.19, N 12.49; found: C 68.91, H 7.48, N 12.42.

Compounds 1–5, general procedure: Compound **A** and NaOH were dissolved in DMSO (2–4 mL). The reaction mixture was stirred

at room temperature for 2 h. The corresponding alkylating agent was then added and the mixture was stirred at room temperature for 30 min and then at 37 °C overnight. After this time, the solvent was removed under vacuum. The crude solid consisted of two regioisomers, separation of which was accomplished for **1**–**4**. All attempts to separate the two isomers of compound **5** were unsuccessful. To separate the two isomers, the crude solid was dissolved in CH_2Cl_2 and the solution filtered through a pad of Celite to remove insoluble salts. The resulting residue was taken up in the minimum amount of CH_2Cl_2, and diethyl ether (5 mL) was added to precipitate the *anti* regioisomers. The filtrate was concentrated under reduced pressure to provide the *syn* regioisomer.

Compounds $\mathbf{1}_{anti}$ and $\mathbf{1}_{syn}$: The reaction was carried out with compound **A** (300 mg, 0.76 mmol), NaOH (62.1 mg, 1.52 mmol), and methyl iodide (96 μL, 1.52 mmol). Yield: 114 mg, 36% (*anti* isomer); 93.9 mg, 30% (*syn* isomer).

$\mathbf{1}_{anti}$: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.01$ (d, $^4J_{H,H} = 1.8$ Hz, 2H, CH_{pyr}), 8.64 (d, $^4J_{H,H} = 1.8$ Hz, 2H, CH_{pyr}), 8.06 (s, 2H, NCHN), 4.50 (s, 6H, NCH_3), 1.66 ppm (s, 18H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 148.9 (C_{qpyr}), 142.0 (NCHN), 139.0 (C_{qpyr}), 127.3(C_{qpyr}), 127.2 (C_{qpyr}), 122.9 (C_{qpyr}), 119.4 (C_{qpyr}), 115.7 (CH_{pyr}), 113.9 (CH_{pyr}), 35.8 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 12.9 ppm (NCH_3); ESI-MS (20 V, *m/z*): 423.3 $[M+H]^+$; elemental analysis calcd for $C_{28}H_{30}N_4$ (422.56): C 79.58, H 7.16, N 13.26; found: C 79.64, H 7.35, N 13.27.

$\mathbf{1}_{syn}$: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.95$ (s, 2H, CH_{pyr}), 8.62 (s, 2H, CH_{pyr}), 7.99 (s, 2H, NCHN), 4.46 (s, 6H, NCH_3), 1.64 (s, 9H, $C(CH_3)_3$), 1.63 ppm (s, 9H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.0$ (C_{qpyr}), 147.7 (C_{qpyr}), 142.3 (NCHN), 139.6 (C_{qpyr}), 126.8 (C_{qpyr}), 126.5 (C_{qpyr}), 123.7 (C_{qpyr}), 119.8 (C_{qpyr}), 119.1 (C_{qpyr}), 115.6 (CH_{pyr}), 113.8 (CH_{pyr}), 35.6 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 29.7 ppm (NCH_3); elemental analysis calcd for $C_{28}H_{30}N_4$ (422.56): C 79.58, H 7.16, N 13.26; found: C 79.74, H 7.57, N 12.80.

Compounds $\mathbf{2}_{anti}$ and $\mathbf{2}_{syn}$: The reaction was carried out with compound **A** (100 mg, 0.25 mmol), NaOH (21.0 mg, 0.51 mmol), and ethyl bromide (39 μL, 0.51 mmol). Yield: 37 mg, 32% (*anti* isomer); 32.5 mg, 28% (*syn* isomer).

$\mathbf{2}_{anti}$: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.01$ (d, $^4J_{H,H} = 1.8$ Hz, 2H, CH_{pyr}), 8.50 (d, $^4J_{H,H} = 1.8$ Hz, 2H, CH_{pyr}), 8.05 (s, 2H, NCHN), 4.85 (m, 4H, NCH_2CH_3), 1.80 (t, $^3J_{H,H} = 6.9$ Hz, 6H, NCH_2CH_3), 1.64 ppm (s, 18H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.9$ (C_{qpyr}), 141.1 (NCHN), 139.5 (C_{qpyr}), 127.3(C_{qpyr}), 126.3(C_{qpyr}), 122.5 (C_{qpyr}), 119.5 (C_{qpyr}), 115.7 (CH_{pyr}), 114.2 (CH_{pyr}), 43.2 (NCH_2CH_3), 35.5 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 16.3 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 451.4 $[M+H]^+$; elemental analysis calcd for $C_{30}H_{34}N_4$ (450.61): C 79.96, H 7.61, N 12.44; found: C 79.64, H 7.35, N 12.27.

$\mathbf{2}_{syn}$: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.98$ (s, 2H, CH_{pyr}), 8.49 (s, 2H, CH_{pyr}), 8.04 (s, 2H, NCHN, 4.81 (m, 4H, NCH_2CH_3), 1.78 (t, $^3J_{H,H} =$ 6.9 Hz, 6H, NCH_2CH_3), 1.65 (s, 9H, $C(CH_3)_3$), 1.64 ppm (s, 9H, $C(CH_3)_3$);^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.2$ (C_{qpyr}), 147.9 (C_{qpyr}), 141.6 (NCHN), 140.2 (C_{qpyr}), 126.7 (C_{qpyr}), 126.1 (C_{qpyr}), 123.6 (C_{qpyr}), 120.1 (C_{qpyr}), 119.2 (C_{qpyr}), 115.8 (CH_{pyr}), 114.2 (CH_{pyr}), 43.3 (NCH_2CH_3), 35.8 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 16.5 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 451.4 $[M+H]^+$; elemental analysis calcd for $C_{30}H_{34}N_4$ (450.61): C 79.96, H 7.61, N 12.44; found: C 79.74, H 7.57, N 12.80.

Compounds $\mathbf{3}_{anti}$ and $\mathbf{3}_{syn}$: The reaction was carried out with compound **A** (100 mg, 0.25 mmol), NaOH (21.0 mg, 0.51 mmol), and *n*-propyl bromide (47 μL, 0.51 mmol). Yield: 22.2 mg, 18% (*anti* isomer); 34.5 mg, 28% (*syn* isomer).

$\mathbf{3}_{anti}$: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.00$ (d, $^4J_{H,H} = 1.8$ Hz, 2H, CH_{pyr}), 8.47 (d, $^4J_{H,H} = 1.8$ Hz, 2H, CH_{pyr}), 8.02 (s, 2H, NCHN), 4.73 (t, $^3J_{H,H} =$ 7.2 Hz, 4H, $NCH_2CH_2CH_3$), 2.21 (m, 4H, $NCH_2CH_2CH_3$), 1.65 (s, 18H, $C(CH_3)_3$), 1.14 ppm (t, $^3J_{H,H} = 7.2$ Hz, 6H, $NCH_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.0$ (C_{qpyr}), 142.1 (NCHN), 139.7 (C_{qpyr}), 127.5(C_{qpyr}), 126.5 (C_{qpyr}), 122.8 (C_{qpyr}), 119.6 (C_{qpyr}), 115.8 (CH_{pyr}), 114.4 (CH_{pyr}), 50.2 ($NCH_2CH_2CH_3$), 35.7 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 24.0 ($NCH_2CH_2CH_3$), 11.2 ppm ($NCH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 479.4 $[M+H]^+$; elemental analysis calcd for $C_{32}H_{38}N_4$ (478.66): C 80.29, H 8.00, N 11.71; found: C 79.97, H 7.80, N 11.31.

$\mathbf{3}_{syn}$: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.98$ (s, 2H, CH_{pyr}), 8.48 (s, 2H, CH_{pyr}), 8.02 (s, 2H, NCHN, 4.72 (t, $^3J_{H,H} = 7.2$ Hz, 4H, $NCH_2CH_2CH_3$), 2.20 (m, 4H, $NCH_2CH_2CH_3$), 1.64 (s, 9H, $C(CH_3)_3$), 1.60 (s, 9H, $C(CH_3)_3$), 1.12 ppm (t, $^3J_{H,H} = 7.2$ Hz, 6H, $NCH_2CH_2CH_3$), ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.2$ (C_{qpyr}), 147.8 (C_{qpyr}), 142.4 (NCHN), 140.2 (C_{qpyr}), 126.6 (C_{qpyr}), 126.0 (C_{qpyr}), 123.6 (C_{qpyr}), 120.2 (C_{qpyr}), 119.1 (C_{qpyr}), 115.8 (CH_{pyr}), 114.2 (CH_{pyr}), 50.3 ($NCH_2CH_2CH_3$), 35.7 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 24.0 ($NCH_2CH_2CH_3$), 11.2 ppm ($NCH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 479.4 $[M+H]^+$; elemental analysis calcd for $C_{32}H_{38}N_4$ (478.66): C 80.29, H 8.00, N 11.71; found: C 79.98, H 8.22, N 11.53.

Compounds $\mathbf{4}_{anti}$ and $\mathbf{4}_{syn}$: The reaction was carried out with compound **A** (100 mg, 0.25 mmol), NaOH (21.0 mg, 0.51 mmol), and *n*-butyl bromide (58 μL, 0.51 mmol). Yield: 33.7 mg, 26% (*anti* isomer); 52.7 mg, 41% (*syn* isomer).

$\mathbf{4}_{anti}$: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.00$ (d, $^4J_{H,H} = 1.8$ Hz, 2H, CH_{pyr}), 8.47 (d, $^4J_{H,H} = 1.8$ Hz, 2H, CH_{pyr}), 8.00 (s, 2H, NCHN), 4.75 (t, $^3J_{H,H} =$ 7.2 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 2.15 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.65 (s, 18H, $C(CH_3)_3$), 1.56 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.02 ppm (t, $^3J_{H,H} =$ 7.2 Hz, 6H, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.0$ (C_{qpyr}), 142.0 (NCHN), 139.7 (C_{qpyr}), 127.5(C_{qpyr}), 126.5 (C_{qpyr}), 122.8 (C_{qpyr}), 119.6 (C_{qpyr}), 115.7 (CH_{pyr}), 114.4 (CH_{pyr}), 48.5 ($NCH_2CH_2CH_2CH_3$), 35.7 ($C(CH_3)_3$), 32.8 ($NCH_2CH_2CH_2CH_3$), 32.0 ($C(CH_3)_3$), 20.2 ($NCH_2CH_2CH_2CH_3$), 13.8 ppm ($NCH_2CH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 507.4 $[M+H]^+$; elemental analysis calcd for $C_{34}H_{42}N_4$ (506.72): C 80.59, H 8.35, N 11.06; found: C 80.55, H 8.62, N 11.06.

$\mathbf{4}_{syn}$: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.97$ (s, 2H, CH_{pyr}), 8.48 (s, 2H, CH_{pyr}), 8.02 (s, 2H, NCHN), 4.75 (t, $^3J_{H,H} = 7.2$ Hz, 4H, $NCH_2CH_2CH_2CH_3$), 2.14 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.65 (s, 9H, $C(CH_3)_3$), 1.59 (s, 9H, $C(CH_3)_3$), 1.54 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.02 ppm (t, $^3J_{H,H} = 7.5$ Hz, 6H, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.1$ (C_{qpyr}), 147.6 (C_{qpyr}), 142.2 (NCHN), 140.0 (C_{qpyr}), 126.5 (C_{qpyr}), 125.9 (C_{qpyr}), 123.5 (C_{qpyr}), 120.0 (C_{qpyr}), 119.0 (C_{qpyr}), 115.7 (CH_{pyr}), 114.1 (CH_{pyr}), 48.4 ($NCH_2CH_2CH_2CH_3$), 35.6 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 32.6 ($NCH_2CH_2CH_2CH_3$), 31.8 ($C(CH_3)_3$), 20.0 ($NCH_2CH_2CH_2CH_3$), 13.7 ppm ($NCH_2CH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 507.4 $[M+H]^+$; elemental analysis calcd for $C_{34}H_{42}N_4$ (506.72): C 80.59, H 8.35, N 11.06; found: C 80.49, H 8.55, N 11.02.

Compound 5: The reaction was carried out with compound **A** (100 mg, 0.25 mmol), NaOH (21.0 mg, 0.51 mmol), and benzyl bromide (62 μL, 0.51 mmol). The crude solid showed the presence of a 1:1 mixture of the two regioisomers, but attempts to separate them were unsuccessful. Yield: 73.5 mg, 51%. Compound **5** was also obtained starting from 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone. The tetraone (100 mg, 0.27 mmol), benzylamine (88.5 μL, 0.80 mmol), paraformaldehyde (34 mg, 1.07 mmol), and ammonium acetate (63 mg, 0.80 mmol) were heated to reflux in a mixture of methanol (20 mL) and glacial acetic acid (20 mL) for 2 h. Once at room temperature, the solvent was evaporated, and the residue was extracted with CH_2Cl_2. The combined extracts were washed with H_2O, dried over anhydrous magnesium sulfate, and concentrated by rotary evaporation. Diethyl ether (5 mL) was added to the residue. The solid thus formed, which contained **5** as a 1:1 mixture of the *anti* and *syn* regioisomers, was collected by filtration and washed with cold diethyl ether. Yield: 111 mg, 72%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.04$ (s, 2H, CH_{pyr}), 8.93 (d, $^4J_{H,H} = 1.2$ Hz, 2H,

CH_{pyr}), 8.16 (d, $^4J_{H,H}=1.5$ Hz, 2H, CH_{pyr}), 8.11 (s, 2H, CH_{pyr}), 8.10 (s, 2H, NCHN), 8.03 (s, 2H, NCHN), 7.33–7.14 (m, 20H, NCH_2Ph), 6.01 (s, 4H, NCH_2Ph), 5.95 (s, 4H, NCH_2Ph), 1.70 (s, 18H, $C(CH_3)_3$), 1.37 ppm (s, 18H, $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=150.1$ (C_{qpyr}), 148.9 (C_{qpyr}), 147.6 (C_{qpyr}), 142.7 (NCHN), 142.4 (NCHN), 139.9 (C_{qpyr}), 139.5 (C_{qpyr}), 135.9 (C_{qpyr}), 129.2 (C_{qpyr}), 128.0 (C_{qpyr}), 127.0 (C_{qpyr}), 126.4 (C_{qpyr}), 125.7 (C_{qpyr}), 122.7 (C_{qpyr}), 122.1 (C_{qpyr}), 120.0 (C_{qpyr}), 119.7 (C_{qpyr}), 115.8 (CH_{pyr}), 115.6 (CH_{pyr}), 115.4 (CH_{pyr}), 114.0 (CH_{pyr}), 51.5 (NCH_2Ph), 35.7 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$). 31.6 ($C(CH_3)_3$), 31.3 ppm ($C(CH_3)_3$); ESI-MS (20 V, *m/z*): 597.4 $[M+Na]^+$; elemental analysis calcd for $C_{40}H_{40}N_4$ (576.76): C 83.29, H 6.99, N 9.72; found: C 83.54, H 6.53, N 9.67.

Synthesis of bis-imidazolium salts 6–8

Compound 6: Compound **A** (100 mg, 0.25 mmol) and NaOH (21.0 mg, 0.51 mmol) were dissolved in DMSO (2 mL). The reaction mixture was stirred at room temperature for 2 h. Methyl iodide (32 μL, 0.51 mmol) was then added and the mixture was stirred at room temperature for 30 min and thereafter at 37 °C overnight. After this time, the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and the solution filtered through a pad of Celite to remove insoluble salts. The solvent was removed under vacuum and the isolated yellow solid was placed in a thick-walled tube together with methyl iodide (0.64 mL, 10.15 mmol). The mixture was stirred at 100 °C for 24 h. During this time, the desired product precipitated as a red solid, which was collected by filtration and washed with diethyl ether. Yield: 166.3 mg, 93%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=9.83$ (s, 2H, NCHN), 9.08 (s, 4H, CH_{pyr}), 4.75 (s, 12H, NCH_3), 1.68 ppm (s, 18H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=150.3$ (C_{qpyr}), 143.0 (NCHN), 127.0 (C_{qpyr}), 120.9 (C_{qpyr}), 120.0 (C_{qpyr}), 118.4 (CH_{pyr}), 38.4 (NCH_3), 35.6 ($C(CH_3)_3$), 31.2 ppm ($C(CH_3)_3$); ESI-MS (20 V, *m/z*): 226.4 $[M]^{2+}$; elemental analysis calcd for $C_{30}H_{36}N_4I_2$ (706.28): C 51.00, H 5.14, N 7.93; found: C 51.80, H 5.31, N 7.97

Compound 7: Compound **A** (100 mg, 0.25 mmol) and NaOH (21.0 mg, 0.51 mmol) were dissolved in DMSO (2 mL). The reaction mixture was stirred at room temperature for 2 h. Ethyl bromide (39 μL, 0.51 mmol) was then added and the mixture was stirred at room temperature for 30 min and thereafter at 37 °C overnight. After this time, the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and the solution filtered through a pad of Celite to remove insoluble salts. The solvent was removed under vacuum and the isolated yellow solid was placed in a thick-walled tube together with ethyl bromide (0.8 mL, 10.15 mmol). The mixture was stirred at 130 °C for 3 d. During this time, the desired product precipitated as a yellow solid, which was collected by filtration and washed with diethyl ether. Yield: 88.4 mg, 52%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=9.98$ (s, 2H, NCHN), 8.92 (s, 4H, CH_{pyr}), 5.20 (m, 8H, NCH_2CH_3), 1.81 (t, $^3J_{H,H}=6$ Hz, 12H, NCH_2CH_3), 1.68 ppm (s, 18H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=150.5$ (C_{qpyr}), 142.0 (NCHN), 126.6 (C_{qpyr}), 120.6 (C_{qpyr}), 120.0 (C_{qpyr}), 118.5 (CH_{pyr}), 46.2 (NCH_2CH_3), 35.7 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 14.3 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 254.3 $[M]^{2+}$; elemental analysis calcd for $C_{34}H_{44}N_4Br_2$ (668.34): C 61.08, H 6.63, N 8.38; found: C 61.36, H 6.57, N 8.17.

Compound 8: Compound **A** (100 mg, 0.25 mmol) and NaOH (21.0 mg, 0.51 mmol) were dissolved in DMSO (2 mL). The reaction mixture was stirred at room temperature for 2 h. *n*-Butyl iodide (58 μL, 0.51 mmol) was then added and the mixture was stirred at room temperature for 30 min and thereafter at 37 °C overnight. After this time, the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and the solution filtered through a pad of Celite to remove insoluble salts. The solvent was removed under vacuum and the isolated yellow solid was placed in a thick-walled tube together with *n*-butyl iodide (1.68 mL, 10.15 mmol). The mixture was stirred at 130 °C for 3 d, during which the desired product precipitated as a yellow-orange solid, which was collected by filtration and washed with diethyl ether. Yield: 115 mg, 52%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=10.0$ (s, 2H, NCHN), 8.88 (s, 4H, CH_{pyr}), 5.16 (t, $^3J_{H,H}=6.9$ Hz, 8H, $NCH_2CH_2CH_2CH_3$), 2.14 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.67 (s, 18H, $C(CH_3)_3$), 1.57 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.01 ppm (t, $^3J_{H,H}=7.2$ Hz, 12H, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=150.4$ (C_{qpyr}), 142.7 (NCHN), 126.7 (C_{qpyr}), 120.5 (C_{qpyr}), 120.2 (C_{qpyr}), 118.6 (CH_{pyr}), 50.6 ($NCH_2CH_2CH_2CH_3$), 35.6 ($C(CH_3)_3$), 31.1 ($NCH_2CH_2CH_2CH_3$), 30.5 ($C(CH_3)_3$), 19.1 ($NCH_2CH_2CH_2CH_3$), 13.5 ppm ($NCH_2CH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 310.4 $[M]^{2+}$; elemental analysis calcd for $C_{42}H_{60}N_4I_2$ (874.44): C 57.67, H 6.91, N 6.40; found: C 57.64, H 6.90, N 6.47.

Synthesis of bis-imidazolium salts 9–11, general procedure

Compound $\mathbf{2}_{anti}$, $\mathbf{3}_{anti}$, or $\mathbf{4}_{anti}$ (0.11 mmol) was placed in a thick-walled tube together with an excess of methyl iodide (4.40 mmol). The tube was then sealed with a Teflon cap, and the mixture was heated at 100 °C for 24 h. On cooling of the mixture to ambient temperature, the desired salts ($\mathbf{9}_{anti}$, $\mathbf{10}_{anti}$, and $\mathbf{11}_{anti}$, respectively) were separated by filtration and washed with diethyl ether. The same experimental procedure was followed to prepare salts $\mathbf{9}_{syn}$, $\mathbf{10}_{syn}$,and $\mathbf{11}_{syn}$ starting from $\mathbf{2}_{syn}$, $\mathbf{3}_{syn}$, and $\mathbf{4}_{syn}$, respectively.

Compound $\mathbf{9}_{anti}$: Yield: 68.1 mg, 83%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=9.97$ (s, 2H, NCHN), 9.06 (s, 2H, CH_{pyr}), 8.92 (s, 2H, CH_{pyr}), 5.22 (m, 4H, NCH_2CH_3), 4.78 (s, 6H, NCH_3), 1.82 (t, $^3J_{H,H}=6$ Hz, 4H, NCH_2CH_3), 1.69 ppm (s, 18H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=150.4$ (C_{qpyr}), 142.4 (NCHN), 127.5 (C_{qpyr}), 126.2 (C_{qpyr}), 121.0 (C_{qpyr}), 120.5 (C_{qpyr}), 120.0 (C_{qpyr}), 118.5 (CH_{pyr}), 118.4 (CH_{pyr}), 46.1 (NCH_2CH_3), 38.6 (NCH_3), 35.7 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 14.3 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 240.3 $[M]^{2+}$; elemental analysis calcd for $C_{32}H_{40}N_4I_2$ (734.48): C 52.33, H 5.49, N 7.63; found: C 52.64, H 5.35, N 7.27.

Compound $\mathbf{9}_{syn}$: Yield: 59.0 mg, 72%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=9.95$ (s, 2H, NCHN), 9.06 (s, 2H, CH_{pyr}), 8.92 (s, 2H, CH_{pyr}), 5.20 (m, 4H, NCH_2CH_3), 4.78 (s, 6H, NCH_3), 1.82 (t, $^3J_{H,H}=6.0$ Hz, 6H, NCH_2CH_3), 1.69 ppm (s, 18H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=150.4$ (C_{qpyr}), 142.4 (C_{qpyr}), 127.5 (NCHN), 127.0 (C_{qpyr}), 126.3 (C_{qpyr}), 120.8 (C_{qpyr}), 120.6 (C_{qpyr}), 120.1 (C_{qpyr}), 120.0 (C_{qpyr}), 118.9 (CH_{pyr}), 118.5 (CH_{pyr}), 46.1 (NCH_2CH_3), 38.6 (NCH_3), 35.7 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 14.3 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 240.3 $[M]^{2+}$; elemental analysis calcd for $C_{32}H_{40}N_4I_2$ (734.48): C 52.33, H 5.49, N 7.63; found: C 52.34, H 5.40, N 7.62.

Compound $\mathbf{10}_{anti}$: Yield: 60.2 mg, 76%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=9.92$ (s, 2H, NCHN), 9.06 (s, 2H, CH_{pyr}), 8.86 (s, 2H, CH_{pyr}), 5.13 (t, $^3J_{H,H}=7.5$ Hz, 4H, $NCH_2CH_2CH_3$), 4.77 (s, 6H, NCH_3), 2.19 (m, 4H, $NCH_2CH_2CH_3$), 1.68 (s, 18H, $C(CH_3)_3$), 1.12 ppm (t, $^3J_{H,H}=7.5$ Hz, 6H, $NCH_2CH_2CH_3$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=150.4$ (C_{qpyr}), 143.0 (NCHN), 127.7 (C_{qpyr}), 126.1 (C_{qpyr}), 121.0 (C_{qpyr}), 120.4 (C_{qpyr}), 120.0 (C_{qpyr}), 118.6 (CH_{pyr}), 118.4 (CH_{pyr}), 51.9 ($NCH_2CH_2CH_3$), 38.4 (NCH_3), 35.6 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 22.0 ($NCH_2CH_2CH_3$), 10.5 ppm ($NCH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 254.3 $[M]^{2+}$; elemental analysis calcd for $C_{34}H_{44}N_4I_2$ (763.53): C 53.55, H 5.82, N 7.35; found: C 53.65, H 5.83, N 7.32.

Compound $\mathbf{10}_{syn}$: Yield: 59.1 mg, 74%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=9.97$ (s, 2H, NCHN), 9.07 (s, 2H, CH_{pyr}), 8.86 (s, 2H, CH_{pyr}), 5.13 (t, $^3J_{H,H}=6.9$ Hz, 4H, $NCH_2CH_2CH_3$), 4.78 (s, 6H, NCH_3), 2.19 (m, 4H, $NCH_2CH_2CH_3$), 1.68 (s, 18H, $C(CH_3)_3$), 1.13 ppm (t, $^3J_{H,H}=9.0$ Hz, 6H, $NCH_2CH_2CH_3$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=$

150.4 (C_{qpyr}), 143.0 (C_{qpyr}), 127.6 (NCHN), 127.0 (C_{qpyr}), 126.0 (C_{qpyr}), 120.8 (C_{qpyr}), 120.5 (C_{qpyr}), 120.1 (C_{qpyr}), 119.9 (C_{qpyr}), 118.6 (CH_{pyr}), 118.3 (CH_{pyr}), 51.9 ($NCH_2CH_2CH_3$), 38.6 (NCH_3), 35.6 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 21.9 ($NCH_2CH_2CH_3$), 10.5 ppm ($NCH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 254.3 $[M]^{2+}$; elemental analysis calcd for $C_{34}H_{44}N_4I_2$ (763.53): C 53.55, H 5.82, N 7.35; found: C 53.61, H 5.85, N 7.35.

Compound 11_{anti}: Yield: 54.2 mg, 69%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.94 (s, 2H, NCHN), 9.06 (s, 2H, CH_{pyr}), 8.86 (s, 2H, CH_{pyr}), 5.16 (t, $^3J_{H,H}$ = 7.5 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 4.76 (s, 6H, NCH_3), 2.12 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.68 (s, 18H, $C(CH_3)_3$), 1.58 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.00 ppm (t, $^3J_{H,H}$ = 6.9 Hz, 6H, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 150.4 (C_{qpyr}), 142.9 (NCHN), 127.7 (C_{qpyr}), 126.1 (C_{qpyr}), 121.0 (C_{qpyr}), 120.4 (C_{qpyr}), 120.0 (C_{qpyr}), 118.6 (CH_{pyr}), 118.4 (CH_{pyr}), 50.3 ($NCH_2CH_2CH_2CH_3$), 38.4 (NCH_3), 35.7 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 30.5 ($NCH_2CH_2CH_2CH_3$), 19.7 ($NCH_2CH_2CH_2CH_3$), 13.5 ppm ($NCH_2CH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 268.4 $[M]^{2+}$; elemental analysis calcd for $C_{36}H_{48}N_4I_2$ (790.58): C 54.69, H 6.12, N 7.09; found: C 54.64, H 6.33, N 7.17.

Compound 11_{syn}: Yield: 59.4 mg, 76%. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.51 (s, 2H, NCHN), 8.81 (s, 2H, CH_{pyr}), 8.63 (s, 2H, CH_{pyr}), 4.86 (t, $^3J_{H,H}$ = 7.2 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 4.50 (s, 6H, NCH_3), 2.00 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.70 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.46 (s, 18H, $C(CH_3)_3$), 0.82 ppm (t, $^3J_{H,H}$ = 7.2 Hz, 6H, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, CD_3CN): δ = 152.0 (C_{qpyr}), 142.7 (C_{qpyr}), 129.3 (NCHN), 128.8 (C_{qpyr}), 128.0 (C_{qpyr}), 122.3 (C_{qpyr}), 122.1 (C_{qpyr}), 121.7 (C_{qpyr}), 119.8 (C_{qpyr}), 119.7 (CH_{pyr}), 52.0 ($NCH_2CH_2CH_2CH_3$), 39.9 (NCH_3), 36.6 $C(CH_3)_3$), 31.9 ($NCH_2CH_2CH_2CH_3$), 31.7 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 20.3 ($NCH_2CH_2CH_2CH_3$), 13.9 ppm ($NCH_2CH_2CH_2CH_3$); ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.97 (s, 2H, NCHN), 9.06 (s, 2H, CH_{pyr}), 8.86 (s, 2H, CH_{pyr}), 5.16 (t, $^3J_{H,H}$ = 6.9 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 4.77 (s, 6H, NCH_3), 2.14 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.69 (s, 18H, $C(CH_3)_3$), 1.58 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.01 ppm (t, $^3J_{H,H}$ = 6.9 Hz, 6H, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 150.4 (C_{qpyr}), 142.9 (C_{qpyr}), 127.6 (NCHN), 127.0 (C_{qpyr}), 126.1 (C_{qpyr}), 120.9 (C_{qpyr}), 120.6 (C_{qpyr}), 119.9 (C_{qpyr}), 118.6 (C_{qpyr}), 118.5 (CH_{pyr}), 118.4 (CH_{pyr}), 50.4 ($NCH_2CH_2CH_2CH_3$), 38.4 (NCH_3), 35.6 $C(CH_3)_3$), 31.2 ($NCH_2CH_2CH_2CH_3$), 30.6 ($C(CH_3)_3$), 19.2 ($NCH_2CH_2CH_2CH_3$), 13.5 ppm ($NCH_2CH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 268.4 $[M]^{2+}$; elemental analysis calcd for $C_{36}H_{48}N_4I_2$ (790.58): C 54.69, H 6.12, N 7.09; found: C 54.64, H 6.22, N 7.09.

Synthesis of the salts 9-BF_4 and 11-BF_4, general procedure

A solution of compound $\mathbf{9}_{anti}$ or $\mathbf{11}_{anti}$ (0.14 mmol) in anhydrous CH_2Cl_2 (25 mL) was treated with $Et_3O{\cdot}BF_4$ (0.27 mmol). The mixture was stirred at room temperature for 1 h. The solution was concentrated, and diethyl ether (5 mL) was added to induce precipitation. The yellow solid thus formed was collected by filtration and washed with diethyl ether (5 mL). The same experimental procedure was followed to prepare salts $\mathbf{9}_{syn}$-BF_4 and $\mathbf{11}_{syn}$-BF_4 starting from $\mathbf{9}_{syn}$ and $\mathbf{11}_{syn}$, respectively.

Compound $\mathbf{9}_{anti}$-BF_4: Yield: 81.7 mg, 92%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.90 (s, 2H, NCHN), 9.06 (s, 2H, CH_{pyr}), 8.91 (s, 2H, CH_{pyr}), 5.19 (m, 4H, NCH_2CH_3), 4.76 (s, 6H, NCH_3), 1.80 (t, $^3J_{H,H}$ = 6 Hz, 6H, NCH_2CH_3), 1.68 ppm (s, 18H, $C(CH_3)_3$); ^{19}F NMR (282 MHz, [D$_6$]DMSO): δ = −148.4 ppm (s, BF_4); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 150.4 (C_{qpyr}), 142.4 (NCHN), 127.5 (C_{qpyr}), 126.2 (C_{qpyr}), 121.0 (C_{qpyr}), 120.5 (C_{qpyr}), 120.0 (C_{qpyr}), 118.5 (CH_{pyr}), 118.4 (CH_{pyr}), 46.1 (NCH_2CH_3), 38.6 (NCH_3), 35.7 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 14.3 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 240.3 $[M]^{2+}$; elemental analysis calcd for $C_{32}H_{40}N_4B_2F_8$ (654.09): C 58.74, H 6.16, N 8.56; found: C 58.31, H 6.68, N 8.53.

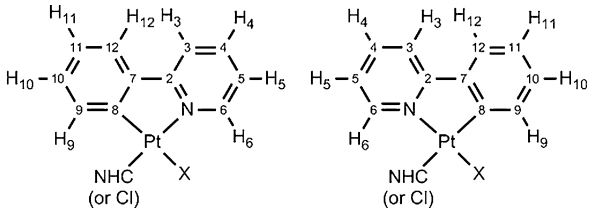
Compound $\mathbf{9}_{syn}$-BF_4: Yield: 80.3 mg, 90%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.90 (s, 2H, NCHN), 9.06 (s, 2H, CH_{pyr}), 8.91 (s, 2H, CH_{pyr}), 5.19 (m, 4H, NCH_2CH_3), 4.76 (s, 6H, NCH_3), 1.80 (t, $^3J_{H,H}$ = 6.0 Hz, 6H, NCH_2CH_3), 1.68 ppm (s, 18H, $C(CH_3)_3$); ^{19}F NMR (282 MHz, [D$_6$]DMSO): δ = −148.4 ppm (s, BF_4); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 150.4 (C_{qpyr}), 142.5 (C_{qpyr}), 127.5 (NCHN), 127.1 (C_{qpyr}), 126.3 (C_{qpyr}), 120.8 (C_{qpyr}), 120.6 (C_{qpyr}), 120.1 (C_{qpyr}), 119.9 (C_{qpyr}), 119.2 (CH_{pyr}), 118.5 (CH_{pyr}), 46.1 (NCH_2CH_3), 38.5 (NCH_3), 35.7 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 14.3 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 240.3 $[M]^{2+}$; elemental analysis calcd for $C_{32}H_{40}N_4B_2F_8$ (654.09): C 58.74, H 6.16, N 8.56; found: C 58.27, H 6.13, N 8.54.

Compound $\mathbf{11}_{anti}$-BF_4: Yield: 66.3 mg, 74%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.90 (s, 2H, NCHN), 9.06 (s, 2H, CH_{pyr}), 8.86 (s, 2H, CH_{pyr}), 5.15 (t, $^3J_{H,H}$ = 9 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 4.76 (s, 6H, NCH_3), 2.12 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.68 (s, 18H, $C(CH_3)_3$), 1.58 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.00 ppm (t, $^3J_{H,H}$ = 6 Hz, 6H, $NCH_2CH_2CH_2CH_3$); ^{19}F NMR (282 MHz, [D$_6$]DMSO): δ = −148.4 ppm (s, BF_4); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 150.4 (C_{qpyr}), 143.0 (NCHN), 127.7 (C_{qpyr}), 126.1 (C_{qpyr}), 121.0 (C_{qpyr}), 120.4 (C_{qpyr}), 120.0 (C_{qpyr}), 118.6 (CH_{pyr}), 118.4 (CH_{pyr}), 50.3 ($NCH_2CH_2CH_2CH_3$), 38.3 (NCH_3), 35.7 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 30.5 ($NCH_2CH_2CH_2CH_3$), 19.0 ($NCH_2CH_2CH_2CH_3$), 13.4 ppm ($NCH_2CH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 268.4 $[M]^{2+}$; elemental analysis calcd for $C_{36}H_{48}N_4B_2F_8$ (711.09): C 60.86, H 6.81, N 7.89; found: C 60.84, H 6.85, N 7.77.

Compound $\mathbf{11}_{syn}$-BF_4: Yield: 70.9 mg, 79%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.90 (s, 2H, NCHN), 9.06 (s, 2H, CH_{pyr}), 8.85 (s, 2H, CH_{pyr}), 5.15 (t, $^3J_{H,H}$ = 6 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 4.76 (s, 6H, NCH_3), 2.12 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.68 (s, 18H, $C(CH_3)_3$), 1.57 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.0 ppm (t, $^3J_{H,H}$ = 6 Hz, 6H, $NCH_2CH_2CH_2CH_3$); ^{19}F NMR (282 MHz, [D$_6$]DMSO): δ = −148.4 ppm (s, BF_4); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 150.4 (C_{qpyr}), 143.0 (NCHN), 127.6 (C_{qpyr}), 127.0 (C_{qpyr}), 126.1 (C_{qpyr}), 120.9 (C_{qpyr}), 120.6 (C_{qpyr}), 120.1 (C_{qpyr}), 119.9 (C_{qpyr}), 118.6 (CH_{pyr}), 118.4 (CH_{pyr}), 50.3 ($NCH_2CH_2CH_2CH_3$), 38.4 (NCH_3), 35.6 $C(CH_3)_3$), 31.2 ($NCH_2CH_2CH_2CH_3$), 30.6 ($C(CH_3)_3$), 19.0 ($NCH_2CH_2CH_2CH_3$), 13.4 ppm ($NCH_2CH_2CH_2CH_3$); ESI-MS (20 V, *m/z*): 268.4 $[M]^{2+}$; elemental analysis calcd for $C_{36}H_{48}N_4B_2F_8$ (711.09): C 60.86, H 6.81, N 7.89; found: C 60.80, H 6.85, N 7.87.

Synthesis of the Pt^{II}-based complexes

For the H and C numbering scheme of the 2-phenylpyridinate ligand, see Scheme 3.



Scheme 3. H and C numbering Scheme for the 2-phenylpyridinate ligand.

Synthesis of 12: A solution of $\mathbf{9}_{syn}$ (50 mg, 0.068 mmol), [{Pt(ppy)(μ-Cl)}$_2$] (52 mg, 0.068 mmol) and NaCl (8 mg, 0.136 mmol) in DMSO (8 mL) was heated at 100 °C overnight. The solution was concentrated under vacuum, and water (5 mL) was added. The orange-red solid thus formed was collected by filtration and successively washed with water (5 mL) and diethyl ether (5 mL). Yield: 81.1 mg, 90%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.91 (s, 2H, NCHN), 9.27 (d, 2H, $^2J_{H,H}$ = 6 Hz, H_6), 8.98 (s, 2H, CH_{pyr}), 8.83 (s, 2H, CH_{pyr}), 8.10 (d, 2H, $^2J_{H,H}$ = 8 Hz, H_9), 7.82 (m, 4H, H_3 and H_4), 7.57 (d,

2H, $^2J_{H,H}=6$ Hz, H_{12}), 7.34 (m, 2H, H_5), 7.12 (m, 4H, H_{10} and H_{11}), 5.15 (m, 4H, NCH_2CH_3), 4.75 (s, 6H, NCH_3), 1.82 (t, $^3J_{H,H}=7$ Hz, 6H, NCH_2CH_3), 1.68 ppm (s, 18H, $C(CH_3)_3$);^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=164.7$ (C_q C8), 150.3 (C_{qpyr}), 148.8 (C_q C2), 144.2 (C_q C7), 142.3 (C_{qpyr}), 141.2 (CH C3), 140.7 (CH C4), 133.2 (CH C9), 129.2 (CH C11), 128.6 (CH C6), 127.3 (NCHN), 126.9 (C_{qpyr}), 126.2 (C_{qpyr}), 124.7 (CH C10), 124.0 (CH C12), 122.5 (CH C5), 120.8 (C_{qpyr}), 120.5 (C_{qpyr}), 120.0 (C_{qpyr}), 119.1 (CH_{pyr}), 118.4 (CH_{pyr}), 118.3 (CH_{pyr}), 46.1 (NCH_2CH_3), 38.5 (NCH_3), 35.6 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 14.3 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 625.4 [C32H$_{40}$N$_4$ Pt(CN)Cl$_2$]$^{2+}$; elemental analysis calcd for $C_{54}H_{56}N_6Cl_4Pt_2$(1320.68): C 49.09, H 4.27, N 6.36; found: C 49.12, H 4.29, N 6.27.

Synthesis of 13a,b: A solution of $\mathbf{9}_{syn}$ (100 mg, 0.136 mmol), [Pt(ppy)(μ-Cl)]$_2$ (105 mg, 0.136 mmol), NaOAc (22 mg, 0.272 mmol), and NaCl (204 mg, 1.362 mmol) in DMSO (8 mL) was heated at 100 °C overnight. The solution was concentrated under vacuum, and CH_2Cl_2 (10 mL) was added to the solid residue. The mixture was filtered through Celite to eliminate the salts thus formed. The filtrate was evaporated to dryness and the residue was dissolved in CH_2Cl_2 and purified by column chromatography. Elution with CH_2Cl_2 afforded a yellow band that contained the desired product. The reaction yielded a mixture of isomers **13a** and **13b** in a 6:4 ratio, which could not be separated. Yield: 86.2 mg, 44%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=10.19$ (m, 2H, H_6, **13a**), 9.00 (s, 2H, CH_{pyr}, **13a**), 8.99 (s, 2H, CH_{pyr}, **13b**), 8.93 (m, 2H, H_6, **13b**), 8.87 (s, 2H, CH_{pyr},**13a**), 8.86 (s, 2H, $CH_{pyr\,anti}$, **13b**), 7.90 (m, 2H, H_4, **13a**), 7.83 (m, 2H, H_4, **13b**), 7.62 (m, 2H, H_9, **13b**), 7.60 (m, 2H, H_9, **13a**), 7.36 (m, 2H, H_5, **13a**), 7.30 (m, 4H, H_5, **13b**), 7.21 (m, 4H, H_{10}, **13a** and **13b**), 7.13 (m, 4H, H_{11}, **13a** and **13b**), 6.90 (t, 4H, $^2J_{H,H}=6$ Hz, H_3, **13a**), 6.82 (t, 4H, $^2J_{H,H}=9$ Hz, H_3, **13b**), 6.44 (d, 4H, $^2J_{H,H}=6$ Hz, H_{12}, **13a**), 6.34 (d, 4H, $^2J_{H,H}=9$ Hz H_{12}, **13b**), 5.64 (m, 4H, NCH_2CH_3), 5.01 (s, 6H, NCH_3, **13b**), 4.93 (s, 6H, $NCH_{3\,syn}$, **13a**), 1.84 (t, $^3J_{H,H}=9$ Hz, 6H, NCH_2CH_3), 1.65 (s, 18H, $C(CH_3)_3$, **13a**), 1.64 ppm (s, 18H, $C(CH_3)_3$, **13b**); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=170.0$ (C_q C8), 165.2 (C_q C8), 154.5 (C_{qpyr}), 154.4 (C_{qpyr}), 150.0, 149.6, 146.6, 146.3, 145.3, 145.2, 139.9, 138.6, 138.0, 134.3, 134.0, 131.7, 131.2, 130.9, 129.6, 128.5, 124.2, 124.0, 123.8, 123.7, 123.5, 122.3, 121.7, 120.0, 119.4, 118.7, 116.5, 47.2 (NCH_2CH_3, **13a**), 46.3 (NCH_2CH_3, **13b**), 41.0 (NCH_3, **13a**), 40.2 (NCH_3, **13b**), 36.0 ($C(CH_3)_3$), 35.9 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 15.1 (NCH_2CH_3), 14.5 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 1344.5 [*M*−I+MeCN]$^+$, 629.3 [*M*−2I+2MeCN]$^{2+}$, 1345.3 [*M*+H]$^+$ in MeOH; elemental analysis calcd for $C_{54}H_{54}N_6I_2Pt_2$ (1430.68): C 45.32, H 3.80, N 5.87; found C 45.33, H 3.85, N 5.87.

Synthesis of 14a,b: $AgBF_4$ (20 mg, 0.102 mmol) was added to a solution of **13** (67 mg, 0.047 mmol) in dry CH_2Cl_2 (10 mL). After 1 h of stirring in the absence of light, the suspension was filtered over a solution of NaCN (9 mg, 0.186 mmol) in CH_2Cl_2 (10 mL). The reaction was stirred at room temperature overnight. After this time, the suspension was collected by filtration through Celite. The filtrate was concentrated and pentane (5 mL) was added to induce precipitation. The yellow precipitate formed was collected by filtrationand washed with pentane (5 mL). The reaction yielded a mixture of isomers **14a** and **14b** in a 1:1 ratio, which could not be separated. Yield: 59.7 mg, 98%. IR (CH_2Cl_2): 2145 cm^{-1} ($\nu_{Pt\text{-}CN}$). ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta=9.56$ (d, 2H, $^2J_{H,H}=4$ Hz, H_6, **14a**), 9.16 (d, 2H, H_6, **14b**), 9.13 (s, 2H, CH_{pyr}, **14a**), 9.11 (br s, 2H, CH_{pyr}, **14b**), 8.98 (br s, 2H, CH_{pyr}, **14b**), 8.66 (s, 2H, CH_{pyr}, **14a**), 8.35 (m, 4H, H_9, **14a** and **14b**), 8.13 (m, 2H, H_4, **14a**), 8.06 (m, 2H, H_{10}, **14b**), 7.93 (m, 2H, H_4, **14b**), 7.78 (m, 2H, H_{11}, **14a**), 7.76 (m, 2H, H_3, **14b**), 7.48 (m, 2H, H_5, **14a**), 7.29 (m, 2H, H_{10}, **14a**), 7.21 (m, 2H, H_5, **14b**), 7.05 (m, 2H, H_3, **14a**), 6.88 (m, 2H, H_{11}, **14b**), 6.68 (d, 2H, H_{12}, **14b**), 6.63 (d, 2H, H_{12}, **14a**), 5.60 (m, 4H, NCH_2CH_3, **14b**), 5.58 (m, 4H, NCH_2CH_3, **14a**), 5.01 (s, 6H, NCH_3, **14b**), 4.93 (s, 6H, NCH_3, **14a**), 1.82 (t, $^3J_{H,H}=9$ Hz, 12H, NCH_2CH_3, **14a** and **14b**), 1.69 (s, 18H, $C(CH_3)_3$, **14b**), 1.67 ppm (s, 18H, $C(CH_3)_3$, **14a**); ^{13}C NMR (75 MHz, [D$_6$]acetone): $\delta=178.1$ (C_q C8), 170.0 (C_q C8), 153.4 (C_{qpyr}), 153.1 (C_{qpyr}), 153.1 (C_{qpyr}), 150.3, 149.6, 143.0, 140.6, 139.7, 139.3, 138.9, 138.4, 138.1, 137.5, 137.4, 131.2, 130.5, 124.9, 124.7, 124.5, 124.4, 124.1, 123.9, 123.4, 120.2, 119.4, 48.1 (NCH_2CH_3), 47.4 (NCH_2CH_3), 41.5 (NCH_3), 41.2 (NCH_3), 40.5 (NCH_3), 36.4 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 15.4 (NCH_2CH_3), 13.8 ppm (NCH_2CH_3); ESI-MS (20 V, *m/z*): 1243.3 [*M*−CN+MeCN]$^+$, 629.3 [*M*−2CN+2MeCN]$^{2+}$; elemental analysis calcd for $C_{54}H_{54}N_8Pt_2$ (1228.92): C 53.81, H 4.52, N 9.30; found C 54.33, H 4.85, N 9.42.

Acknowledgements

We gratefully ackowledge financial support from MINECO of Spain (CTQ2014-51999-P) and StartUJI (VAL-2013-01). The authors are grateful to the Serveis Centrals d'Instrumentació Científica (SCIC) of the Universitat Jaume I for providing spectroscopic and X-ray facilities. We would also like to thank the Ramón y Cajal Program (M.P.). A.G. would like to thank the Generalitat Valenciana for finantial support (Institute of Nanotecnologies for Clean Energies, ISIC/2012/008).

Keywords: luminescence · nitrogen heterocycles · photophysics · platinum · polycycles

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Received: March 25, 2015
Published online on June 10, 2015