Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 8648



Photophysical and electrochemical properties of 1,3-bis(2-pyridylimino)isoindolate platinum(II) derivatives[†]

Kenneth Hanson,^a Luke Roskop,^b Niral Patel,^a Laurent Griffe,^a Peter I. Djurovich,^a Mark S. Gordon^{*b} and Mark E. Thompson^{*a}

Received 15th February 2012, Accepted 25th April 2012 DOI: 10.1039/c2dt30354j

A series of twelve platinum(II) complexes of the form (N^N^N)PtX have been synthesized and characterized where N^N^N is 1,3-bis(2-pyridylimino)isoindolate ligands (BPI) or BPI ligands whose aryl moieties are substituted with *tert*-butyl, nitro, alkoxy, iodo or chloro groups, and X is a chloride, fluoride, cyano, acetate, phenyl or 4-(dimethylamino)phenyl ligand. All complexes display at least one irreversible oxidation and two reversible reduction waves at potentials dependent on the position and the electron donating or withdrawing nature of both X and the substituted N^N^N ligand. Broad room temperature phosphorescence ranging in energy from 594 to 680 nm was observed from the complexes, with quantum efficiencies ranging from 0.01 to 0.05. The efficiency of emission is dictated largely by nonradiative processes since the rate constants for nonradiative deactivation [(1.1–100) × 10⁵ s⁻¹] show greater variation than those for radiative decay [(0.57–4.0) × 0⁴ s⁻¹]. Nonradiative deactivation for compounds with X = Cl follow the energy gap law, *i.e.* the nonradiative rate constants increase exponentially with decreasing emission energy. Deactivation of the excited state appears to be strongly influenced by a non-planar distortion of the BPI ligand.

Introduction

Square planar platinum(II) complexes are known to exhibit a rich array of photophysical properties and many potential applications have been suggested to exploit their luminescent characteristics.¹⁻⁴ Chelating ligands that have been used to produce these square planar complexes include bidentate, tridentate and tetradentate ligands.⁵ Of these, the tridentate ligands possess two notable advantages. First, they can inhibit square planar to tetrahedral (D_{2d}) distortions⁶ that promote nonradiative decay. Second, unlike tetradentate ligands, tridentate ligands provide an available coordination site that permits further modification of the complex. This feature enables one to use either anionic (*e.g.*, Cl, NCS, OH, OMe, or alkyne) or neutral (*e.g.*, amines, pyridines) ligands to alter the charge and/or spectroscopic properties of the parent structure.⁷⁻¹⁰

A variety of tridentate ligands have been used to prepare luminescent Pt(II) complexes. Perhaps the most studied of these is 2,2':6',2''-terpyridine (terpy) and related ligands that coordinate

to platinum through three imine nitrogen atoms.^{4,11} Analogs of terpy have also been investigated in which a phenyl group is substituted for one or two of the imine moieties to produce monoand dianionic ligands of the type (C^N^N) or (N^C^N) or $(C^N^C)^{2-2-5}$ However, there are few examples of Pt(II) complexes with monoanionic (N^N^N)⁻ ligands,¹²⁻¹⁵ and even fewer reports of luminescence from complexes with these kinds of ligands.^{12,16,17} One interesting version of a (N^N^N)⁻ ligand is 1,3-bis(2-pyridylimino)isoindolate (BPI). BPI ligands are used for a variety of different applications $^{18-22}$ because they are thermally stable, readily synthesized²³ and easily modified. BPI has been used as a chelate for a number of metals, including platinum.¹⁵ Reports on these metal-BPI complexes have been focused primarily on catalytic properties, and only minimal data has appeared regarding the photophysical characteristics of these compounds.24

Recently, a series of (BPI)PtCl derivatives were synthesized and their photophysical properties investigated.^{25,26} The parent (BPI)PtCl was found to display phosphorescent emission at 631 nm with a quantum efficiency of 0.54% in CH₂Cl₂. Replacing the coordinating chloride anion with a neutral *N*-heterocyclic ligand has a minimal effect on absorption/emission energies and efficiencies. Additionally, unlike the significant changes in photophysical properties of $[(terpy)PtCl]^{+1}$ when the chloride ligand is replaced with an acetylene group,²⁷ the (BPI) Pt acetylene complex has similar absorption/emission spectra to the parent (BPI)PtCl, with the emission efficiency decreasing to 0.36%. This result is contrary to the expectation that the addition of a strong field ligand will increase the platinum d–d energy

^aDepartment of Chemistry, University of Southern California,

Los Angeles, CA 90089, USA. E-mail: met@usc.edu

^bDepartment of Chemistry, Iowa State University, Ames, Iowa 50011,

USA. E-mail: mark@si.msg.chem.iastate.edu

[†] Electronic supplementary information (ESI) available: Calculated HOMO/LUMO orbitals for 1–12, emission spectra at 77 K for 1–12, the calculated transitions of 6, cyclic voltammograms for 1, 6–12, $^{1}H/^{13}C$ NMR spectra of 1–12 and crystallographic data for 6. CCDC reference number 867303. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30354j

	R_5 R_4 R_3			
Complex	X	R ₃	R ₄	R ₅
1	C1	Н	Н	Н
2	F	Н	Н	Н
3	CN	Н	Н	Н
4	OAc	Н	Н	Н
5	C_6H_5	Н	Н	Н
6	p-(NMe ₂)C ₆ H ₄	Н	Н	Н
7	Cl	Н	t-Bu	Н
8	Cl	NO_2	Н	Н
9	Cl	Н	NO_2	Н
10	Cl	Н	OC_5H_{11}	Н
11	C1	Н	Ι	Н
12	Cl	Н	Cl	Cl

 $\overline{}$

Fig. 1 Structure of substituted BPI platinum complexes 1–12.

separation and thus, reduce non-radiative deactivation through ligand field states.^{7,28–30} On the other hand, the platinum chloride complexes with 1,3-bis(2-pyridylimino)isoindolate ligands appended with electron donating (NH₂) and electron withdrawing (NO₂) groups display significant variations in electrochemical properties, emission wavelength and efficiency relative to (BPI)PtCl.²⁶

To better understand this new class of emitter, (BPI)PtX, it is important to expand the investigation into how perturbations on either the BPI or anionic monodentate ligand affect its luminescent properties. Herein we report the synthesis, photophysical and electrochemical characterization of a series of platinum(II) complexes of the form (R-BPI)PtX, where R-BPI is an assortment of substituents (R) on the BPI ligand and X represents various anionic monodentate ligands (Fig. 1). The photophysical data indicate that structural distortion of the BPI ligand in an electronic excited state imparts a significant contribution to the rate of nonradiative decay.

Experimental section

General information

2-Aminopyridine, 1,2-dicyanobenzene, 1,5-cyclooctadiene, 4-*tert*-butylphthalonitrile, 4-iodophthalonitrile, 4-(*N*,*N*-dimethyl)aniline magnesium bromide, phenylmagnesium bromide, silver(1) fluoride, potassium silver(1) cyanide, silver acetate (Aldrich),

1,2-dicyanonaphthalene, 4,5-dichlorophthalonitrile, 3-nitrophthalonitrile, 4-nitrophthalonitrile, 4-pentoxyphthalonitrile, 4-iodophthalonitrile (TCI America), calcium chloride (J.T. Baker), and K₂PtCl₄ (Pressure Chemical Company) were purchased from the corresponding supplier (in parentheses) and used without further purification for synthesis. (COD)PtCl₂,³¹ 1,3-bis(2-pyridylimino)isoindole,²³ 4-NO₂BPI,²⁶ 1,3-bis(2-pyridylimino)isoindolate platinum(II) chloride (1),¹⁵ (COD)PtPh₂,³² and (COD)Pt(Ph-4-NMe₂)₂³³ were synthesized according to literature procedures. All reported NMR spectra were obtained on a Bruker AC-250 MHz FT NMR or a Varian 400 MHz NMR with all shifts relative to residual solvent signals. Solid probe mass spectrometer (MS) spectra were taken with a Hewlett-Packard MS instrument with electron impact ionization and model 5973 mass selective detector. Mass spectra were also recorded using a Voyager-DE STR mass spectrometer using a positive MALDI-TOF method without matrix. Elemental analyses (CHN) were performed at the Microanalysis Laboratory at the University of Illinois, Urbana-Champaign, IL.

(BPI)PtF (2)

400 mg (0.76 mmol) 1 and 491 mg (3.79 mmol) AgF were rigorously stirred in 100 mL CH₂Cl₂ for 24 hours. The solution was then passed through a plug of silica eluting with CH₂Cl₂ and evaporated to dryness under reduced pressure. The resultant solid was dissolved in a minimal amount of CH₂Cl₂ followed by lavered addition of methanol. After gradual diffusion, precipitate began to form. The precipitate was collected by filtration, washed with methanol and dried under vacuum to give 0.325 g (84%), orange solid. ¹H NMR (400 MHz, CDCl₃, δ) 9.91 (dd, $J_{\rm HH} = 6.4$ Hz, $J_{\rm HF} = 10.8$ Hz, 2H), 8.08 (dd, J = 5.6 and 3.2 Hz, 2H), 8.0 (t, J = 7.2 Hz, 2H), 7.68 (d, J = 8 Hz, 2H), 7.61 (dd, J = 5.2 and 2.8 Hz, 2H), 7.2 (t, J = 6.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ)148.8, 145.9, 145.6, 137.6, 131.1, 127.7, 122.0, 119.62, 119.58. MS m/z (relative intensity): 511.10 (83.16%), 512.05 (100%), 513.00 (78.45%), 514.10 (15.67%), 515.00 (18.28%). UV-vis (CH₂Cl₂) λ_{max} , nm ($\varepsilon/10^4$ M⁻¹ cm⁻¹): 250 (4.20), 277 (2.61), 349 (1.88), 387 (0.87), 476 (1.00), 497 (0.91). Elemental analysis for C₁₈H₁₂N₅PtF·CH₂Cl₂: calcd: C 38.20, H 2.36, N 11.72; found: C 38.82, H 2.09, N 11.87.

(BPI)PtCN (3)

500 mg (0.95 mmol) **1** and 995 mg (5 mmol) KAg(CN)₂ were rigorously stirred in 250 mL CH₂Cl₂ for 24 hours. The solution was then evaporated to dryness under reduced pressure. The product was extracted using a Soxhlet apparatus with 250 mL refluxing CH₂Cl₂. When the extracting solution was no longer yellow, the solution was cooled to room temperature and then to -40 °C. After one day of cooling, the precipitate was collected and the solvent in the remaining solution was reduced and cooled again. This process was repeated several times to yield 0.210 g (43%) of dark red needles. ¹H NMR (400 MHz, CDCl₃, δ) 10.17 (d, $J_{\text{HH}} = 6.4$ Hz, ³ $J_{\text{PtH}} = 26$ Hz, 2H), 8.02 (dd, J = 5.2 and 3.2 Hz, 2H), 7.93 (t, J = 7.6 Hz, 2H), 7.66 (d, J = 8 Hz, 2H), 7.59 (dd, J = 5.6 and 3.2 Hz, 2H), 6.98 (t, J = 6.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ) 157.6, 152.4, 150.8, 138.5,

137.6, 131.7, 128.8, 122.6, 120.8. MS *m/z* (relative intensity): 518.25 (85.76%), 519.20 (100%), 520.20 (72.19%), 521.21 (17.13%), 522.25 (17.19%). UV-vis (CH₂Cl₂) λ_{max} , nm ($\varepsilon/10^4$ M⁻¹ cm⁻¹): 245 (4.46), 268 (2.21), 342 (2.24), 437 (1.69), 465 (1.96). Elemental analysis for C₁₉H₁₂N₆Pt: calcd: C 43.93, H 2.33, N 16.18; found: C 43.97, H 2.05, N 15.33.

(BPI)PtOOCCH₃ (4)

300 mg (0.57 mmol) 1 and 440 mg (3 mmol) silver(1) acetate (AgOAc) were rigorously stirred in 50 mL CH₂Cl₂ for 24 hours. The solution was then passed through a plug of Celite eluting with CH₂Cl₂. The volume was reduced to 15 mL under reduced pressure followed by slow evaporation at room temperature. The precipitate was collected by filtration and washed with methanol to give 0.155 g (49%), orange plates. ¹H NMR (400 MHz, CDCl₃, δ) 9.36 (dd, $J_{\rm HH}$ = 6.8 and 1.6 Hz, $J_{\rm PtH}$ = 11.6 Hz, 2H), 8.08 (dd, J = 5.6 and 3.2 Hz, 2H), 7.95 (ddd, J = 8.4, 6.8 and 1.6 Hz, 2H), 7.66 (dd, J = 7.2 and 1.6 Hz, 2H), 7.62 (dd, J = 5.2 and 2.8 Hz, 2H), 7.09 (td, J = 5.2 and 1.6 Hz, 2H), 2.3 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, δ) 177.6, 151.2, 150.0, 147.1, 137.7, 137.6, 131.3, 128.1, 122.2, 119.8, 24.7. MS m/z (relative intensity): 551.10 (83.66%), 552.10 (100%), 553.10 (78.57%), 554.10 (17.36%), 555.45 (18.56%). UV-vis (CH₂Cl₂) λ_{max} , nm $(\varepsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1})$: 249 (4.86), 278 (2.93), 349 (2.21), 464 (1.34), 488 (1.31). Elemental analysis for C₁₉H₁₂N₆Pt: calcd: C 43.48, H 2.74, N 12.68; found: C 43.44, H 2.52, N 12.17.

(BPI)PtPh (5)

0.095 g (0.208 mmol) (COD)PtPh₂ and 0.072 g (0.192 mmol) BPI were suspended in 20 ml of methanol. To this solution 0.038 ml (0.208 mmol) triethylamine was added and the solution was heated to 50 °C under nitrogen overnight. A precipitate began to form upon cooling to room temperature. The precipitate was collected by filtration and washed with methanol. The product was then recrystallized from a minimal amount of CH₂Cl₂ followed by a layered addition of methanol to give 0.044 g (37%), orange needles. ¹H NMR (400 MHz, CDCl₃, δ) 8.57 (d, $J_{\rm HH}$ = 6.4 Hz, $J_{\rm PtH}$ = 28 Hz, 2H), 8.08–8.05 (m, 2H), 7.76 (td, J = 7.6 and 2 Hz, 2H), 7.65–7.55 (m, 6H), 7.13 (t, J =7.6 Hz, 2H), 7.03 (t, J = 7.2 Hz, 1H), 6.49 (td, J = 6.8 and 2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ) 156.9, 154.0, 153.6, 152.2, 139.0, 136.9, 136.8, 130.9, 129.3, 128.7, 123.5, 122.2, 118.7. MS m/z (relative intensity): 568.15 (75.44%), 569.10 (100%), 570.15 (95.29%), 571.20 (48.40%), 572.15 (39.80%). UV-vis (CH₂Cl₂) λ_{max} , nm ($\epsilon/10^4$ M⁻¹ cm⁻¹): 249 (4.35), 289 (2.37), 352 (1.99), 472 (1.17), 497 (1.13). Elemental analysis for C₂₄H₁₇N₅Pt: calcd: C 50.53, H 3.00, N 12.28; found: C 50.83. H 2.81, N 11.98.

(BPI)Pt(Ph-4-NMe₂) (6)

0.100 g (0.18 mmol) (COD)Pt(Ph-4-NMe₂)₂ and 0.049 g (0.165 mmol) BPI were suspended in 5 ml of methanol. To this solution 0.030 ml (0.18 mmol) triethylamine was added and the solution was heated to 60 °C under nitrogen for 4 days. Precipitate began to form upon cooling to room temperature. The

precipitate was collected by filtration and washed with methanol. The product was then recrystallized from a minimal amount of CH₂Cl₂ followed by layered addition of methanol to give 0.054 g (49%), black crystals. ¹H NMR (400 MHz, CDCl₃, δ ppm) 8.81 (dd, J = 6.8 and 1.6 Hz, J_{PtH} = 26.8 Hz, 2H), 8.12 (dd, J = 5.2 and 2.8 Hz, 2H), 7.82 (ddd, J = 6.8, 5.6 and 1.6 Hz, 2H), 7.68–7.62 (m, 4H), 7.48 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.59 (td, J = 6.8 and 1.6 Hz, 2H), 2.98 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ ppm) 154.2, 153.5, 152.2, 147.6, 139.1, 136.6, 136.4, 130.8, 128.6, 122.1, 118.6, 115.3, 110.0. MS m/z (relative intensity): 612.15 (99.94%), 613.15 (100%), 614.15 (84.14%), 615.15 (22.34%), 616.15 (13.26%). UV-vis (CH₂Cl₂) λ_{max} , nm ($\epsilon/10^4$ M⁻¹ cm⁻¹): 252 (4.91), 287 (2.87), 342 (1.78), 470 (0.94). Elemental analysis for C₂₆H₂₂N₆Pt: calcd: C 50.90, H 3.61, N 13.70; found: C 51.09, H 3.40, N 13.36.

4-t-BuBPI

A solution of 1 g (5.43 mmol) 4-*tert*-butylphthalonitrile, 1.28 g (13.6 mmol) 2-aminopyridine and 0.12 g (1.0 mmol) CaCl₂ in 20 ml 1-butanol was refluxed under N₂ for 5 days. Upon cooling to room temperature, the solution was poured into 50 mL of water and precipitate began to form. The precipitate was collected by filtration and was then chromatographed on silica gel eluting with CH₂Cl₂. A fluorescent blue fraction of 4-*tert*-butylphthalonitrile starting material was collected first, followed by a yellow fraction containing the desired product. The yellow fraction . 0.439 g (23%), yellow solid. ¹H NMR (250 MHz, CDCl₃, δ) 8.61 (d, *J* = 5 Hz, 2H), 8.1 (d, *J* = 1 Hz, 1H), 8.0 (d, *J* = 8 Hz, 1H), 7.82–7.67 (m, 3H), 7.46 (dd, *J* = 8, 5 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 2H), 1.64 (s, 9H).

(4-t-BuBPI)PtCl (7)

0.2 g (0.54 mmol) (COD)PtCl₂ and 0.173 g (0.486 mmol) 4-t-BuBPI were suspended in 15 ml of methanol. To this solution 0.074 ml (0.54 mmol) triethylamine was added and the solution was heated overnight to 50 °C under nitrogen. A bright orange precipitate began to form upon cooling to room temperature. The precipitate was collected by filtration and washed with methanol. The solid was recrystallized from a minimal amount of CH₂Cl₂ followed by layered addition of hexane to give 0.171 g (70%), orange plates. ¹H NMR (400 MHz, CDCl₃, δ) 10.4–10.2 (m, 2H), 8.13 (dd, J = 1.6, 0.4 Hz, 1H), 7.99 (dd, J = 8.0, 0.4 Hz, 1H), 7.97-7.90 (m, 2H), 7.69 (dd, J = 8.0, 1.6 Hz, 1H), 7.68–7.61 (m, 2H), 7.07–7.01 (m, 2H), 1.46 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, δ) 155.7, 152.4, 151.5, 151.3, 150.1, 150.0, 138.1, 137.5, 134.8, 128.8, 127.5, 127.4, 122.1, 119.7, 119.6, 119.3, 35.6, 31.4. MS m/z (relative intensity): 583.15 (86.21%), 584.15 (100%), 585.10 (96.98%), 586.15 (48.63%), 587.10 (41.17%). UV-vis (CH₂Cl₂) λ_{max} , nm ($\varepsilon/10^4$ M⁻¹ cm⁻¹): 250 (5.36), 278 (3.86), 352 (2.49), 472 (1.33), 486 (1.32). Elemental analysis for C₂₂H₂₀N₅PtCl: calcd: C 45.17, H 3.45, N 11.97; found: C 45.16, H 3.27, N 11.65.

3-NO₂BPI

A solution of 0.86 g (4.79 mmol) 3-nitrophthalonitrile, 0.98 g (10.4 mmol) 2-aminopyridine and 0.10 g (0.89 mmol) CaCl₂ in 15 ml 1-butanol was refluxed under N2 for 4 days. Upon cooling to room temperature, precipitate began to form. The precipitate was collected by filtration and the crude product was dissolved in ethylacetate and passed through a plug of silica. The yellow fraction was evaporated to dryness and used without further purification. 0.703 g (41%), yellow solid. ¹H NMR (250 MHz, $CDCl_3$, δ) 8.92 (d, J = 2 Hz, 2H), 8.29 (d, J = 7 Hz, 1H), 7.85–7.72 (m, 4H), 7.45 (t, J = 8 Hz, 2H), 7.20–7.10 (m, 2H).

(3-NO₂BPI)PtCl (8)

0.1 g (0.268 mmol) (COD)PtCl₂ and 0.084 g (0.243 mmol) 3-NO₂BPI were suspended in 15 ml of methanol. To this solution 0.037 ml (0.268 mmol) triethylamine was added and the solution was heated to 50 °C under nitrogen overnight. Upon cooling to room temperature, precipitate began to form. The precipitate was collected by filtration and washed with water and methanol. The orange solid was then recrystallized by dissolving hot CH₂Cl₂ and cooled to -40 °C overnight. The precipitate was collected by filtration and washed with methanol to give 0.097 g (64%), maroon powder. ¹H NMR (400 MHz, CDCl₃, δ) 10.33 (t, J = 6.4 Hz, 2H), 8.31 (d, J = 6.8 Hz, 1H), 7.99–7.93 (m, 2H), 7.81–7.74 (m, 2H), 7.64 (d, J = 8 Hz, 1H), 7.58 (d, J = 8 Hz, 1H), 7.13–7.06 (m, 2H). MS (MALDI-TOF): *m*/*z* = 574.11. UVvis (CH₂Cl₂) λ_{max} , nm ($\epsilon/10^4$ M⁻¹ cm⁻¹): 235 (3.23), 278 (2.75), 338 (1.53), 483 (1.05), 505 (1.05). Elemental analysis for C₁₈H₁₁N₆O₂PtCl: calcd: C 37.67, H 1.93, N 14.64; found: C 37.44, H 1.78, N 13.70.

(4-NO₂BPI)PtCl (9)

0.1 g (0.268 mmol) (COD)PtCl₂ and 0.084 g (0.243 mmol) 4-NO₂BPI were suspended in 20 ml of methanol. To this solution 0.037 ml (0.268 mmol) triethylamine was added and the solution was heated to 50 °C under nitrogen overnight. Upon cooling to room temperature, precipitate began to form. The precipitate was collected by filtration and washed with methanol. The orange solid was then recrystallized by dissolving the solid in hot CH₂Cl₂ and then cooling the solution to -40 °C overnight. The precipitate was collected by filtration and washed with methanol to give 0.092 g (60%), maroon powder. ¹H NMR (400 MHz, CDCl₃, δ) 10.5–10.3 (m, 2H), 8.92 (d, J = 2.0 Hz, 1H), 8.53 (dd, J = 8.0, 2.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.04–7.98 (m, 2H), 7.70 (t, *J* = 6.8 Hz, 2H). MS (MALDI-TOF): m/z = 574.01. UV-vis (CH₂Cl₂) λ_{max} , nm ($\varepsilon/10^4$ M⁻¹ cm⁻¹): 232 (3.23), 277 (3.41), 346 (2.14), 492 (1.09), 511 (1.08). Elemental analysis for C₁₈H₁₁N₆O₂PtCl: calcd: C 37.67, H 1.93, N 14.64; found: C 37.58, H 1.74, N 14.04.

4-OC₅H₁₁BPI

A solution of 1.0 g (4.67 mmol) 4-pentoxyphthalonitrile, 1.10 g (11.68 mmol) 2-aminopyridine and 0.10 g (0.89 mmol) CaCl₂ in 10 ml 1-butanol was refluxed under N₂ for 11 days. Upon cooling to room temperature, the solution was poured into 50 mL of water and precipitate began to form. The precipitate was collected by filtration, washed with water and used without further purification. 1.56 g (87%), yellow powder. ¹H NMR (250 MHz, CDCl₃, δ) 8.59 (t, J = 4.75 Hz, 2H), 7.94 (d, J = 8.5Hz, 1H), 7.80-7.70 (m, 2H), 8.23 (d, J = 2.25 Hz, 1H), 7.42(dd, J = 8, 4.75 Hz, 2H), 7.20–7.05 (m, 3H), 4.12 (t, J = 10.8Hz, 2H), 1.94-1.77 (m, 4H), 1.58-1.32 (m, 2H), 0.95 (t, J = 10.8 Hz, 3H).

(4-OC₅H₁₁BPI)PtCl (10)

0.1 g (0.268 mmol) (COD)PtCl₂ and 0.094 g (0.243 mmol) 4-OC₅H₁₁BPI were suspended in 10 ml of methanol. To this solution 0.037 ml (0.268 mmol) triethylamine was added and the solution was heated to 50 °C under nitrogen overnight. Upon cooling to room temperature, precipitate began to form. The precipitate was collected by filtration and washed with water and methanol. The orange solid was then recrystallized by dissolving it in a minimal amount of CH₂Cl₂ followed by layered addition of hexane to give 0.078 g (52%), red powder. ¹H NMR (400 MHz, CDCl₃, δ) 10.3 (dd, J = 6.4, 2 Hz, 1H), 10.27 (dd, J = 6.4, 2 Hz, 1H), 7.95–7.86 (m, 3H), 7.61–7.55 (m, 2H), 7.54 (d, J = 2.4 Hz, 1H), 7.12 (dd, J = 8.0, 2.4 Hz, 1H), 7.04-6.98(m, 2H), 4.13 (t, J = 6.4 Hz, 2H), 1.91–1.82 (m, 2H), 1.55–1.37 (m, 4H), 0.96 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, δ) 162.7, 152.4, 151.1, 151.0, 150.1, 150.0, 139.6, 138.0, 129.2, 127.4, 127.3, 123.7, 119.6, 119.4, 118.7, 107.0, 68.7, 28.9, 28.2, 22.4, 14.0. MS m/z (relative intensity): 613.15 (81.44%), 614.10 (100%), 615.05 (95.62%), 616.10 (47.02%), 617.10 (41.05%). UV-vis (CH₂Cl₂) λ_{max} , nm ($\epsilon/10^4$ M⁻¹ cm⁻¹): 261 (4.13), 280 (3.69), 351 (1.74), 386 (1.63), 472 (0.90), 492 (0.83). Elemental analysis for C₂₃H₂₂N₅OPtCl: calcd: C 44.92, H 3.61, N 11.39; found: C 45.06, H 3.49, N 10.82.

4-IBPI

A solution of 1 g (3.94 mmol) 4-iodophthalonitrile, 0.927 g (9.85 mmol) 2-aminopyridine and 0.085 g (0.75 mmol) CaCl₂ in 12 ml 1-butanol was refluxed under N₂ for 2 days. Upon cooling to room temperature precipitate began to form. The precipitate was collected by filtration, washed with water and used without further purification. 1.42 g (85%), green powder. ¹H NMR (250 MHz, CDCl₃, δ) 8.63 (dd, J = 3.2, 1.2 Hz, 1H), 8.61 (dd, J = 3.2, 1.2 Hz, 1H), 8.44 (dd, J = 2.4, 1.2 Hz, 1H), 7.98 (dd, J = 12.8, 2.4 Hz, 1H), 7.84–7.73 (m, 3H), 7.45 (d, J = 12.8 Hz, 2H), 7.17–7.10 (m, 2H).

(4-IBPI)PtCl (11)

0.1 g (0.268 mmol) (COD)PtCl₂ and 0.103 g (0.243 mmol) 4-IBPI were suspended in 10 ml of methanol. To this solution 0.037 ml (0.268 mmol) triethylamine was added and the solution was heated to 50 °C under nitrogen overnight. Upon cooling to room temperature, precipitate began to form. The precipitate was collected by filtration and washed with water and methanol. The orange solid was then recrystallized by dissolving hot CH₂Cl₂ and cooling the solution to -40 °C overnight. The precipitate was collected by filtration and washed with methanol to give 0.085 g (53%), orange powder. ¹H NMR (400 MHz, CDCl₃, δ) 10.33 (d, J = 6.8 Hz, 2H), 8.64 (dd, J = 1.6, 0.8 Hz, 1H), 8.00 (dd, J = 8.0, 1.6 Hz, 1H), 7.98–7.93 (m, 2H), 7.83 (dd, J = 8.0, 0.8 Hz, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.07 (t, J = 6.8 Hz, 2H). MS *m*/*z* (relative intensity): 653.00 (79.09%), 653.95 (100%), 654.95 (94.33%), 655.95 (45.88%), 657.00 (31.88%). UV-vis (CH₂Cl₂) λ_{max} , nm (ε /10⁴ M⁻¹ cm⁻¹): 257 (3.80), 279 (3.57), 353 (2.04), 478 (1.00), 497 (0.97). Elemental analysis for C₁₈H₁₁N₅IPtCl: calcd: C 33.02, H 1.69, N 10.70; found: C 32.79, H 1.54, N 10.06.

4,5-diClBPI

A solution of 1.0 g (5.1 mmol) 4,5-dichlorophthalonitrile, 1.2 g (12.75 mmol) 2-aminopyridine and 0.12 g (1 mmol) CaCl₂ in 15 ml 1-butanol was refluxed under N₂ for 2 days. Upon cooling to room temperature, precipitate began to form. The precipitate was collected by filtration and washed with water to give 1.80 g (96%), light green solid. ¹H NMR (250 MHz, CDCl₃, δ) 8.60 (d, J = 5.0, 2H), 8.17 (s, 1H), 7.78 (td, J = 8.0, 1.5 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 5.0 Hz, 2H).

(4,5-diClBPI)PtCl (12)

0.1 g (0.268 mmol) (COD)PtCl₂ and 0.106 g (0.29 mmol) 4,5diCIBPI were suspended in 10 ml of methanol. To this solution 0.043 ml (0.29 mmol) triethylamine was added and the solution was heated to 50 °C under nitrogen overnight. Upon cooling to room temperature, precipitate began to form. The precipitate was collected by filtration and washed with water and methanol to give 129 mg crude product (81%). A 40 mg sample of this crude product was sublimed at 315 °C ($\sim 10^{-4}$ torr) to give 26 mg (sublimation yield: 65%), dark orange needles. ¹H NMR (400 MHz, $CDCl_3$, δ) 10.35 (dd, J = 6.4, 1.6 Hz, 2H), 8.20 (s, 2H), 7.97 (td, J = 7.2, 1.6 Hz, 2H), 7.64 (dd, J = 8.4, 2.0 Hz, 2H), 7.09 (td, J = 6.4, 1.6 Hz, 2H). MS m/z (relative intensity): 594.95 (53.66%), 595.95 (72.475%), 596.95 (100%), 597.95 (69.59%), 598.95 (71.85%), 599.90 (30.89%), 600.95 (26.56%). UV-vis $(CH_2Cl_2) \lambda_{max}$, nm ($\varepsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 257 (4.60), 279 (3.62), 351 (1.90), 479 (1.06), 498 (1.05). Elemental analysis for C₁₈H₁₀N₅PtCl₃: calcd: C 36.17, H 1.69, N 11.72; found: C 36.12, H 1.50, N 11.42.

X-ray crystallography

A clear, intense red prism-like specimen of **6** obtained from CH₂Cl₂–MeOH was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX II CCD system equipped with a TRIUMPH curved-crystal monochromator and a MoK α fine-focus tube source ($\lambda = 0.71073$ Å). The data collection was performed at room temperature due to a crystal phase transition that occurred at 100 K. A total of 2520 frames were collected over a total exposure time of 14.0 hours. The frames were integrated with the Bruker SAINT V7.68A software package⁵⁶ using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent

 Table 1
 Crystal and structure refinement parameters for complex 6, (BPI)Pt(Ph-4-NMe₂)

Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions	$C_{26}H_{22}N_6Pt$ 613.59 296(2) K 0.71073 Å Monoclinic C 2/c a = 11.1436(7) Å b = 23.4283(13) Å c = 9.3583(6) Å	$\alpha = 90^{\circ}$ $\beta = 115.0110(10)^{\circ}$ $\gamma = 90^{\circ}$
Volume	2214.1(2) Å ³	7 90
Z	4	
Density (calculated)	1.841 Mg m^{-3}	
Absorption coefficient	6.365 mm^{-1}	
F(000)	1192	
Crystal size	$0.29 \times 0.17 \times 0.10$ mm	n ³
θ range for data collection	2.20 to 30.53°	
Index ranges	$-15 \le h \le 15, -32 \le -13 \le l \le 13$	$k \leq 33,$
Reflections collected	26 464	
Independent reflections	3363 [<i>R</i> (int) = 0.0251]
Completeness to theta = 30.53°	99.2%	
Absorption correction	Semi-empirical from e	equivalents
Max. and min. transmission	0.54 and 0.46	2
Refinement method	Full-matrix least-square	res on F^2
Data/restraints/parameters	3363/0/153	
Goodness-of-fit on F^2	1.143	0.405
Final <i>K</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0186, WR_2 = 0$.042/
K indices (all data)	$K_1 = 0.0221, WR_2 = 0$.0452 -3
Largest diff. peak and hole	1.301 and -1.003 e A	<u> </u>

transmission was 0.815. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2562 and 0.5629. The structure was solved and refined using the Bruker SHELXTL V6.12 software package.⁵⁷ Additional refinement details and the resulting factors for **6** are given in Table 1 and the ESI.[†]

Electrochemical and photophysical characterization

All cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using an EG&G Potentiostat/Galvanostat model 283. DMF (purchased from VWR) was used as the solvent under inert atmosphere with 0.1 M tetra(*n*-butyl) ammonium hexafluorophosphate (Aldrich) as the supporting electrolyte or a solution of anhydrous 0.1 M NBu₄ClO₄ in CH₂Cl₂ (VWR) as indicated. A glassy carbon rod, a platinum wire and a silver wire were used as the working electrode, the counter electrode, and the pseudo reference electrode, respectively. CV was used to establish electrochemical reversibility using the peak separation between the forward and reverse scans, while all redox potentials were determined using DPV and reported relative to a decamethylferrocenium/ferrocene or ferrocenium/ferrocene (Fc⁺/Fc) redox couple used as an internal standard.³⁴

The UV-visible spectra were recorded on a Hewlett-Packard 4853 diode array spectrophotometer. Steady state emission experiments at room temperature and 77 K were performed on a Photon Technology International QuantaMaster Model C-60SE

spectrofluorimeter. Quantum efficiency measurements were carried out using a Hamamatsu C9920 system equipped with a xenon lamp, calibrated integrating sphere and model C10027 photonic multichannel analyzer.

Samples for transient luminescent decay measurements were prepared in 2-MeTHF solution. All phosphorescent lifetimes were measured by time-correlated single-photon counting using an IBH Fluorocube instrument equipped with a 405 nm LED excitation source.

Computational methods

All theoretical properties reported here are determined from first principles electronic structure methods using the GAMESS (General Atomic and Molecular Electronic Structure System) electronic structure code.³⁵ As previously reported, density functional theory (DFT) was shown to reliably predict X-ray crystallographic, electrochemical and photophysical properties of several (BPI)PtCl derivatives including complex 1,³⁶ thus similar treatments are applied to complexes 2–12.

Platinum is described using the small core model core potential MCPtzp (triple zeta + polarization basis set) while chlorine and iodine use MCPdzp (double zeta + polarization basis set).³⁷ All remaining atoms are treated with the all-electron cc-pVDZ basis set.³⁸ Geometry optimizations for **1–12** are performed with the DFT hybrid B3LYP functional.^{39–43} All stationary points are confirmed as minima on the ground state potential energy surface by calculating and diagonalizing the Hessian (matrix of energy second derivatives). Vertical excitation energies are computed with time dependent density functional theory (TDDFT) using the B3LYP functional. The effects of solvent on the geometry and vertical excitation energies are studied using the Conductor-like Polarizable Continuum Model (CPCM).⁴⁴

The Tamm–Dancoff approximation to TDDFT (TDA-TDDFT) is used here for the purposes of conveniently analyzing the excitation energies.⁴⁵ The TDA-TDDFT provides an analog to the simple configuration interaction with single excitations (CIS) method. This is a crucial feature since an excited state dominated by a single CIS configuration can be approximately characterized using simple orbital arguments.³⁶ Similar use of an orbital argument is justified here if the TDA-TDDFT method predicts an excited state dominated by a single excitation (*i.e.* HOMO \rightarrow LUMO).

Results and discussion

Synthesis

The BPI ligand was synthesized according to literature procedures,²³ followed by platination with (COD)PtCl₂ to give 1.¹⁵ Complexes **2–4** were synthesized in 43–84% yield by the addition of AgF, KAg(CN)₂ and AgOAc, respectively, to the parent complex 1. Unlike in the preparation of several [Pt(terpy)-X]⁺ complexes from Pt(terpy)Cl]⁺, where exchange of the chloride ligand is facile,^{8,46} attempts to synthesize (BPI)PtX derivatives **2–4** by simple nucleophilic substitution of **1** were found to be unsuccessful. The (BPI)Pt(Ph–R) complexes **5** (R = H) and **6** (R = NMe₂) were synthesized in 37 and 49% yield from



Fig. 2 ORTEP diagram of 6 from single crystal X-ray analysis with thermal ellipsoids at the 50% probability level. Selected hydrogen atoms omitted for clarity.

the corresponding aryl platinum precursor (COD)Pt(Ph–R)₂.^{13,47} Complexes 1–6 are soluble in common organic solvents, with solubility decreasing along the trend 6 > 5-4 > 2-1 > 3.

The BPI substituted ligand precursors for 7-12 were synthesized using the method developed by Siegl, metal-ion-catalyzed nucleophilic addition of aromatic amines to dicyano aromatics.²³ Reaction progress was monitored by thin layer chromatography (eluting with CH₂Cl₂) for disappearance of the fluorescent blue dicyanobenzene starting material. The reaction time is affected by both steric and electronic effects of the dicyanobenzene substituent. The addition of electron withdrawing groups (NO₂, I, Cl) at the 4- and 5-positions results in short (<2 days) reaction times, whereas electron donating groups (t-Bu, OC_5H_{11}) at the 4-position increases reaction times (5–10 days). The reaction rates are presumably altered due to changes in the electron density at the site of 2-aminopyridine addition. A nitro substituent at the 3-position (8) increases the reaction time, presumably due to steric hindrance, since starting material is still present after 4 days. The substituted ligands were metalated using (COD)PtCl₂ to give complexes 7-12 in 52-81% yield. All complexes are air-stable and were obtained as yellow to red solids, except for complex 6, which would range from a red powder to a black crystalline solid. The complexes were fully characterized by NMR spectroscopy, mass spectrometry and elemental analysis.

A single crystal X-ray analysis was performed on complex **6** (Fig. 2). The complex has a near ideal square planar geometry (N1–Pt–N3 = 89.3°, N1–Pt–C10 = 90.6°, N1–Pt–N5 = 180.88°, N3–Pt–C10 = 180.00°) with the aryl ring oriented perpendicular to the N1–N3–N1′–C10 coordination plane (89.12°). Steric congestion between the aryl ligand and the *ipso*-hydrogens (C10…H1 = 2.276 Å) causes the pyridyl groups in the BPI to warp 8.4° away from the coordination plane. The Pt–C10 (2.022 Å) and Pt–N1 (2.053 Å) distances are unexceptional whereas the Pt–N3 distance (2.038 Å) is *ca.* 0.05 Å longer than values reported for other (BPI)PtX (X = Cl,^{15,25} ethynylaryl²⁵ and pyridyl²⁶) derivatives due to the strong *trans* influence of the *p*-dimethylaminophenyl group.

Complex	HOMO energy (eV)	LUMO energy (eV)	TDA-TDDFT vertical excitation energy (nm)	Exp. lowest energy absorption peak (nm)	TDDFT vertical xcitation energy (nm)	Square of HOMO \rightarrow LUMO TDA-TDDFT coefficient
1	-5.77	-2.64	478	487	489	0.84
2	-5.76	-2.63	480	497	492	0.91
3	-6.00	-2.70	430	465	444	0.91
4	-5.84	-2.64	458	488	471	0.91
5	-5.68	-2.52	462	497	475	0.91
6	-4.83	-2.48	660	470	661	0.99
7	-5.75	-2.61	481	486	491	0.92
8	-5.86	-2.89	503	505	515	0.94
9	-5.89	-3.07	524	511	537	0.95
10	-5.72	-2.54	480	492	490	0.91
11	-5.81	-2.73	487	497	498	0.92
12	-5.90	-2.81	481	498	494	0.92

Table 2 HOMO-LUMO energies, TDA-TDDFT and TDDFT vertical excitation energies, experimental absorption peaks, and the square of the HOMO \rightarrow LUMO TDA-TDDFT coefficient for the CPCM solvated complexes

Computational results

In accordance with our previous report,³⁶ excitation energies incorporating solvation effects using the CPCM are in better agreement with experiment than are the gas-phase calculations. Consequently, only CPCM-B3LYP excitation energies computed with TDDFT and TDA-TDDFT are reported for structures 1–12 (Table 2). The platinum chloride complexes, 1 and 7–12, have relatively small variations (489–537 nm) in the lowest energy transitions compared to the chloride substituted complexes 2–6 (444–661 nm).

Since the squares of the HOMO \rightarrow LUMO TDA-TDDFT coefficients for 1–12 are close to unity (0.84–0.99), it is clear that the HOMO \rightarrow LUMO excitation dominates the lowest energy transitions within the TDA-TDDFT approximation (Table 2). In addition, the TDA-TDDFT excitation energies are in good qualitative agreement with the trends established by TDDFT and experiment (except for complex 6). Thus it is reasonable to use Kohn–Sham orbitals as a means to understand the observed trends in the lowest energy excitations for complexes 1–5 and 7–12.

The HOMO and LUMO energy values for the ground state structures of 1-12 can be seen in Table 2 and schematics of the associated Kohn–Sham orbitals can be found in the ESI (Fig. S1†). The HOMO of 1 is largely localized on the [(2-pyri-dylimino)3,4-pyrrolate]PtCl portion of the molecule and the LUMO is localized over the entire BPI ligand, with decreased orbital character on the platinum center and chlorine atom (Fig. 3). Similar HOMO and LUMO characteristics are seen for all complexes reported with the exception of **6**. For structure **6**, the HOMO resides on the *p*-(dimethylmino)phenyl moiety.

Electrochemistry

The electrochemical properties of 1-12 were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The results of these measurements are shown in Table 3 (all values are reported relative to the ferrocenium/ferrocene couple). All of the complexes reported here display at least one irreversible oxidation from 0.58 to 0.97 V and at least two reversible reduction peaks from -1.15 to -2.39 V. In good agreement with values reported by Wen *et al.*,²⁵ the parent complex 1



Fig. 3 HOMO (solid, left) and LUMO (transparent, right) of 1. With carbon, chlorine, hydrogen and nitrogen indicated by black, green, white and blue spheres respectively.

displays an irreversible oxidation ($E_{pa} = 0.79$ V) and two reversible reduction waves ($E_{1/2} = -1.44$ V, -1.87 V). The initial oxidation and reduction potentials of a series of benzannulated (BPI)PtCl derivatives have been shown to display good correlation with both the location and the relative energies of the calculated HOMO and LUMO, respectively.³⁶ With respect to the spatial features of the HOMO and LUMO of **1**, replacing the chloride with a different ligand would be expected to have a larger effect on the oxidation potentials than the reduction potentials, which it does. Conversely, substitution at the 3–5-positions of the BPI ligand is expected to have a larger effect on the reduction potentials than the oxidation potentials, as observed.

Complexes 2–5 all display a single irreversible oxidation wave between 0.69 and 0.97 V. The most pronounced changes in oxidation potential were found in complexes with cyano (3, $E_{pa} =$ 0.97 V) and phenyl (5, $E_{pa} = 0.69$ V) ligands. The shifts in oxidation potential are due to the electron withdrawing (CN) or donating (Ph) nature of the ligands. The addition of a *p*-(dimethylamino)phenyl donor in 6 shifts the irreversible oxidation peak by -0.11 V relative to 5. An additional reversible oxidation wave ($E_{1/2} = 0.08$ V) in 6 is assigned to a process centered on the *p*-(dimethylamino)phenyl moiety (HOMO of 6). The first reduction potential of 2–6 is between -1.42 to -1.67 V. Again the most pronounced changes in reduction potential are found in complexes with cyano (3, $E_{1/2} = -1.42$ V) and *p*-(dimethylamino)phenyl (6, $E_{1/2} = -1.67$ V) ligands.

Table 3 Electrochemical potentials for 1–12 reported in volts (V) relative to Fc^+/Fc^- Electrochemical oxidations are irreversible and reductions are reversible, unless otherwise noted

Complex	$E_{\rm pa}^{\rm ox} \left({\rm V} \right)^b$	$E_{1/2}^{\text{red1}}$ (V)	$E_{1/2}^{\text{red}}(\mathbf{V})$	$\Delta E_{1/2} \left(\mathbf{V} \right)^c$
1	0.79	$-1.44(69)^d$	$-1.87(70)^{d}$	2.23
2	0.73	-1.51	-2.01	2.24
3	0.97	-1.42	-1.86	2.39
4	0.88	-1.51	-1.96	2.39
5	0.69	-1.62	-2.09	2.31
6 ^{<i>e</i>}	$0.08,^{f}0.58$	$-1.67(63)^d$	$-2.12(78)^{d}$	1.75, ^g 2.25
7	0.83	$-1.47(80)^{d}$	$-1.90(79)^d$	2.30
8	0.95	$-1.24(66)^d$	$-1.93 (101)^d$,	2.19
			$-1.81(90)^{d}$	
		,	$-1.60(65)^{a}$	
9	0.93	$-1.15(102)^{a}$	$-2.39(94)^{a},$	2.08
			$-1.42(135)^{a}$	
10	0.84	$-1.48(89)^{a}$	$-1.92(88)^{a}$	2.32
11	0.84	$-1.36(62)^d$	$-1.89(100)^{d}$,	2.20
		,	-1.75^{n}	
12	0.84	$-1.30(56)^d$	$-1.69(81)^{d}$	2.14

^{*a*} Measurements were performed in an anhydrous solution of 0.1 M NBu₄PF₆ in DMF. ^{*b*} Peak anodic potential. ^{*c*} $\Delta E_{1/2} = E_{pa}^{\text{ox}} - E_{1/2}^{\text{red1}}$. ^{*d*} The $E_{pa} - E_{pc}$ separation (in mV) are in parentheses. ^{*e*} Measured using decamethylferrocene as the internal standard and corrected for -0.57 V vs. Fc⁺/Fc. ^{*f*} Reversible oxidation. ^{*g*} $\Delta E_{1/2} = E_{1/2}^{\text{ox1}} - E_{1/2}^{\text{red1}}$. ^{*h*} Irreversible reduction.

The complexes with substituted BPI ligands (7-12) all display a single irreversible oxidation, and at least two reversible reduction waves. The irreversible oxidation potentials of 7-12 range from 0.83 to 0.95 V (Table 3). On the other hand, the first reduction shows greater variation, ranging from -1.15 to -1.48 V. The addition of electron donating (C(CH₃)₃, OC₅H₁₁) or electron withdrawing (NO₂, Cl, I) groups to 1 result in either an anodic (7 and 10) or a cathodic shift (8, 9, 11 and 12) in the first reduction potential (Table 3). Similar shifts in redox potentials upon substitution of the ligand have been observed with (4-R-terpy)PtCl⁴⁸ and (4-R-BPI)PtCl complexes.²⁶ Although 8 and 9 both have NO₂ substituents on the BPI ligand, attachment at the 4-position leads to a reduction potential that is ~ 0.1 V more negative than substitution at the 3-position. If one were to consider only inductive effects, it might be expected that substitution with NO₂ at either position would lead to similar reduction potentials. However, a calculated structure of 8 shows that steric hindrance at the 3-position forces a 45° out-of-plane rotation of the nitro group. This out-of-plane rotation reduces the π -electron withdrawing ability of NO₂ and, as a result, complex 8 is more difficult to reduce than 9.

Additional reduction waves, not present in 1, are observed for complexes 8, 9 and 11. These additional reduction waves are presumably due to reversible reduction of the nitro groups in 8, 9 and the irreversible reductive elimination of the iodo substituent of 11 at -1.75 V.⁴⁹

Absorption spectroscopy

The photophysical properties of BPI, (BPI)PtCl (1) and several $(BPI)Pt(4-X-pyridine)^+$ complexes have recently been described.^{25,26} The BPI ligand displays several absorption bands between 300–425 nm. According to TDDFT calculations, the



Fig. 4 Absorption spectra of complexes 1, 3, 5 (top) and 7, 9, 10 (bottom) at room temperature in $\rm CH_2Cl_2$.

lowest energy transition in BPI (calculated: 391 nm) is dominated by transitions from the HOMO to the LUMO (84%). The HOMO is a π orbital localized on the (2-pyridylimino)3,4pyrrole portion of the molecule, with minimal character on the benzene ring, whereas the LUMO is delocalized over the entire molecule. The lowest energy absorption in BPI is thus qualitatively assigned as a π - π * transition.

The absorption spectra for complexes 1-12 were recorded in CH₂Cl₂. Representative spectra are shown in Fig. 4, and the remaining spectra are available in the ESI.[†] Upon platination of the BPI derivatives, the ligand centered (LC) π - π * transitions undergo a red shift to ~350 nm ($\varepsilon = 1.5-2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) while a new, low energy transition appears between 425-550 nm $(\varepsilon \approx 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$. DFT calculations predict that the low energy absorption (calculated for 1 at 489 nm) is predominately a HOMO to LUMO transition (84%). Upon platination, the HOMO is destabilized and now includes contributions from the platinum and ancillary ligand portions of the molecule, whereas the LUMO is stabilized and remains localized on the BPI ligand with minimal metal character (Fig. 3). The nature of the frontier orbitals suggests that the low energy absorption band is best described as a combined metal-to-ligand/intraligand chargetransfer (CT) transition. TDDFT calculations are in good agreement with experiment, as deviations are less than 30 nm



Fig. 5 (a) Absorption spectra of complex 6 at room temperature in CH_2Cl_2 . Calculated transitions are shown as vertical bars with heights equal to the oscillator strength. (b) The relative intensities and orbitals involved in the two lowest energy transitions of 6 found by TDDFT.

(Table 4). To confirm the nature of the absorption transitions, the highly soluble (4-*tert*-butylBPI)PtCl complex (7) was examined in solvents of varying polarity. While the energy of the LC absorption band remains constant, the low energy CT band exhibits a negative solvatochromic effect, shifting from 505 nm in hexane to 485 nm in acetonitrile (Fig. S4†). Hypsochromic shifts in polar solvents are attributed to a decrease in the molecular dipole moment upon excitation.⁵⁰ Since the calculated dipole moment in the ground state ($\mu = 3.5$ D) is oriented along the Pt–Cl bond, and the LUMO has electron density that is shifted away from this portion of the complex, the solvatochromic shifts support the assigned HOMO \rightarrow LUMO charge transfer description for this transition.

The energy of the CT band in complexes 1–12 is altered by both the type of anionic ligand (X) and substituents (R) on the BPI ligand. Relative to 1, the greatest perturbation is observed in 3 (X = CN) as the CT band energy is blue shifted by ~50 nm and becomes highly structured with a vibronic spacing of ~1400 cm⁻¹ (Fig. 4(top)). The blue shift is primarily due to a 0.23 eV stabilization of the HOMO by the cyano ligand that diminishes the metal character of the CT band and shifts the Franck–Condon factors in favor of the 0–0 transition. Other ligands have a smaller effect on the energy of the CT band. Fluoride (2) and phenyl (5) ligands red shift the transition by 10 nm, whereas the acetate ligand causes little change in **4**. The addition of electron donating groups at the 4-position of the BPI ligand in **7** ($R = C(CH_3)_3$) and **10** ($R = OC_5H_{11}$) has a minimal effect on the absorption onset and peak positions relative to **1**. Electron withdrawing groups, on the other hand, red shift the absorption onset according to the trend **9** ($R_4 = NO_2$) > **8** ($R_3 = NO_2$) > **12** ($R_{4,5} = Cl$) > **11** ($R_4 = I$). As already noted based on the TDA-TDDFT coefficients, the lowest energy vertical excitations of these complexes are dominated by a HOMO \rightarrow LUMO transition. The relatively small variability in the HOMO of **8**, **9**, **11** and **12** (<0.1 eV) indicates that stabilization of the LUMO in the absolute value order **9** (-3.07 eV) > **8** (-2.89 eV) > **12** (-2.81 eV) > **11** (-2.73 eV) is likely responsible for the observed trends in this absorption band.

In complex 6, with a *p*-(dimethylamino)phenyl ligand, the CT band appears as a single structureless feature from 400 to 550 nm (Fig. 5a). The twenty lowest energy transitions of 6 identified by TDDFT (Table S1[†]) are indicated by vertical bars in Fig. 5a with heights equal to the oscillator strength. Shown in Fig. 5b are the valence orbitals associated with lowest CT states. As mentioned earlier in the computation section, the HOMO for this complex resides primarily on the *p*-(dimethylamino)phenyl ligand and a low energy HOMO \rightarrow LUMO transition at 661 nm is predicted from the calculation. However, due to the minimal orbital overlap between the HOMO and LUMO, the oscillator strength of this transition ($f = 7.3 \times 10^{-4}$) is three orders of magnitude lower than the oscillator strength at 476 nm (f = 0.23). On the other hand, since the orbitals that dominate the latter transition (81% HOMO-1 \rightarrow LUMO) closely resemble the HOMO and LUMO of the parent complex (Fig. 5b), a molar absorptivity similar to 1 is observed for this transition.

Emission spectroscopy

Complexes 1–5 and 7–12 display broad emission spectra at room temperature in CH₂Cl₂ with λ_{max} ranging from 594 to 680 nm. Spectra for 1, 3, 5, 7, 9 and 10 are shown in Fig. 6; data for the emissive properties of complexes 1–12 are listed in Table 4. Emission spectra for 2, 4, 8, 11 and 12 recorded at room temperature and for complexes 1–12 at low temperature (77 K) in glassy solvent (2-MeTHF) are given in the ESI (Fig. S7†). Spectra recorded at 77 K undergo rigidochromic blue-shifts of 30–50 nm and display a structured manifold with a vibronic progression of ~1500 cm⁻¹. The luminescent decay lifetimes at 77 K are in the microsecond regime, and therefore assigned to emission from a metal-perturbed, ligand-centered triplet state.

The emission energies for complexes 1–5 and 7–12 at room temperature follow the same general trends as found in the CT absorption bands. Relative to 1 ($\lambda_{max} = 641$ nm), emission is blue-shifted by the electron withdrawing cyano ligand in 3 (λ_{max} = 594 nm) and red-shifted by the electron donating phenyl ligand in 5 ($\lambda_{max} = 656$ nm). Conversely, addition of electron donating groups at the 4-position of the BPI ligand leads to a small blue shift in 7 ($\lambda_{max} = 638$ nm) and 10 ($\lambda_{max} = 635$ nm), whereas a red shift in emission maxima is observed for derivatives substituted with electron withdrawing groups. The red shift follows a trend 9 (680 nm) > 8 (678 nm) > 12 (657 nm) > 11

Table 4 TDDFT vertical excitation energies and photophysical properties of complexes 1-12

			Emission at rt^c					Emission at 77 K ^d	
	Absorbance λ (nm) (ε , ×10 ⁴ M ⁻¹ cm ⁻¹) ^{<i>a</i>}	TDDFT vertical excitation energy $(nm)^b$	λ_{\max} (nm)	τ (μs)	$arPsi_{ ext{PL}}$	$k_{\rm r} (10^4 {\rm s}^{-1})^e$	$k_{\rm nr} (10^5 {\rm s}^{-1})^{f}$	λ_{\max} (nm)	τ (μs)
1	250(5.37), 277(3.51), 348(2.24), 473(1.36), 487(1.35)	489(2)	641	0.99	0.014	1.4	10	595	6.8
2	250(4.20), 277(2.61), 349(1.88), 387(0.87), 476(1.00), 497(0.91)	492(5)	620	0.84	0.011	1.3	12	592	6.6
3	245(4.46), 268(2.21), 342(2.24), 437(1.69), 465(1.96)	444(21)	594	8.4	0.048	0.57	1.1	567	35
4	249(4.86), 278(2.93), 349(2.21), 464(1.34), 488(1.31)	471(17)	620	0.60	0.011	1.8	17	584	11.5
5	249(4.35), 289(2.37), 352(1.99), 472(1.17), 497(1.13)	475(22)	656 [615]	0.1 [2.6]	0.004 [0.018]	4.0 [0.69]	100 [3.8]	603	3.5
6	252(4.91), 287(2.87), 342(1.78), 470(0.94)	476(6) ^g	_	_	_			594	7.6
7	250(5.36), 278(3.86), 352(2.49), 472(1.33), 486(1.32)	491(5)	638 [610]	1.1 [2.4]	0.018 [0.029]	1.6 [1.2]	8.9 [4.1]	593	7.3
8	235(3.23), 278(2.75), 338(1.53), 483(1.05), 505(1.05)	515(10)	678	0.32	0.003	0.90	31	625	2.9
9	232(3.23), 277(3.41), 346(2.14), 492(1.09), 511(1.08)	537(26)	680	0.30	0.004	1.3	33	632	2.4
10	261(4.13), 280(3.69), 351(1.74), 386(1.63), 472(0.90), 492(0.83)	490(2)	635	0.93	0.014	1.5	11	592	6.9
11	257(3.80), 279(3.57), 353(2.04), 478(1.00), 497(0.97)	498(1)	650	0.73	0.01	1.4	14	607	5.2
12	257(4.60), 279(3.62), 351(1.90), 479(1.06), 498(1.05)	494(4)	657	0.63	0.007	1.1	16	615	3.5

^{*a*} In CH₂Cl₂. ^{*b*} The absolute difference between calculated HOMO \rightarrow LUMO and experimental transitions, reported in nm, is given in parentheses. ^{*c*} In toluene deaerated with N₂. ^{*d*} In 2-MeTHF. ^{*e*} $k_{\rm r} = \Phi/\tau$. ^{*f*} $k_{\rm nr} = (1 - \Phi)/\tau$. 2% complex by weight doped in [PMMA]. ^{*g*} HOMO-1 \rightarrow LUMO transition.

(650 nm) that is similar to the observed variation in $\Delta E_{1/2}$ values.

The luminescent quantum yields (Φ) measured at room temperature for the complexes vary between 0.003-0.048, with 6 being non-emissive. The non-emissive nature of 6 at room temperature may be due to the formation of a transient charge separated state, involving a ligand-to-ligand electron transfer from the p-(dimethylamino)phenyl moiety to the electron deficient BPI portion of the complex. On the basis of the electrochemical potentials, the free energy for the formation of such a chargeseparated species in fluid solution (Table 3, $\Delta E_{1/2} = 1.75$ eV, 709 nm) is favored over emission ($E_{0-0} = 2.09$ eV, 594 nm at 77 K). The other complexes have radiative rate constants (k_r) that vary between $0.57-4.0 \times 10^4$ s⁻¹, with most being near $1.5 \times$ 10^4 s⁻¹. The ancillary ligand exerts the greatest effect on k_r since the complexes with the lowest and highest values are those with electron withdrawing cyano (3, $k_r = 0.47 \times 10^4 \text{ s}^{-1}$) or electron donating phenyl (5, $k_r = 4.0 \times 10^4 \text{ s}^{-1}$) ligands. The difference most likely reflects a respective lower and higher degree of metal character in the triplet state. However, since the overall values of $k_{\rm r}$ deviate by less than an order of magnitude, the variations in photoluminescent efficiency of 1-5 and 7-12 are largely due to much greater variations in the nonradiative rate constants ($k_{\rm nr}$ = $1.1-100 \times 10^5 \text{ s}^{-1}$).

To better understand the nonradiative decay channels of the (BPI)PtX complexes, the highly soluble *tert*-butyl substituted derivative 7 was investigated with respect to concentration, solvent media and temperature. The quantum yield of 7 in toluene remains constant ($\Phi = 0.018$) over concentrations ranging from 3 to 80 μ M, and indicates that excimer-type

dynamic bimolecular interactions do not contribute to nonradiative decay. On the other hand, variations in solvent polarity, while only having a minimal effect on the emission energies, significantly alter the quantum efficiency (Table 5). The highest quantum yields are observed in non-polar solvents ($\Phi_{\text{hexane}} =$ 0.022, $\Phi_{\text{cyclohexane}} = 0.018$), gradually decrease with increased solvent polarity ($\Phi_{2-MeTHF} = 0.011$, $\Phi_{acetone} = 0.010$, $\Phi_{acetonitrile}$ = 0.006) until finally, there is no observed emission in the most polar solvent, DMSO. The decrease in the quantum efficiency of 7 in coordinating solvents, (2-MeTHF and CH₃CN) relative to hydrocarbon solvents (hexane and toluene) suggests that formation of a 7-solvent exciplex is a contributing process for nonradiative decay.^{51–54} However, the low photoluminescent (PL) efficiency in alkane solvents indicates that exciplex formation is not the predominant deactivation pathway. Moreover, when 7 is doped in PMMA (2%, w/w) the PL efficiency ($\Phi = 0.029$) and excited state lifetime ($\tau = 2.4 \ \mu s$) only double relative to fluid solution (Table 3). Since the radiative rate constant of 7 is nearly invariant in solid matrix ($k_{r(PMMA)} = 1.2 \times 10^4 \text{ s}^{-1}$) and solution $(k_{r(toluene)} = 1.6 \times 10^4 \text{ s}^{-1})$, the increased efficiency in PMMA is due to a decrease in the rate of nonradiative decay $(k_{nr(PMMA)} =$ $4.1 \times 10^5 \text{ s}^{-1}$, $k_{\text{nr(toluene)}} = 8.9 \times 10^5 \text{ s}^{-1}$). Finally, temperaturedependent decay mechanisms are typically associated with thermal population of a ligand field (d-d) type of excited state. However, the lifetime of the complex in 2-MeTHF at 77 K $(\tau = 7.3 \text{ } \mu\text{s})$ is only three times longer than the value in PMMA at room temperature. Consequently, the estimated quantum yield at 77 K is still far below unity, which implies that nonradiative decay of the excited state is not a thermally activated process.



Fig. 6 Emission spectra of complexes 1, 3, 5 (top) and 7, 9, 10 (bottom) at room temperature in $\rm CH_2Cl_2$.

 Table 5
 Emission properties of 7 in various solvents at room temperature

Solvent	λ_{\max} (nm)	$arPsi_{ ext{PL}}$	τ (μs)	$k_{\rm r} (10^4 {\rm s}^{-1})$	$k_{\rm nr} (10^5 {\rm s}^{-1})$
Hexane	632	0.022	1.1	2.1	9.1
Cyclohexane	635	0.018	0.98	1.8	10
Toluene	638	0.018	1.1	1.6	8.9
Benzene	639	0.017	1.1	1.6	8.9
Heptane	630	0.017	1.1	1.6	8.9
CH ₂ Cl ₂	636	0.015	1.1	1.4	9.0
Diethyl ether	634	0.014	1.1	1.3	9.4
2-MeTHF	637	0.011	0.77	1.4	13
Acetone	639	0.010	0.92	1.1	11
Acetonitrile	638	0.006	0.64	0.94	16

The energy gap law (EGL) states that the nonradiative decay rate will decrease exponentially with increasing energy of emission for molecules with similar vibrational coupling between the excited and ground states.⁵⁵ The plot of the natural log of the nonradiative rate constant *versus* emission energy (E_{em}) for 1–12 can be seen in Fig. 7. Complexes 1 and 7–12, all with a Pt–Cl bond, exhibit a linear relationship with a slope of –1.2 and *y*-intercept of 33.2. However, (BPI)Pt–X complexes 1–5 do not follow the same linear relationship found for the Pt–Cl derivatives. These deviations imply that substitution of the



Fig. 7 Plot of emission energy *vs.* $\ln(k_{nr})$ for 1–12 in toluene. 5' and 7' are $\ln(k_{nr})$ values in PMMA (open symbols).

monodentate anionic ligands results in different vibrational coupling paths from the excited state to the ground state. For example, the role played by molecular distortion is evidenced in the pronounced change in the nonradiative rate constant of 5 depending on the solvent viscosity, decreasing from 1.0 \times 10^7 s^{-1} in toluene to $3.8 \times 10^5 \text{ s}^{-1}$ in PMMA (5' in Fig. 7). The large decrease in $k_{\rm nr}$ for this species (and to a lesser extent in 7) in rigid media suggests a large amplitude vibrational mode may be responsible for the higher k_{nr} value in fluid solution. In particular, various degrees of out-of-plane deformations of the BPI ligand are found in all of the reported X-ray structures of (BPI)Pt derivatives.^{15,25,26} These distortions, similar to those observed in the X-ray structure of 6, are caused by steric repulsion with the monodentate ligand and are likely present in 5 as well. Libration of the phenyl ring around the Pt-Ph bond axis would further exacerbate the warp in the BPI ligand and thus, enhance the rate of surface crossing back to the ground state.

Conclusion

In this report we describe the synthesis and the photophysical and electrochemical characterization of a series of platinum(II) complexes of the form $(N^N^N)PtX$ where N^N^N is an assortment of substituted 1,3-bis(2-pyridylimino)isoindolate ligands and X represents various anionic monodentate ligands. Relative to the parent (BPI)PtCl, variation in X and substitution at the BPI ligand are found to have the most pronounced effect on the oxidation and reduction potentials, respectively. The shift in potential is dependent on the electron donating or withdrawing nature of the substituent. The photophysical properties of the complexes are also dictated by the nature of the substituent. The most blue- and red-shifted absorption–emission spectra are found for the (BPI)PtCN and the (4-NO₂BPI)PtCl complexes respectively.

As with our previous report, molecular orbital based arguments are used to rationalize the experimental observations. The use of molecular orbitals for this purpose is valid since the square of the HOMO \rightarrow LUMO TDA-TDDFT coefficients are close to unity (0.84–0.99) and the TDA-TDDFT excitation

energies are in good qualitative agreement with the trends established by TDDFT and experiment. The spatial features of the HOMO and LUMO of the (R-BPI)PtX complexes were used to rationalize the nature of the electrochemical shifts upon substitution, the solvatochromic shifts in absorption for **7** and the nonemissive nature of **6** (X = p-(dimethylamino)phenyl).

Quantum efficiencies for all of the complexes are primarily dictated by nonradiative deactivation caused by vibrational coupling between the excited and ground states. The nonradiative rate constants of the platinum chloride derivatives are found to correlate with the energy gap law (EGL). The deviation from the linear EGL behavior for (BPI)PtX complexes with X other than Cl implies that substitution of the monodentate anionic ligands results in different vibrational coupling paths from the excited to ground state. Out-of-plane deformation of BPI ligand caused by steric repulsion with the monodentate ligand is suggested to be a dominant vibrational deactivation mode in these complexes.

Acknowledgements

K. H., L. G., N. P., P. I. D. and M. E. T. thank Universal Display Corporation and the Department of Energy for their financial support of this work. L. R. and M. S. G. are grateful for the support of the Air Force Office of Scientific Research. We would like to thank Dr Ralf Haiges for assistance with the X-ray structure analysis. The X-ray diffractometer was purchased with support from NSF CRIF grant 1048807.

References

- J. A. G. Williams, S. Develay, D. L. Rochester and L. Murphy, *Coord. Chem. Rev.*, 2008, **252**, 2596.
- 2 Highly Efficient OLEDs with Phosphorescent Materials, ed. H. Yersin, Wiley-VCH, 2007.
- 3 B. A. DeGraff and J. N. Demas, in *Luminescence-based oxygen sensors*, ed. C. D. Geddes, 2005.
- 4 I. Eryazici, C. N. Moorefield and G. R. Newkome, *Chem. Rev.*, 2008, 108, 1834.
- 5 J. A. G. Williams, Top. Curr. Chem., 2007, 281, 205.
- 6 V. Balzani and V. Carassiti, J. Phys. Chem., 1968, 72, 383.
- 7 H.-K. Yip, L.-K. Cheng, K.-K. Cheung and C.-M. Che, J. Chem. Soc., Dalton Trans., 1993, 2933.
- 8 T. K. Aldridge, E. M. Stacy and D. R. McMillin, *Inorg. Chem.*, 1994, 33, 722.
- 9 S.-W. Lai, C.-W. Chan, K.-K. Cheung and C.-M. Che, *Organometallics*, 1999, 18, 3327.
- K. M.-C. Wong and V. W.-W. Yam, *Coord. Chem. Rev.*, 2007, **251**, 2477.
 K. L. Garner, L. F. Parkes, J. D. Piper and J. A. G. Williams, *Inorg.*
- *Chem.*, 2010, **49**, 476.
- H. Zhang, B. Zhang, Y. Li and W. Sun, *Inorg. Chem.*, 2009, 48, 3617.
 S. B. Harkins and J. C. Peters, *Organometallics*, 2002, 21, 1753.
- 14 D. Patra, P. Pattanayak, J. L. Paratihar and S. Chattopadhyay, *Polyhedron*,
- 2007, **26**, 5484.
- 15 M. Meder, C. H. Galka and L. H. Gade, *Monatsh. Chem.*, 2005, 136, 1693.
- 16 J.-L. Chen, S.-Y. Chang, Y. Chi, K. Chen, Y.-M. Cheng, C.-W. Lin, G.-H. Lee, P.-T. Chou, C.-H. Wu, P.-I. Shih and C.-F. Shu, *Chem.–Asian J.*, 2008, **3**, 2112.
- 17 K.-W. Wang, J.-L. Chen, Y.-M. Cheng, M.-W. Chung, C.-C. Hsieh, G.-H. Lee, P.-T. Chou, K. Chen and Y. Chi, *Inorg. Chem.*, 2010, 49, 1372.

- 18 L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fischer and R. Weiss, J. Am. Chem. Soc., 1985, 107, 3534.
- 19 C. A. Tolman, J. D. Druliner, P. J. Krusic, M. J. Nappa, W. C. Seidel, I. D. Williams and S. D. Ittel, *J. Mol. Catal.*, 1988, **48**, 129.
- 20 B. K. Langlotz, H. Wadepohl and L. H. Gade, Angew. Chem., Int. Ed., 2008, 47, 4670.
- 21 J. Kaizer, T. Csay, P. Kovari, G. Speier and L. Parkanyi, J. Mol. Catal. A: Chem., 2008, 280, 203.
- 22 J. Kaizer, G. Barath, R. Csonka, G. Speier, L. Korecz, A. Rockenbauer and L. Parkanyi, *J. Inorg. Biochem.*, 2008, **102**, 773.
- 23 W. O. Siegl, J. Org. Chem., 1977, 42, 1872.
- 24 P. T. Selvi, H. Stoeckli-Evans and M. Palaniandavar, J. Inorg. Biochem., 2005, 99, 2110.
- 25 H.-M. Wen, Y.-H. Wu, Y. Fan, L.-Y. Zhang, C.-N. Chen and Z.-N. Chen, *Inorg. Chem.*, 2010, 49, 2210.
- 26 H.-M. Wen, Y.-H. Wu, L.-J. Xu, L.-Y. Zhang, C.-N. Chen and Z.-N. Chen, *Dalton Trans.*, 2011, 40, 6929.
- 27 V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong and K.-K. Cheung, Organometallics, 2001, 20, 4476.
- 28 S.-W. Lai, M. C. W. Chan, K.-K. Cheung and C.-M. Che, *Inorg. Chem.*, 1999, 38, 4262.
- 29 M. H. Wilson, L. P. Ledwaba, J. S. Field and D. R. McMillin, *Dalton Trans.*, 2005, 2754.
- 30 G. S.-M. Tong and C.-M. Che, Chem.-Eur. J., 2009, 15, 7225.
- 31 J. X. McDermott, J. F. White and G. M. Whitesides, J. Am. Chem. Soc., 1976, 98, 6521.
- 32 R. L. Brainard, W. R. Nutt, T. R. Lee and G. M. Whitesides, Organometallics, 1988, 7, 2379.
- 33 S. Shekhar and J. F. Hartwig, J. Am. Chem. Soc., 2004, 126, 13016.
- 34 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, 1980, 19, 2854.
- 35 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. J. Montgomery, *J. Comput. Chem.*, 1993, 14, 1347.
- 36 K. Hanson, L. Roskop, P. I. Djurovic, F. Zahariev, M. S. Gordon and M. E. Thompson, J. Am. Chem. Soc., 2010, 132, 16247.
- 37 H. Mori, K. Ueno-Noto, Y. Osanai, T. Noro, M. Fujiwara, M. Klobukowski and E. Miyoshi, *Chem. Phys. Lett.*, 2009, 476, 317.
- 38 T. H. Dunning Jr., J. Chem. Phys., 1989, 90, 1007.
- 39 P. Hohenberg, Phys. Rev., 1964, 136, B864.
- 40 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, J. Phys. Chem., 1994, 98, 11623.
- 41 R. H. Hertwig and W. Koch, Chem. Phys. Lett., 1997, 268, 345.
- 42 A. D. Becke, J. Chem. Phys., 1993, 98, 5648.
- 43 W. Kohn and L. J. Sham, Phys. Rev., 1965, 140, A1133.
- 44 M. Cossi and V. Barone, J. Chem. Phys., 2001, 115, 4708.
- 45 A. Dreuw and M. Head-Gordon, Chem. Rev., 2005, 105, 4009.
- 46 S. D. Cummings, Coord. Chem. Rev., 2009, 253, 449.
- 47 G. Arena, G. Calogero, S. Campagna, L. M. Scolaro, V. Ricevuto and R. Romeo, *Inorg. Chem.*, 1998, 37, 2763.
- 48 D. R. McMillin and J. J. Moore, Coord. Chem. Rev., 2002, 229, 113.
- 49 J. S. Jaworski, A. Kacperczyk and M. K. Kalinowski, J. Phys. Org. Chem., 1992, 5, 119.
- 50 A. P. Wilde, K. A. King and R. J. Watts, J. Phys. Chem., 1991, 95, 629.
- 51 D. K. Crites Tears and D. R. McMillin, Coord. Chem. Rev., 2001, 211,
- 195.
 52 W. L. Fleeman and W. B. Connick, *Comments Inorg. Chem.*, 2002, 23, 205
- 53 B. Ma, P. I. Djurovich and M. E. Thompson, *Coord. Chem. Rev.*, 2005, 249, 1501.
- 54 M. D. Perez, P. I. Djurovich, A. Hassan, G. Y. Cheng, T. J. Stewart, K. Aznavour, R. Bau and M. E. Thompson, *Chem. Commun.*, 2009, 4215.
- 55 J. V. Caspar and T. J. Meyer, Inorg. Chem., 1983, 22, 2444.
- 56 Bruker, SAINT v7.68A; Bruker AXS Inc.: Madison, WI, 2009; G. M, Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- 57 Bruker, SHELXTL v6.12; Bruker AXS Inc.: Madison, WI, 2002.