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Pincers and other hemilabile ligands

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PAPER

Palladium(II)- and platinum(II)phenyl-2,6-bis(oxazole) pincer complexes: Syntheses, crystal structures, and photophysical properties†

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Phenyl-2,6-bis(oxazole) ligands have been explored for the synthesis of novel palladium(II) and platinum(II) pincer complexes. The materials were characterized by spectroscopic methods and by X-ray crystallography. Investigations of the photophysical properties revealed that the lowest triplet states of the materials are largely centred at the bis(oxazole) ligands. The platinum(II) compounds are moderately emissive in fluid solution at ambient temperature. Introduction of both strong donors and strong acceptors leads to a significant red shift of the emission. Due to the facile synthesis of bis(oxazole) based complexes with electronically tuneable oxazole moieties, these materials might be promising alternatives to the well-established phenyl-2,6-bipyridyl systems.

A Introduction

The robustness of metal pincer complexes[1] has been invaluable for their applications in catalysis or material science. Important subclasses of pincer complexes are those with NCN-ligands,[2] featuring for example amines, pyridines, and most relevant to this study oxazolines[3] as nitrogen donors. The latter moiety has proved to be especially versatile in the coordination of metals,[4] moreover, its readily accessibility from the abundant pool of amino acids allows their synthesis in a large structural variety.[5] However, the inherent instability of oxazolines against Brønsted and Lewis acids hampers their application as materials when longevity is a requirement.

The oxazole moiety offers the same advantages like oxazolines with respect to availability and variability, however, its use as a ligand for metal complexes has been scarcely explored.[6] In this work, we utilized such ligands to synthesize new palladium(II) and platinum(II) bis(oxazole) complexes. We reasoned that the oxazole moiety could be easily tuned in its electronic properties by introducing electron donating or electron withdrawing substituents, following our previously developed synthetic route to ligand **2a** that served as a precursor for the corresponding palladium complex **6a**.[6]

Due to the relatively strong spin–orbit coupling (SOC) induced by the central metal ion[7] and the high molecular rigidity - both being important for high emission quantum yields - platinum(II) pincer compounds with structurally closely related dipyridinebenzene (dpyb) ligands have been established as efficient phosphorescent emitters in organic light emitting diodes (OLEDs).[8,9] Further, several Pt(II) complexes with CNC[10,11] and NNC ligands[12,13] have been reported to exhibit efficient room temperature phosphorescence. The latter materials were also successfully applied as OLED emitters.[13] In order to evaluate the potential of the here reported bis(oxazole) compounds and to study the effects of donor/acceptor-substitution, investigations of the photophysical properties of the new complexes were carried out.

B Results and Discussion

B1 Synthesis of 1-bromo-phenyl-2,6-oxazole ligands

Starting from 2-bromoisophthaloyl dichloride **1**[14] amination with ethyl glycinate hydrochloride or 1-amino-3,3-dimethylbutan-2-one hydrochloride followed by dehydrative cyclisation smoothly gave rise to bis-ethoxy substituted **2a** and bis-*t*-butyl substituted **2b**, respectively (Scheme 1). Likewise, the analogous bis-phenyl substituted bis(oxazole) can be obtained, however, this ligand turned out to be sparsely soluble in most common organic solvents and was therefore not evaluated further. Following the same sequence but starting from isophthaloyl dichloride, we also could successfully synthesise the debrominated analogues to **2a** and **2b**,

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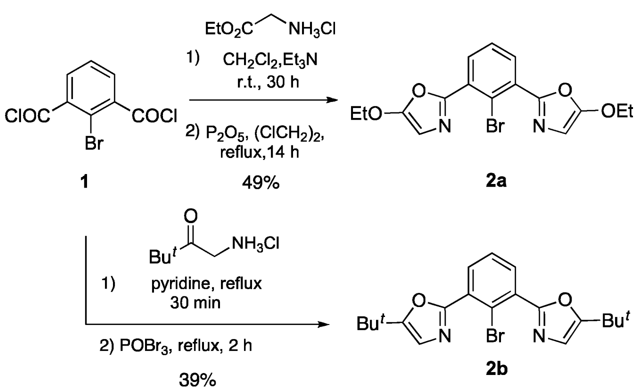
† Electronic supplementary information (ESI) available: Details on the X-ray structure analyses, absorption spectra of the ligands **2a–2c** at ambient temperature, emission spectra of the palladium(II) compounds **6a–6c** and the platinum(II) compounds **7a–7c** at 77 K. CCDC reference numbers 630898, 817026, 817027 and 817028. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10369e

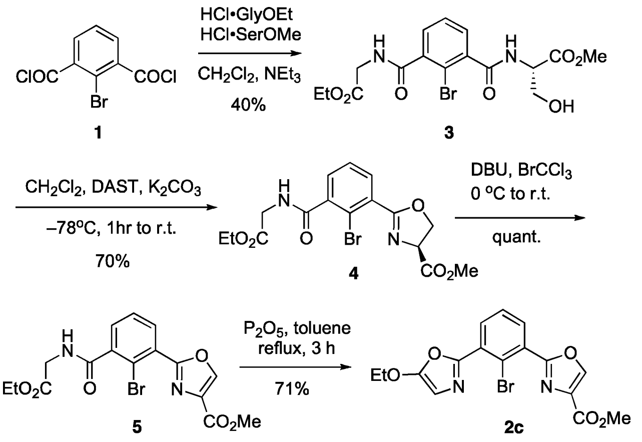
‡ These authors contributed equally to this work.



Scheme 1 Synthesis of 1-bromo-phenyl-2,6-bis(oxazole) ligands **2a** and **2b** with strong and weak donor substituents in the oxazole moieties.

which also turned out to be difficult to be further processed due to low solubility.

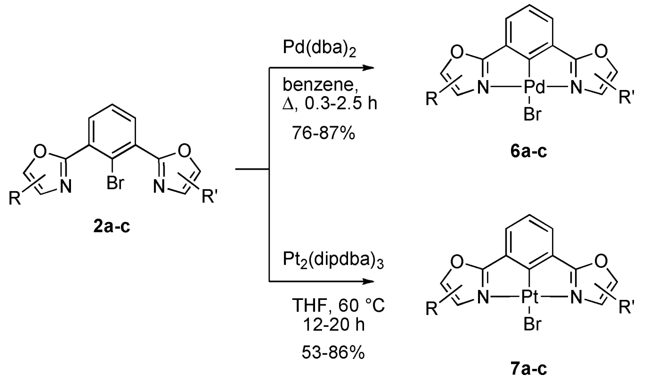
In order to arrive at a donor–acceptor substituted bis(oxazole) ligand (Scheme 2), we reacted in a one pot procedure a 1 : 1 : 1 mixture of **1a**, ethyl glycinate hydrochloride and methyl serinate hydrochloride to obtain the desired unsymmetrical coupling product **3** in 40% yield along with the two symmetrical coupling products (15 and 17% respectively). Selective activation of the serinate amide with DAST to the oxazoline **4** followed by oxidation with DBU/$BrCCl_3$[15] established the acceptor-substituted oxazole **5**. The donor substituted oxazole ring was readily set up by dehydrative cyclisation of **5** along the lines already demonstrated in the synthesis of **2a** to arrive at the targeted ligand **2c**.



Scheme 2 Synthesis of 1-bromo-phenyl-2,6-bis(oxazole) ligand **2c** with electron donor and acceptor substituents in the oxazole moieties.

B2 Synthesis and crystal structures of palladium(II)- and platinum(II)phenyl-2,6-oxazole complexes

Ligands **2** proved to be suitable precursors for palladium(II) and platinum(II) by oxidative addition with Pd(0) or Pt(0) salts in contrast to their debrominated analogs, which could not be converted into metal complexes by direct cyclometalation following a previously established protocol[16] for the synthesis of NCN pincer complexes.[17] Thus, **2a–2c** were treated with $Pd(dba)_2$ or with $Pt_2(dipdba)_3$, respectively, to cleanly give the palladium complexes **6a–c** and platinum complexes **7a–7c** in good yields. All six complexes could be fully characterized by standard spectroscopic methods, moreover, X-ray structure analyses could be performed for **6a**,[6,18] **6c**,[18] **7a**,[18] and **7c**[18] (Scheme 3, Fig. 1, Table 1 and 2).



Scheme 3 Synthesis of palladium(II) and platinum(II) phenyl-2,6-oxazole complexes **6** and **7**.

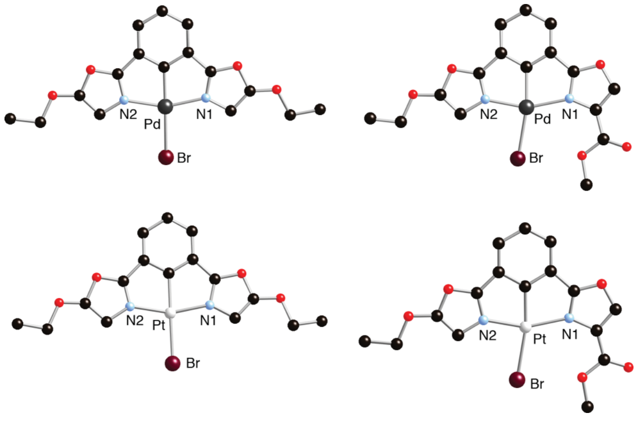


Fig. 1 Molecular structures of palladium complexes **6a/6c** (top) and platinum complexes **7a/7c** (bottom) as determined by X-ray crystallography; hydrogens are omitted for clarity.

All four complexes are very similar in their geometry, displaying an only slightly distorted square planar geometry around the metal centre. Bond lengths and angles are well within the range of Pd- and Pt-NCN pincer complexes reported before.[19] The differences between **6a/6c** and **7a/7c** due to electronic differences caused by the substituents in the oxazole moieties are reflected in the change of the metal-nitrogen bond lengths: Donor substitution causes a shortening of those bonds, suggesting a stronger coordination between that part of the ligand and the metal. Moreover, the nitrogen-metal-bromine angle is significantly smaller with the nitrogen belonging to the donor substituted (N2) with respect to the acceptor substituted (N1) oxazole moiety, being most likely a consequence of avoiding 1,3-allylic strain (Pd–N1–C(oxazole) representing an allylic system) between the ester and the bromine substituent.

B3 Photophysical properties

Several platinum(II) pincer compounds with dipyridinebenzene (dpyb) ligands show remarkably high emission quantum yields[20]

Table 1 Crystal data and structure refinements for compounds **6a**, **6c**, **7a** and **7c**

	6a	6c	7a	7c
Formula	$C_{16}H_{15}BrN_2O_4Pd$	$C_{16}H_{13}BrN_2O_5Pd$	$C_{16}H_{15}BrN_2O_4Pt$	$C_{16}H_{13}BrN_2O_5Pt$
Mr	485.62	499.60	574.28	588.26
Crystal system	Monoclinic	Triclinic	Monoclinic,	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	7.5601(8)	9.656(1)	33.697(4)	9.696(1)
b/Å	9.3101(6)	10.061(1)	5.2354(4)	10.073(1)
c/Å	24.686(3)	10.590(1)	19.994(2)	10.436(1)
α (°)		107.99(1)		107.82(1)
β (°)	90.83(1)	112.14(1)	96.70(1)	111.73(1)
γ (°)		100.06(1)		10.00(1)
V/Å^3	1737.4(3)	855.5(2)	3503.2(6)	852.7(2)
Z	4	2	8	2
Temperature (K)	173(1)	173(1)	173(1)	173(1)
Reflections collected/unique	19590/3360	10880/3756	6524/1688	10760/3422
R_{int}	0.0360	0.0326	0.0834	0.0339
GOF on F^2	0.969	0.963	1.021	1.029
R_1, wR_2[$I > 2\sigma(I)$]^a	0.0226/0.0560	0.0238/0.0580	0.0461/0.1225	0.0233/0.0563
R_1, wR_2 (all data)^a	0.0272/0.0571	0.0293/0.0596	0.0513/0.1272	0.0265/0.0572

^{a} $R_1 = \sum(|F_o| - |F_c|)/\sum |F_o|$; $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum w F_o^{\,2}]^{1/2}$

Table 2 Selected bond lengths and angles of Pd(II)- and Pt(II) pincer complexes with ligands **2a** and **2c**

	6a[6]	**6c**
Pd–N1 [Å]	2.0591(18)	2.138(2)
Pd–N2 [Å]	2.0605(18)	2.045(2)
Pt–C [Å]	1.959(2)	1.959(2)
Pd–Br [Å]	2.5125(4)	2.5382(5)
N1–Pd–N2 [°]	158.81(7)	157.94(8)
C–Pd–N1 [°]	79.40(7)	78.89(10)
C–Pd–N2 [°]	79.41(7)	79.06(10)
N1–Pd–Br [°]	101.15(5)	111.11(6)
N2–Pd–Br [°]	100.04(5)	90.94(6)
N1–Pd–N2–C [°]	0.1(3)	2.0(4)
	7a	**7c**
Pt–N1 [Å]	2.027(9)	2.097(4)
Pt–N2 [Å]	2.024(10)	2.024(4)
Pd–C [Å]	1.975(13)	1.937(5)
Pt–Br [Å]	2.4973(17)	2.5267(6)
N1–Pt–N2 [°]	159.2(4)	158.47(16)
C–Pt–N1 [°]	79.1(4)	79.17(19)
C–Pt–N2 [°]	80.1(4)	79.30(19)
N1–Pt–Br [°]	101.8(3)	110.67(11)
N2–Pt–Br [°]	99.0(3)	90.86(12)
N1–Pt–N2–C [°]	1.2(8)	0.1(6)

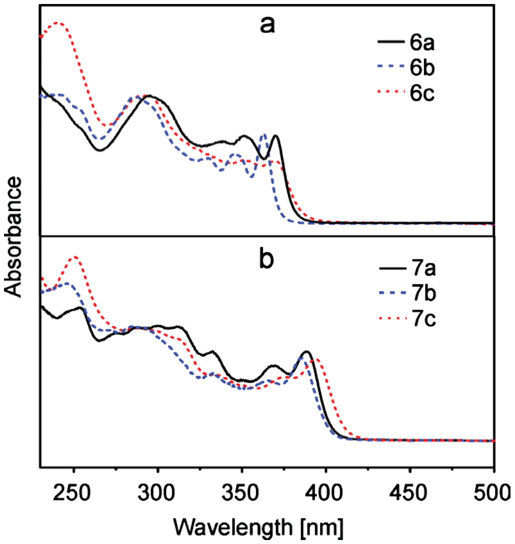


Fig. 2 Absorption spectra of (a) **6a–6c** and (b) **7a–7c** at ambient temperature in CH_2Cl_2.

and therefore have been employed as efficient emitters in OLEDs.[8] Consequently, it seems attractive to investigate the photophysical properties of the reported bis(oxazole) pincer compounds.

Fig. 2 shows the absorption spectra of (a) the palladium(II) compounds **6a–6c** and (b) the platinum(II) compounds **7a–7c**.

Both the Pd(II) and the Pt(II) materials exhibit intense absorption bands below ≈ 325 nm, which can also be found in the absorption spectra of the respective free ligands (see Supporting Information†). Thus, these bands can be assigned to correspond to singlet states which are largely centred at the bis(oxazole) ligands (^{1}LC states). The intense absorptions at longer wavelengths, on the other hand, are absent in the spectra of the ligands. Consequently, they represent transitions to singlet states of strong metal-to-ligand charge-transfer (MLCT) character. In the Pd(II) compounds, the maxima of the lowest ^{1}MLCT states are found between 363 and 370 nm, while the corresponding bands in the Pt(II) compounds lie between 385 and 393 nm. At the applied concentration of ≈ 10^{-5} mol L^{-1}, absorptions from the singlet ground state to the lowest triplet state T_1 could not be observed for any of the studied materials, indicating relatively weak spin–orbit coupling between the T_1 and higher lying MLCT states in both the Pd(II) and Pt(II) compounds. This fits to the assignment of the T_1 states as being largely centred at the bis(oxazole) ligands.

The emission properties of the materials are summarized in Table 3. The Pt(II) pincer compounds **7a–7c** are emissive in solution at ambient temperature (Fig. 3). The spectra are structured and show a series of resolved bands. The high-energy bands with maxima between 508 and 542 nm correspond to the electronic transition from the lowest triplet state T_1 to the singlet ground state, while the bands at lower energy represent vibrational

Table 3 Emission properties of the Pd(II) (**6a–6c**) and Pt(II) (**7a–7c**) bis(oxazole) compounds at 298 K in CH_2Cl_2 and at 77 K in ethanol

Compound	**6a**	**6b**	**6c**	**7a**	**7b**	**7c**
λ_{em} (298 K) [nm][a]	—	—	—	535	508	542
τ (298 K) [μs]	—	—	—	3.0	8.0	1.8
ϕ_{PL}	—	—	—	0.05	0.27	0.02
k_r [s^{-1}][b]	—	—	—	1.7×10^4	3.4×10^4	1.1×10^4
k_{nr} [s^{-1}][b]	—	—	—	32×10^4	9.1×10^4	54×10^4
λ_{em} (77 K) [nm][a]	520	488	534	532	504	538
τ (77 K) [μs]	45	149	33	4.1	10.4	3.3

[a] Electronic $T_1 \rightarrow S_0$ transition. [b] Calculated according to $\phi_{PL} = \frac{k_r}{k_{nr} + k_r} = \tau \cdot k_r$

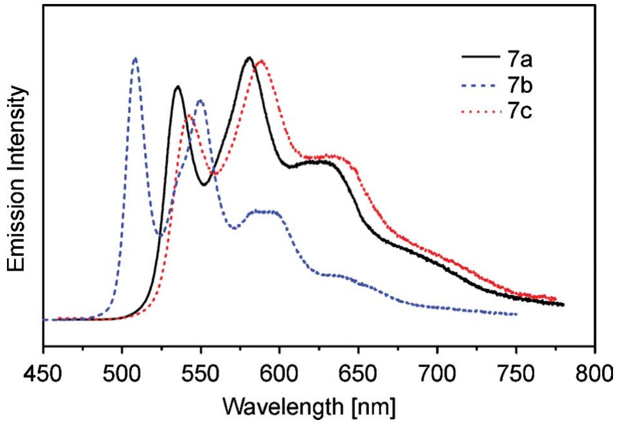


Fig. 3 Emission spectra of **7a–7c** at ambient temperature in CH_2Cl_2.

satellites corresponding to ground state modes as well as to combinations and/or progressions of these modes. For all three compounds, spacings of ≈ 1500 cm^{-1} can be observed, indicating that the vibrational bands mainly stem from stretching vibrations of the aromatic rings.[21]

Similarly as observed for the absorptions to the lowest ^{1}MLCT states (*vide supra*), the emission energy of the compounds decreases in the order **7b** → **7a** → **7c**. However, the energy shifts in emission are much larger than in absorption, indicating an emitting triplet state of largely ligand centred character with both the HOMO and the LUMO strongly influenced by the electronically different substituents in the oxazole moieties. A large red shift of ≈ 1000 cm^{-1} is observed after the introduction of stronger donors by replacing the *t*-butyl groups by ethoxy groups (**7b** → **7a**). An additional red shift of ≈ 250 cm^{-1} is found when going to the donor–acceptor substituted compound (**7a** → **7c**). For Pt(II) pincer compounds with dpyb ligands, on the other hand, a blue shift of the emission was reported after inserting electron-donating groups at the pyridine rings.[22] This different behaviour that the electronic structures of the emitting triplet states in the bis(oxazole) and dipyridinebenzene compounds seem to exhibit significant dissimilarities. However, without further experimental data or the results of quantum chemical calculations, no reasonable explanation for the observed behaviour can be given.

The emission quantum yields in deaerated solutions amount to 0.05 (**7a**), 0.27 (**7b**), and 0.02 (**7c**), with decay times of 3.0 μs (**7a**), 8.0 μs (**7b**), and 1.8 μs (**7c**). From the quantum yields and decay times, the radiative and nonradiative deactivation rates k_r and k_{nr} can be calculated (see Table 3). The radiative rates, lying between 1.1×10^4 (**7c**) and 3.4×10^4 s^{-1} (**7b**), are significantly lower than those of some Pt(II) pincer compounds with dpyb ligands, which exhibit k_r values of up to 1×10^5 s^{-1}.[20] Thus, spin–orbit coupling to higher lying singlet MLCT states, facilitating the radiative decay from the T_1 state to the singlet ground state,[7] is weaker in the reported bis(oxazole) compounds than in the related dipyridinebenzene complexes.

The nonradiative decay rate of the Pt(II) compounds increases with decreasing electronic transition energy in the order **7b** → **7a** → **7c**. Furthermore, the intensities of the vibrational emission bands increase in the same order, indicating increasing geometrical distortions of the T_1 state with respect to the singlet ground state. Since the experimental results are in agreement with the energy gap law for radiationless transitions, which predicts an increase of k_{nr} with decreasing transition energy and increasing geometrical distortions upon excitation,[23] nonradiative decay for **7a–7c** at ambient temperature can be assumed to occur mainly *via* vibrational coupling to ground state modes.

At 77 K in glassy ethanol, the emission spectra of the platinum(II) bis(oxazole) compounds **7a–7c** are more structured, while the decay times are only slightly longer (see Table 3 and Supporting Information†). The good correspondence of the decay times at ambient temperature and at 77 K supports the assumption that the nonradiative decay is mainly governed by vibrational coupling to ground state modes, while the thermal population of higher lying metal-centered dd* states, as observed for several blue emitting Pt(II) compounds,[7,24] can probably be neglected even at ambient temperature.

For Pd(II) compounds, spin–orbit coupling is much weaker than for Pt(II) compounds.[7,25] As a consequence and due to lower lying metal centred dd* states (which quench the emission), no phosphorescence at ambient temperature can be observed for the bis(oxazole) complexes **6a–6c**. However, at 77 K, the materials are emissive (see Table 3 and Supporting Information†). With respect to the transition energies, the same trend as found for the Pt(II) compounds can be observed, *i.e.* the $T_1 \rightarrow S_0$ energies decrease in the order **6b** → **6a** → **6c**. The decay times of the complexes are about one order of magnitude longer than those of the respective Pt(II) compounds. This is in agreement with the weaker SOC induced by Pd(II) compared to Pt(II).

Interestingly, the materials coordinated by ligand **2c**, *i.e.* **6c** and **7c**, have a strong tendency to form intermolecular aggregates in frozen solution even at low concentrations, leading to intense and broad low energy emission bands centred at 750 nm (**6c**) and 690 nm (**7c**).[26] For the compounds with the ligands **2a** and **2b**, on the other hand, corresponding low energy emission bands at 77 K are completely absent (see Supporting Information†). Discussion of the aggregate formation at low temperature is beyond the focus of this contribution.

C Conclusion

Bis(oxazole)phenyl ligands of type **2** can be readily synthesized in a modular fashion, allowing the variation of their electronic properties by introducing donor and/or acceptor substituents into the oxazole moieties. This provides an alternative to the more commonly employed electronic tuning of such types of ligand in the central ring.[19,20] As representative examples, three different palladium(II) and platinum(II) pincer complexes could be synthesized having two weak donors, two strong donors, and one strong donor and one strong acceptor (push-pull approach) present in the oxazole moieties. The energies of absorptions to ^{1}MLCT states are only slightly affected by those substitutions, but the emission energies are distinctly red shifted by two strong donors, with a further slight red shift achieved by substitution of one strong donor by one strong acceptor. Phosphorescence of the Pd(II) compounds can be observed only at 77 K, while the Pt(II) compounds are moderately emissive in ambient temperature solution, exhibiting quantum yields of up to 0.27. A comparison of the photophysical properties of the reported platinum(II) bis(oxazole) compounds with related materials coordinated by dipyridinebenzene pincer ligands shows that the latter ones exhibit stronger spin–orbit coupling, leading to higher radiative decay rates and higher emission quantum yields. Nevertheless, further modifications of the reported bis(oxazole) ligands might lead to materials with improved emission properties.

D Experimental

The synthesis of ligand **2a** and palladium complex **6a** has been described before.[6]

5,5′-Di-*tert*-butyl-2,2′-*m*-(2-bromo-phenylene)-bis-oxazole (2b)

To a stirred mixture of 2-bromo-1,3-benzenedicarbonyl dichloride (**1**) (0.705 g, 2.5 mmol, 1.0 equiv) in 8 ml of dry pyridine was added in portions 1-amino-3,3-dimethyl-butan-2-one hydrochloride (0.758 g, 5.0 mmol, 2.0 equiv) under a nitrogen atmosphere. The mixture was heated to reflux for 30 min. After cooling to room temperature, the mixture was diluted with water. Extraction with CH_2Cl_2 afforded an orange oil (crude: 0.872 g), which was dissolved in CH_2Cl_2 and washed with 10^{-4} mol l^{-1} aqueous HCl solution to remove pyridine. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. The resulting 2-bromo-*N*,*N*′-bis-(3,3-dimethyl-2-oxo-butyl)-isophthalamide (0.715 g of an orange solid, 1.6 mmol, ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.56–7.52 (m, 2H), 7.42 (dd, 1H, *J* = 8.5, 6.6 Hz), 6.81–6.73 (m, 2H), 4.49 (d, 4H, *J* = 4.1 Hz), 1.24 (s, 18H) was used without further purification. A mixture of 2-bromo-*N*,*N*′-bis-(3,3-dimethyl-2-oxo-butyl)-isophthalamide (400 mg, 0.91 mmol, 1.0 equiv) and phosphorus oxybromide (1.82 g, 6.35 mmol, 7.0 equiv) was heated to 140 °C for 2 h. The mixture was allowed to cool to room temperature upon water was added slowly. The aqueous layer was extracted twice with ethyl acetate, the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified on silica (hexanes/EtOAc 5 : 1) afforded **2b** as colourless oil (0.222 g, 0.55 mmol, 39%). R_f (SiO_2, hexanes/EtOAc 5 : 1) = 0.14 (UV); ^{1}H-NMR (300 MHz, $CDCl_3$): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, 2H, *J* = 7.9 Hz), 7.48 (t, 1H, *J* = 7.9 Hz), 6.88 (s, 2H), 1.37 (s, 18H); ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 161.9, 159.1, 132.6, 131.5, 127.3, 120.8 (2 C), 31.9, 28.8; IR (KBr): 3120, 3060, 2960, 2930, 2900, 2860, 1640, 1580, 1545, 1450, 1390, 1360, 1350, 1320, 1275, 1250, 1200, 1120, 1105, 1060, 1030, 980, 960, 935, 825, 805, 755, 730, 690 cm^{-1}; MS (EI-MS): *m*/*z* (%) = 402.1 (36) [M^+], 387.1 (100) [M^+–CH_3], 187.1 (43), 55.1 (44), 41.1 (42), 28.1 (75); $C_{20}H_{23}BrN_2O_2$ (403.31): calc. C 59.56, H 5.75, N 6.95; found C 58.94, H 5.56, N 6.93.

2-Bromo-*N*-(1-hydroxymethyl-2-oxo-2-methoxyethyl)-*N*′-(2-oxo-2-ethoxyethyl)isophthalamide (3)

Isophthaloyl dichloride (**1**, 2.0 g, 7 mmol), methyl serinate hydrochloride (1.1 g, 7.1 mmol) and ethyl glycinate hydrochloride (0.99 g, 7.1 mmol) were suspended in 100 mL of dry CH_2Cl_2, and Et_3N (4.8 mL, 34 mmol) was added dropwise at −15 °C. After being stirred for 12 h with gradual warming to room temperature, the mixture was concentrated to dryness, the residue was purified by column chromatography on silica: I (DCM/EtOAc 1 : 1): 2-bromo-*N*,*N*′-bis(2-oxo-2-ethoxyethyl)isophthalamide (510 mg, yield 17%). -II (EtOAc): **3** (1.24 g, 40%, white solid)- ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.7 Hz, 1H), 7.36 (dd, *J* = 6.9, 8.0 Hz, 2H), 7.26 (dd, *J* = 6.7, 8.4 Hz, 1H), 7.19 (t, *J* = 5.4 Hz, 1H), 4.71–4.66 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.13 (d, *J* = 5.2 Hz, 2H), 4.01–3.90 (m, 2H), 3.74 (s, 3H), 3.39 (brs, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.4, 169.3, 168.1, 167.8, 138.5, 130.1, 127.7, 116.3, 62.6, 61.7, 55.3, 52.7, 41.8, 14.2. MS (ESI, CH_2Cl_2/MeOH + 10 mmol L^{-1} NH_4OAc): *m*/*z* (%) = 450.1 (55), 448.1 (56) [$M+NH_4^+$], 433.0 (100), 431.0 (98) [MH^+]-. III: (EtOAc/MeOH 5 : 1): 2-bromo-*N*,*N*′-bis(1-hydroxymethyl-2-oxo-2-methoxyethyl)isophthalamide (483 mg, yield 15%)- ^{1}H NMR (300 MHz, CD_3OD): δ = 7.56–7.48 (m, 3H), 4.72 (t, *J* = 4.7 Hz, 1H), 3.98 (dd, *J* = 4.8, 11.4 Hz, 2H), 3.91 (dd, *J* = 4.4, 11.3 Hz, 2H), 3.79 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.9, 170.5, 140.7, 130.9, 128.8, 117.5, 62.8, 56.7, 52.9. MS (ESI, MeOH + 10 mmol L^{-1} NH_4OAc): *m*/*z* (%) = 466.0 (26), 464.0 (27) [$M+NH_4^+$], 449.0 (100), 447.0 (98) [MH^+].

2-Bromo-3-(4-methoxycarbonyloxazolin-2-yl)-*N*-(2-oxo-2-ethoxyethyl)benzamid (4)

Diethylaminosulfur trifluoride (DAST, 0.16 mL, 1.2 mmol in 1 mL of dry CH_2Cl_2) was added dropwise to a solution (−78 °C) of **3** (431 mg, 1 mmol) in 14 mL of dry CH_2Cl_2. After stirring for 1 h at −78 °C, anhydrous K_2CO_3 (207 mg, 1.5 mmol) was added in one portion and the mixture was allowed to warm to room temperature. The reaction was quenched with saturated aqueous $NaHCO_3$ (20 mL). The biphasic mixture was extracted with EtOAc (three portions of 40 mL). The combined organic extract was washed with water and saturated aqueous NaCl, dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by column chromatography (silica, EtOAC/hexanes 1 : 1 to EtOAc) to afford **4** (290 mg, 70%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (dd, *J* = 1.9, 7.7 Hz, 1H), 7.53 (dd, *J* = 1.8, 7.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.79 (t, *J* = 4.8 Hz, 1H), 4.98(dd, *J* = 8.0, 10.7 Hz, 1H), 4.75–4.59 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.27–4.19 (m, 2H), 3.81 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1, 169.5, 167.5, 166.0, 139.4, 132.6, 131.2, 130.6, 127.4, 118.9, 70.1, 68.5, 61.7, 52.8, 41.8, 14.2. MS (EI-MS): *m*/*z* (%) = 413.9 (10), 412.0 (7) [M^+], 354.9 (100), 353.0 (88), 311.9 (61), 309.9 (47).

2-Bromo-3-(4-methoxycarbonyloxazol-2-yl)-*N*-(2-oxo-2-ethoxyethyl)benzamide (5)

To a solution of **4** (170 mg, 0.41 mmol) in 4 mL of dry CH_2Cl_2 cooled to 0 °C was added DBU (0.070 mL, 0.47 mmol) and then dropwise $BrCCl_3$ (0.055 mL, 0.55 mmol). The mixture was stirred overnight while warming to room temperature. Saturated aqueous NH_4Cl solution (7 mL) was added, and the biphasic mixture was extracted with EtOAc (three portions of 10 mL). The combined organic extract was washed with water and saturated aqueous NaCl, dried over anhydrous $MgSO_4$ and concentrated. The residue was purified on silica (hexanes/EtOAc) 1 : 1 to EtOAc) to give **5** (166 mg, 98%) of a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.96 (dd, *J* = 1.7, 7.7 Hz, 1H), 7.60 (dd, *J* = 1.8, 7.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 6.44 (t, *J* = 4.7 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.27 (d, *J* = 4.9 Hz, 2H), 3.96 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5, 167.5, 161.4, 160.9, 144.6, 140.0, 134.2, 133.4, 131.1, 129.1, 127.7, 118.8, 61.8, 52.4, 41.9, 14.2. MS (EI-MS): *m/z* (%) = 411.9 (8), 410.0 (8) [M$^+$], 338.8 (11), 336.9 (10), 309.8(100), 307.9 (97). Element Analysis for $C_{16}H_{15}BrN_2O_6$: Found C46.68, H 3.73, N 6.73, Calcd. C 46.73, H 3.68, N 6.81.

2-Bromo-1-(4-methoxycarbonyl-oxazol-2-yl)-3-(5-ethoxy-oxazol-2-yl) benzene (2c)

A mixture of **5** (408 mg, 0.99 mmol) and P_2O_5 (4.8 g, 33 mmol) in 40 mL of dry toluene was refluxed for 3 h. After cooling to room temperature, the mixture was diluted with 30 ml of Et_2O, and then carefully neutralized with cold 10% KOH aqueous solution (50 mL) followed by extraction with Et_2O (two portions of 200 mL). The combined organic layers were washed with water and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified on silica (hexanes/EtOAc 1 : 1) to afford **2c** (280 mg, 71%) as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 7.94 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.84 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 6.32 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.5, 160.4, 159.1, 149.3, 143.5, 133.1, 132.2, 132.1, 129.5, 129.4, 126.4, 119.5, 99.9, 67.3, 51.3, 13.4. MS (EI-MS): *m/z* (%) = 394.0 (34), 392.0 (33) [M$^+$], 309.8 (97), 307.9 (100), 283.0(17), 280.9 (19). Element Analysis for $C_{16}H_{13}BrN_2O_5$: Found C 48.58, H 3.46, N 6.85, Calcd. C 48.88, H 3.33, N 7.12.

Synthesis of 6b

$Pd(dba)_2$ (223 mg, 0.388 mmol, 1.0 equiv) and **2b** (157 mg, 0.389 mmol, 1.0 equiv) were dissolved in dry benzene (14 ml). The solution was degassed (3 × freeze-pump-thaw cycles) and heated to reflux until the purple colour had faded (20 min). The reaction mixture was concentrated, the residue was purified on silica (hexanes/EtOAc 3 : 1) to afforded **6b** (166 mg, 0.326 mmol, 84%) as a yellow solid. R_f (SiO_2, hexanes/EtOAc 3 : 1) = 0.18 (UV); M.p. > 290 °C (decomp.); ^{1}H-NMR (300 MHz, MeOH-d_4): δ = 7.25–7.20 (m, 2H), 7.12 (dd, 1H, *J* = 8.5, 6.6 Hz), 6.89 (s, 2H), 1.42 (s, 18H); ^{13}C-NMR (75.5 MHz, MeOH-d_4): δ = 168.6, 164.7, 162.7, 131.0, 126.0, 123.9, 121.0, 33.1, 29.0; IR (KBr): 3137, 3058, 2966, 2906, 2870, 2369, 1591, 1459, 1397, 1364, 1281, 1211, 1152, 1126, 1030, 1004, 946, 824, 724, 681 cm^{-1}; MS (PI-FDMS): *m/z* (%) = 939.5 (50) [2M$^+$–Br], 510.4 (100) [M$^+$], 429.4 (20) [M$^+$–Br]; $C_{20}H_{23}BrN_2O_2Pd$ (509.73): calc. C 47.13, H 4.55, N 5.50; found C 46.99, H 4.68, N 5.44.

Synthesis of 6c

Under a N_2 atmosphere, a 25 mL Schlenk flask was charged with 2-bromo-1-(4-methoxycarbonyl- oxazol-2-yl)-3-(5-ethoxy-oxazol-2-yl) benzene (89 mg, 0.226 mmol), $Pd(dba)_2$ (130 mg, 0.226 mmol) and 8 mL of dry benzene. The reaction mixture was heated to reflux until the purple color faded (30 min, from purple to dark green or yellow), then cooled to room temperature and stirred for further 2 h, followed by filtration to remove the precipitate. To the filtrate was slowly added hexanes (10 mL) to precipitate the complex. Filtration and subsequent washing with hexanes (three times of 1 mL) gave a yellow powder, which was dissolved in acetone (*ca* 50 mL) and filtered to remove residual palladium black. The filtrate was concentrated, the residue was recrystallised from CH_2Cl_2/EtOAc to yield 86 mg of **6c** (76%) as yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20(s, 1H), 7.31 (dd, *J* = 1.5, 7.3 Hz, 1H), 7.18(dd, *J* = 1.4, 7.7 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.74(s, 1H), 4.24 (q, *J* = 7.0 Hz, 4H), 3.99 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 169.2, 162.4, 159.2, 159.1, 158.4, 142.4, 133.9, 120.6, 128.3, 125.2, 123.3, 123.1,100.5, 69.6, 53.0, 14.5. MS (FI-FDMS): *m/z* (%) = 918.1 (20) [2M$^+$–HBr], 500.2 (100) [M$^+$], 456.2 (9) [M$^+$–CO_2], 419.2 (63) [M$^+$–HBr]. Elemental Analysis for $C_{16}H_{13}BrN_2O_5Pd$: Found C 38.52, H 2.36, N 5.58, Calcd. C 38.46, H 2.62, N 5.61.

Synthesis of 7a

Under a N_2 atmosphere, a 25 mL Schlenk flask was charged with **2a** (227 mg, 0.6 mmol), $Pt_2(dipdba)_3$ (459 mg, 0.34 mmol, 1.1 equiv) and 9 mL of dry THF. The reaction mixture was stirred overnight at 60 °C, and then cooled to room temperature. To the reaction mixture, 10 mL of petroleum ether was slowly added under N_2-pretection, and yellow solid was precipitated. After filtration and washing with hexanes (three portions of 2 mL each), 270 mg (78%) of **7a** were obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (dd, *J* = 7.1, 8.2 Hz, satellite J_{Pt-H} = 7.8 Hz, 2H), 7.16 (dd, *J* = 6.9, 8.5 Hz, 1H), 6.71(s, satellite J_{Pt-H} = 9.2 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 4H), 1.50 (t, *J* = 7.1 Hz, 6H). ^{1}H NMR (300 MHz, acetone-d_6): δ = 7.41 (dd, *J* = 7.1, 8.2 Hz, satellite J_{Pt-H} = 7.8 Hz, 2H), 7.29 (dd, *J* = 6.9, 8.5 Hz, 1H), 6.70(s, satellite J_{Pt-H} = 9.2 Hz, 2H), 4.45 (q, *J* = 7.0 Hz, 4H), 1.51 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 159.0, 157.2, 128.1, 123.4, 121.4 (satellite J_{Pt-C} = 18.7 Hz), 100.2 (satellite J_{Pt-C} = 21.3 Hz), 67.0, 14.5. MS (FI-FDMS): *m/z* (%) = 1147.3 (41) [2M$^+$], 1068.6 (60) [2M$^+$–HBr], 573.9 (100) [M$^+$]. Element Analysis for $C_{16}H_{15}BrN_2O_4Pt$: Found C 33.55, H 2.48, N 4.76, Calcd. C 33.46, H 2.63, N 4.88.

Synthesis of 7b

To a solution of **2a** (60 mg, 0.15 mmol, 1.0 eq) in 3 ml of THF was added $Pt_2(dipdba)_3$ (161 mg, 0.12 mmol, 1.6 equiv "Pt") under a nitrogen atmosphere. The reaction was stirred at 60 °C for 20 h. The mixture was concentrated, and the residue was purified on silica (hexanes/EtOAc 3:1) to afford **7b** as an orange solid (77 mg, 0.13 mmol, 86%). R_f (SiO_2, hexanes/EtOAc 3 : 1) = 0.30 (UV); M.p. > 295 °C (decomp.); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.52–7.43 (m, 2H), 7.31–7.18 (m, 3H), 1.38 (s, 18H); ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 172.2, 162.0, 157.3, 128.0, 123.3, 123.0, 119.8, 32.2, 28.4; IR (KBr): 3140, 3060, 2970, 2870, 1590, 1520, 1460, 1430, 1395, 1365, 1320, 1280, 1210, 1150, 1130, 1110, 1025,

1005, 940, 815, 720, 680 cm^{-1}; MS (PI-FDMS): *m/z* (%) = 1117.1 (40) [$2M^+$–Br], 598.4 (100) [M^+]; $C_{20}H_{23}BrN_2O_2Pt$ (598.39): calc. C 40.14, H 3.87, N 4.68; found C 40.34, H 3.90, N 4.74.

Synthesis of 7c

Following the same procedure as for **7a**, 187 mg (53%) of **7c** were obtained: ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.25$(s, satellite J_{Pt-H} = 3.4 Hz, 1H), 7.45(d, J = 7.7 Hz, satellite J_{Pt-H} = 3.2 Hz, 1H), 7.33(d, J = 6.7 Hz, satellite J_{Pt-H} = 3.1 Hz, 1H), 7.16 (t, J = 6.9 Hz, 1H), 6.82(s, satellite J_{Pt-H} = 10.5 Hz, 1H), 4.30 (q, J = 7.0 Hz, 2H), 3.99 (s, 3H), 1.50(t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 175.4, 164.1, 159.5, 159.1, 156.6, 142.2 (satellite J_{Pt-C} = 15.0 Hz), 134.2, 129.0, 126.8, 123.9, 123.6, 123.3, 99.9 (satellite J_{Pt-C} = 22.8 Hz), 70.5, 53.4, 14.7. MS (FI-FDMS): *m/z* (%) = 1176.0 (16) [$2M^+$], 588.3 (100) [M^+]. Elemental Analysis for $C_{16}H_{13}BrN_2O_5Pt$: Found C 32.78, H 2.18, N 4.74, Calcd. C 32.67, H 2.23, N 4.76.

Spectroscopy

For ambient temperature measurements, the materials were dissolved in CH_2Cl_2, while ethanol was used as solvent at 77 K. All solvents were of spectroscopic grade, the concentration of the solutions was ≈ 10^{-5} mol/L. Absorption spectra were recorded with a Varian Cary 300 double beam spectrometer. Emission spectra at 300 and at 77 K were measured with a steady-state fluorescence spectrometer (Jobin Yvon Fluorolog 3). Luminescence quantum yields were determined with a commercially available system for the measurements of absolute quantum yields (Hamamatsu Photonics C9920-02).[27] The estimated relative error of the quantum yields is about 10%. Fluid solutions were degassed by at least three pump–freeze–thaw cycles with a final vapor pressure at 77 K of ≈ 10^{-5} mbar. A pulsed diode laser (PicoQuant PDL 800-B) with a pulse width of about 500 ps (excitation wavelength of 372 nm) or a nitrogen laser (MNL100, Lasertechnik Berlin) with a pulse width of 3 ns (excitation wavelength of 337 nm) were applied as excitation sources for decay time measurements. Decay times were registered using a FAST Comtec multichannel scaler PCI card with a time resolution of 250 ps.

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