Construction of a photoactive supramolecular system based on a platinum(II) bis-acetylide building block incorporated into a ruthenium(II) polypyridyl complex†

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A new ruthenium(II) polypyridyl-platinum(II) diethynyl triad containing 3-ethynylphenanthroline linked by platinum(II) bis-tributylphosphine organometallics, Ru(II)-Pt(II)-Ru(II), and platinum(II) bis-ethynylphenanthroline complex has been prepared. The ruthenium(II)-metal triads, Ru(II)-M-Ru(II) (M = Pt(II) and Au(I)), showed typical MLCT absorption bands and a lowest energy π–π* absorption involved with the metal perturbation in the 350–500 nm region. Broad emission bands assignable to triplet MLCT transitions were definitely observed in the triads Ru(II)-M-Ru(II), while those of platinum(II) and gold(I) bis-ethynylphenanthroline complexes displayed a phosphorescent band with vibronic progression assignable to the metal-perturbed triplet π–π*(C≡Cphen) transition, which means that the hybrid architecture constructed with Ru(II) polypyridyl and metal bis-acetylide units converts a blue-green metal perturbed π–π* phosphorescence into an orange MLCT-based emission. The transient differential absorption spectra of ruthenium compounds showed the difference of the electron transfer process between [Ru(bipy)(phen)](PF$_6$)$_2$ and triads under the MLCT state. Photophysical data of the triad suggest an efficient energy transfer from the platinum bis-acetylide site to the ruthenium polypyridyl site followed by the supposed charge injection from a ruthenium center to the extended π-conjugated phenanthroline under photo-excitation in this photoactive supramolecular system.

Introduction

Current research regarding platinum(II) acetylide complexes has gained great importance due to their potential applications in the field of optical devices and photocatalyst materials because of their interesting properties as photoactive molecules.[1–6] In addition, co-ordination oligomers and polymers with acetylene derivatives have been developed in recent studies of platinum(II) organometallics, and structural and photophysical studies of platinum(II) bis-acetylide oligomers have been carried out in the recent past.[7–10] In contrast, photoactive molecular systems with ruthenium(II) polypyridyl complexes including ethynyl-substituted bipyridyl and terpyridyl ligands have been extensively studied by Ziessel *et al.* in the past two decades,[11–13] while the recent photophysical studies of ruthenium(II)-platinum(II) heterometallic complexes have been reported by many other research groups.[14] There have also been photophysical studies of ruthenium(II) polypyridyl complexes containing 4-ethynylbipyridine linked by platinum(II) bis-tributylphosphine organometallics, and this supramolecular system does not operate as a molecular wire according to this previous research,[15,16] because such a function is interfered with by the supposed charge injection from the ruthenium center to

the unsubstituted bipyridyl ligand in this system. In this light, we previously reported the first example of the preparation of, and the photophysical and electrochemical properties of, a ruthenium(II) polypyridyl complex containing 3-ethynylphenanthroline linked by a gold(I) cation, a supramolecular triad Ru(II)-Au(I)-Ru(II) system[17] that suggests the possibility of a molecular wire by charge injection from the ruthenium center to the wire skeleton, which contains two ethynyl-substituted phenanthrolines under photoexcitation. However, a recent photophysical study of ruthenium(II) polypyridyl complexes containing 4,4′- and 5,5′-phenylethynyl-substituted bipyridine by Schanze *et al.*,[18] and a study of dinuclear ruthenium(II) polypyridyl complexes containing the bridging ligand of two phenanthroline units linked at the 3- and/or 4-substitution with an acetylide unit by Tor *et al.*[19] suggest a distinguishing difference in the emission energy level from triplet metal to ligand charge transfer (MLCT) transition between these ruthenium(II) complexes including an ethynyl-substituted ligand with a different substituted site.

We therefore became interested in the photophysical properties of ruthenium(II) polypyridyl complexes containing 3-ethynyl-phenanthroline linked by platinum(II) bis-tributylphosphine organometallics; specifically, a triad Ru(II)-Pt(II)-Ru(II) (**1**) supramolecular system (Scheme 1), because the platinum organometallics operate as an insulator or conductor in this system. In this paper, we report the characterization of and the photophysical investigation of the triplet state of **1** and a neutral platinum(II) organometallic (**2**) (Scheme 1) by emission and transient differential absorption spectroscopies.

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Scheme 1   Structures of compounds **1–4**.
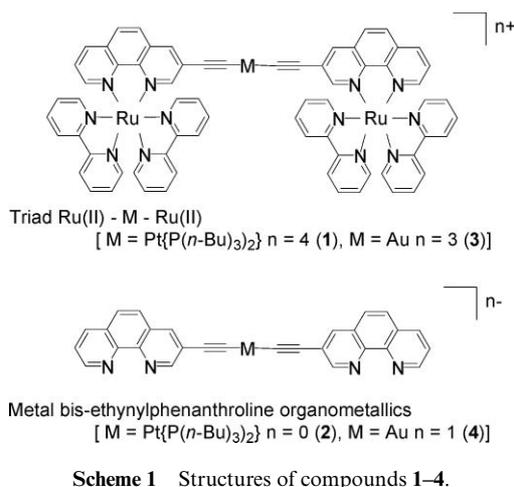
Results and discussion

Synthesis and characterization

Novel triad **1** was synthesized from *trans*-Pt{P(*n*-Bu)$_3$}$_2$Cl$_2$ (P(*n*-Bu)$_3$ = tributylphosphine) and [Ru(bpy)$_2$(3-ethynyl-phenanthroline)](PF$_6$)$_2$ (1 : 2 ratio) using CuI as a catalyst, while the platinum(II) organometallic **2** was prepared by reacting *trans*-Pt{P(*n*-Bu)$_3$}$_2$Cl$_2$ and 3-ethynyl-1,10-phenanthroline (1 : 2 ratio) under similar experimental conditions. These compounds were characterized by ^{1}H- NMR, IR, UV-vis, and electrospray MS spectroscopies and elemental analysis (see Experimental). The IR spectra of both compounds indicate that the metal–carbon bond between platinum and 3-ethynylphenanthroline is the η^1 coordination of σ-bonding. Characteristic v(C≡C) bands were observed at 2091 cm^{-1} (**1**) and 2090 cm^{-1} (**2**), respectively, and the v(CC–H) bands at around 3150 cm^{-1} in both phenanthroline ligands disappeared. The formation of a Pt–C≡C bond is further supported by the ^{1}H-NMR measurement; no signal assignable to ethynyl proton was detected, and all observed signals for **1** and **2** correspond to the protons of their ethynylphenanthrolines and the tributylphosphine (and bipyridine for **1**). Additionally, the upfield shifts on **1** and **2** in the H-2 and H-4 protons of their phenanthroline ligands are triggered by the coordination of the platinum(II) unit because of the π back-donation from the Pt(II) center to each ethynylphenanthroline ligand. A similar phenomenon is reported in our previous study of a Ru(II)-Au(I)-Ru(II) (**3**) (Scheme 1) supramolecular system.[17]

Photophysical and electrochemical properties

Fig. 1(a) shows the absorption and emission spectra of **1** and similar triad ruthenium(II)-gold(I) **3** in acetonitrile, while Fig. 1(b) shows the absorption and emission spectra of **2** and similar gold(I) complex **4** (Scheme 1).[20] The photophysical data of the UV absorption bands at room temperature and of the emission bands at room temperature and at 77 K for **1–4** and the numerical data of emission lifetimes (τ_{em}) and emission quantum yields (ϕ_{em}) for triads are listed in Table 1.[21] The absorption bands in the 300–400 nm region are primarily assigned to metal-perturbed π–π*(C≡Cphen) transitions for all compounds. The spectrum of **1** shows the lowest energy π–π*(C≡Cphen) transition band at 392 nm and a similar absorption is detected in **3** at 362 nm.
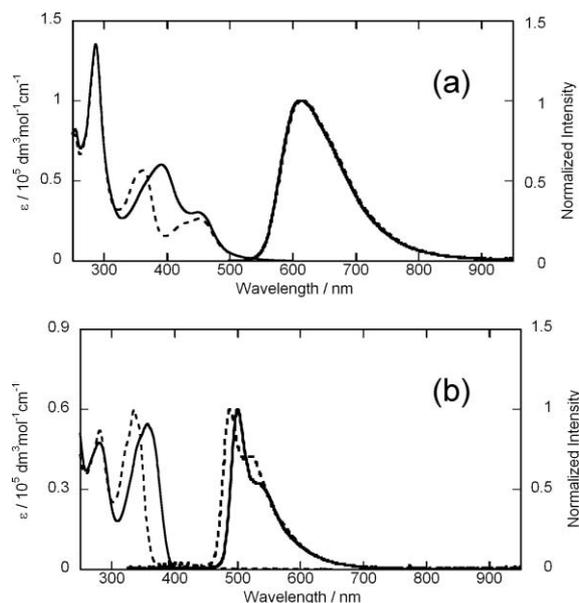
Fig. 1 (a) UV-vis absorption and emission spectra upon excitation at 425 nm of **1** (solid line) and **3** (dash line) in acetonitrile at room temperature. (b) UV-vis absorption spectra in methanol and emission spectra upon excitation at 325 nm in an ethanol of **2** (solid line) and **4** (dash line) at room temperature.

The molar extinction coefficients of **1** for the π–π* and MLCT absorptions are almost equivalent to those of **3**, and a similar relationship of the lowest energy π–π* absorption bands and their molar extinction coefficients was observed between **2** (357 nm) and **4** (336 nm). The lowest energy π–π* absorption of platinum(II) compounds **1** and **2** was comparable to that of the shifts of corresponding gold(I) compounds **3** and **4** to a long wavelength area, the so-called red shift, which is probably due to greater electron delocalization between two ethynylphenanthrolines.

The emission spectra of **1** and **3** shows almost the same phosphorescent bands assignable to the triplet MLCT transition in the long wavelength region (550–900 nm) at room temperature, while the those of **2** and **4** display a similar shape of phosphorescent bands assignable to the metal-perturbed triplet π–π*(C≡Cphen) transition in the middle wavelength region (450–700 nm) at room temperature (Fig. 1). Furthermore, the shape of the emissions of **1** and **3** is the typical broad phosphorescent band of a ^{3}MLCT transition, while that of **2** and **4** is a unique phosphorescent band with vibronic progression even at room temperature. The vibronic structure of **2** and **4** shows an almost identical vibrational spacing of the frequency vibration (v = 1200–1600 cm^{-1}) in accord with the aromatic vibrational mode in phenanthroline ligands. Additionally, the excitation spectra of **1–4** in the 300–500 nm area are approximately compatible with the absorption spectra in this region. These emission data suggest an efficient energy transfer from a platinum bisacetylide site to a ruthenium polypyridyl site because the emission of triads **1** and **3** shows only the phosphorescence of an MLCT transition and does not include that of the metal-perturbed π–π*(C≡Cphen) transition observed in **2** and **4**.

The electrochemical properties of triads, Ru(II)-M-Ru(II), were investigated by cyclic voltammetry technique in an acetonitrile. Their electrochemical data are collected in Table 1. Triads and

Table 1 The photophysical and electrochemical data for compounds **1–4**

Compound	Absorption[a]			Emission[b]		Electrochemical data		
	λ_{abs}/nm ($\varepsilon/10^4$ dm^{3}mol^{-1}cm^{-1}) at r.t.			λ_{phos}/nm (τ/μs, ϕ_{em})[c]		$E_{1/2}$(ox)/V	$E_{1/2}$(red)/V	$\Delta E_{1/2}$/V
				at r.t.	at 77 K			
1	450, (3.1),	392, (6.0),	287 (13.6)	614 (1.13, 0.058)	579, 629, 687	1.30	−1.34	2.64
2	—	357, (5.5),	281 (4.8)	501, 534	496, 534, 553, 580	—	—	—
3	452, (2.6),	362, (5.7),	287 (13.5)	616 (0.82, 0.059)	578, 628, 686	1.28	−1.31	2.59
4	—	336, (6.0),	281 (5.2)	486, 526	481, 520, 535,565, 583	—	—	—
Ru(bpy)$_3$	451, (1.4),	—	287 (8.1)	619 (0.96, 0.062)	579, 628, 687	1.26	−1.36	2.62

[a] UV-vis spectra were measured in an acetonitrile for triad ruthenium compounds and a methanol for mononuclear complexes at room temperature.
[b] These data were phosphorescence peaks. [c] Time-resolved luminescence was measured in a degassed acetonitrile for triad ruthenium compounds at room temperature. Emission quantum yields (ϕ_{em}) were calculated relative to [Ru(bpy)$_3$](PF$_6$)$_2$ in a degassed acetonitrile ($\phi_{em} = 0.062$) as a standard.

Ru(bpy)$_3$(PF$_6$)$_2$ exhibited reversible oxidation waves ($E_{1/2}$(ox)) and reversible first reduction waves ($E_{1/2}$(red)) in the potential range +1.50 V to −1.50 V *versus* SCE. The $E_{1/2}$(ox) of two triads are typical for the Ru$^{3+/2+}$ couple of ruthenium(II) polypyridyl complexes with bipyridine and/or phenanthroline derivatives, while the $E_{1/2}$(red) are assigned to the first reduction process of the ethynylphenanthroline or one of the bipyridine ligands. An interest finding is that the $E_{1/2}$(red) of two triads (**1**: −1.34 V, **3**: −1.31 V) are higher potential than that of Ru(bpy)$_3$(PF$_6$)$_2$ (−1.36 V) under a same measurement condition although the difference of the $E_{1/2}$(red) in these compounds is small. These first reduction potentials of triads might indicate that the first reduction occurred at the ethynylphenanthroline ligands in Ru(II)-M-Ru(II) and it means that an ethynylphenanthroline in triads accepts the electron from a ruthenium center under photoexcited MLCT state. Validity of this explanation is supported by the observation of the transient differential spectra as mentioned below.

Transient differential absorption spectroscopy

The transient differential absorption spectrum of **1** was distinctly different from that of tris(2,2′-bipyridine)ruthenium(II) reported in previous works,[15,22] which was similar to that of [Ru(bipy)$_2$(phen)](PF$_6$)$_2$ (Fig. 2). The specific differences between the spectra of **1** and [Ru(bipy)$_2$(phen)](PF$_6$)$_2$ were strong bleaching of the π–π*(C≡Cphen) absorption band near at 390 nm in **1** and strong absorption near at 370 nm assignable to π–π*(phen$^-$ radical and/or bipy$^-$ radical) absorption in {[Ru(bipy)$_2$(phen)](PF$_6$)$_2$}*. A corresponding distinction between the spectra of **3** and [Ru(bipy)$_2$(phen)](PF$_6$)$_2$ was also confirmed (Fig. 2). The bleaching in **1** of the π–π*(C≡Cphen) absorption band and the absorption band near 400 nm, which is probably assignable to π–π*(C≡Cphen$^-$ radical) absorption, relative to those in **3**, may be attributable to a red shift, as in the case of the π–π*(C≡Cphen) absorption in **1** and **3** mentioned above. Additionally, the lifetimes calculated from these transient differential absorption spectra on **1** and **3** are in agreement with their emission lifetimes τ_{em} on **1** and **3**. The transient differential absorption spectrum of the first example of triad ruthenium(II) polypyridyl complexes containing 4-ethynylbipyridine linked by platinum(II) bis-tributylphosphine
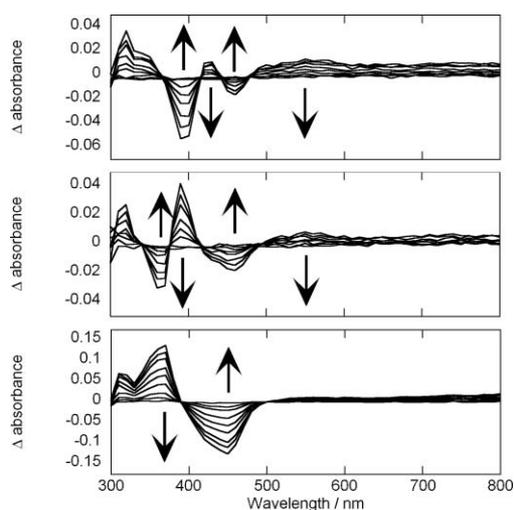
Fig. 2 Transient differential absorption spectra of **1** (upper), **3** (center), and [Ru(bipy)$_2$(phen)](PF$_6$)$_2$ (lower) in acetonitrile at room temperature.

organometallics, which was reported by Ziessel *et al.*, was similar to that of [Ru(bipy)$_3$]Cl$_2$ and it was concluded that the function as a molecular wire is interfered with by the charge injection from the ruthenium center to the unsubstituted bipyridyl ligand in such a system.[12,15] The distinct difference between triad **1** (or **3**) and [Ru(bipy)$_3$]Cl$_2$ in the 300–450 nm region supports the idea that triads **1** and **3** receive the supposed charge injection from a ruthenium center to the extended π-conjugated ethynylphenanthroline under a photoexcited MLCT state.

Conclusion

Novel Ru(II)-Pt(II)-Ru(II) triad **1** and mononuclear platinum(II) bisacetylide complex **2** were synthesized and characterized by spectroscopic means. Triad **1** shows an intense emission assignable to triplet MLCT transition, while **2** shows an emission assignable to triplet π–π*(C≡Cphen) transition. The emission data and transient differential absorption spectra of **1** and **3** suggest an efficient energy transfer from a bisacetylide organometallic site to a ruthenium site and then the supposed charge injection from

a ruthenium center to the extended π-conjugated ethynylphenan-throline, which contains a metal (M = Au or Pt) bisacetylide site under photoexcitation. It is appropriate to highlight the difference in the transient differential absorption spectra between our Ru(II)-Pt(II)-Ru(II) system with 3-ethynylphenthroline and Ziessel's similar system with 4-ethynylbipyridine, because the present system is capable of operating as a conductor between two ruthenium(II) units in contrast to Ziessel's system, which is expressed as an insulator in their article.[15,16] We are currently extending synthetic work on a novel ruthenium(II)-gold(I) and ruthenium(II)-platinum(II) supramolecular system with more π-conjugated ligands of 3,8- diethynylphenanthroline, and are exploring the photoinduced energy transfer process and the electron population under photoexcitation in these photoactive supramolecular systems.

Experimental

Materials and general measurements

All reactions were carried out under an argon atmosphere. Solvents were freshly distilled according to standard procedures. The starting materials were purchased from Aldrich or Nacalai and used without further purification. The starting ruthenium(II) complex, [Ru(bpy)$_2$(3-ethynylphenanthroline)](PF$_6$)$_2$, was synthesized by the similar method of Tor et $al.$[23] and the platinum(II) complex, Pt{P(n-Bu)$_3$}$_2$Cl$_2$, was prepared by Kauffmann et $al.$[24] Characterization of the novel complexes has been done by IR, ^{1}H NMR, UV-vis, emission spectroscopy, and elemental analyses. Elemental analyses were performed for C, H and N elements on a Perkin-Elmer 2400II CHNS/O full-automatic analyzer. Electrospray MS spectra were acquired using an LCT mass spectrometer equipped with an ion spray interface (Micromass Limited, Manchester, U.K.). Samples were introduced using a single syringe pump (KD Scientific Inc.) fitted with Hamilton syringes (Hamilton Co., Reno, NE). The samples employed for spectral measurements were prepared in an acetonitrile (HPLC grade). IR spectra were obtained on a JASCO FT/IR 460 spectrometer using the KBr-pellet method. The ^{1}H NMR spectra were recorded with a Bruker AVANCE NMR spectrometer (600 MHz) at room temperature and the chemical shifts were referenced to TMS.

Electrochemical measurements were performed by using a BAS CV-50W Voltammetric Analyzer. Measurements were made in N$_2$-purged acetonitrile containing 0.1 M [N(n-C$_4$H$_9$)$_4$](PF$_6$) in a three-compartment cell. A platinum coil counter, a platinum wire working, and Ag/AgNO$_3$ reference electrode (+0.37 V $vs.$ SCE; calibrated with Fc$^{+/0}$) were used. The $E_{1/2}$ values were calculated as the average of the anodic and cathodic peak potentials, (E_{pa} + E_{pc})/2 from cyclic voltammograms data. UV-vis spectra were recorded on a SHIMADZU U-1800 spectrophotometer in a CH$_3$CN (spectroscopic grade) for ruthenium compounds and in a methanol (spectroscopic grade) for other compounds at room temperature. Emission and excitation spectra were recorded on a HITACHI F-2500 fluorescence spectrophotometer and corrected emission spectra were measured with a HAMAMATSU C7473 photonic multi-channel analyzer and the spectra at 77 K were measured using a liquid nitrogen in a quarts Dewar. Emission spectra at room temperature were measured in a degassed

acetonitrile for triad ruthenium compounds by argon bubbling (30 min) upon excitation at 425 nm and in a degassed ethanol for mononuclear complexes by freeze-pump-thaw (4 times) upon excitation at 325 nm. All emission spectra at 77 K were measured in a degassed ethanol by freeze-pump-thaw (4 times).

Nanosecond time-resolved transient differential spectra were obtained by using the third harmonic of a Q-switched Nd3+:YAG laser (Continuum Surelite I-10, λ = 355 nm). Sample solutions in a 1 cm quartz cell were deaerated by bubbling with argon for 5 min. White light from a Xe arc lamp was used for acquisition of absorption spectra. For the determination of emission lifetimes, samples were irradiated using the third harmonic pulses of the Nd3+:YAG laser. The emission from the samples was passed through a grating monochromator (H-10, Jobin Yvon) to eliminate scattering light and focused into a Si avalanche photodiode (Si-APD, S5139, Hamamatsu). The photocurrent from the Si-APD was amplified through wide-band amplifier (DC-500 MHz, CLC110) and accumulated on a digitizing oscilloscope (HP 54520 Hewlett-Packard) to get the decay-profile of the emission intensity, which was fit to single-exponential function with convolution of the instrumental response function of the measuring system. The time-resolution of the system is 2 ns.

Syntheses of Ru–Pt triad and Pt complex

Ru(II)-Pt(II)-Ru(II) (**1**). The mixture solution of dry CH$_2$Cl$_2$ (30 mL) and distilled diisopropylamine (3 mL) was added Pt{P(n-Bu)$_3$}$_2$Cl$_2$ (33 mg, 0.05 mmol) and CuI (3mg, 0.015 mmol) under Ar. The [Ru(bpy)$_2$(3-ethynylphenanthroline)](PF$_6$)$_2$ (91 mg, 0.10 mmol) was added to the mixture solution and stirred at 25 °C for 3 d under light shielding. After the reaction period, CH$_2$Cl$_2$ was removed under reduced pressure and added ethanol (3 mL). The resulting red precipitate was collected by filtration with a suction filter and chromatographed on Cosmosil 75C$_{18}$-OPN (Nacalai Tesque), eluted with CH$_3$CN. The red powder **1** (71 mg, 59%) was dried at 40 °C under vacuum for 5 h. (Found: C 44.64, H 4.05, N 6.79. Calcd for C$_{92}$H$_{100}$N$_{12}$P$_6$F$_{24}$Pt$_1$Ru$_2$·3H$_2$O: C 44.80, H 4.33, N 6.81%); Positive ES-MS: ion at m/z 458.4 (M^{4+}, 100%); IR (cm^{-1}) ν(C≡C): 2091; ^{1}H NMR (600 MHz, CD$_3$OD, Me$_4$Si): δ 8.563 (dd, J = 8.0 and 1.2 Hz, 1 H, phen-H7), 8.533 (m, 2 H, bpy-H6), 8.497 (m, 2 H, bpyH6), 8.299 (d, J = 1.7 Hz, 1 H, phen-H4), 8.174 (d, J = 9.0 Hz, 1 H, phen-H5), 8.105 (m, 2 H, bpy-H5), 8.095 (d, J = 9.0 Hz, 1 H, phen-H6), 8.025 (dd, J = 5.3 and 1.2 Hz, 1 H, phen-H9), 8.010 (m, 2 H, bpy-H5′), 7.848 (d, J = 4.8 Hz, 1 H, bpyH3α), 7.808 ((d, J = 4.8 Hz, 1 H, bpyH3β), 7.683 (dd, J = 8.3 and 5.3 Hz, 1 H, phen-H8), 7.682 (d, J = 1.7 Hz, 1 H, phen-H2), 7.581 (d, J = 4.8 Hz, 1 H, bpy-H3′α), 7.547 (d, J = 4.8 Hz, 1 H, bpy-H3′β), 7.442 (m, 2 H, bpy-H4), 7.242 (m, 2 H, bpy-H4′), 1.927 (m, 6 H, α-CH$_2$), 1.464 (m, 6 H, β-CH$_2$), 1.285 (qt, J = 7.4 and 7.4 Hz, 6 H, γ-CH$_2$), 0.764 (t, J = 7.4 Hz, 9 H, –CH$_3$).

Platinum(II) bis-ethynylphenanthroline (**2**). The dry CH$_2$Cl$_2$ solution (12 mL) of 3-ethynylphenanthroline (56 mg, 0.27 mmol) was added Pt{P(n-Bu)$_3$}$_2$Cl$_2$ (84 mg, 0.13 mmol) and CuI (3 mg, 0.015 mmol) under Ar. The distilled diisopropylamine (2 mL) was added to the mixture solution and stirred at 25 °C for 4 d under light shielding. After the reaction period, MeOH (5 mL) was added, and the solvent and excess diisopropylamine were removed under reduced pressure. The resulting residue was

chromatographed on Al_2O_3 (Merck), eluted with CH_2Cl_2–MeOH (99 : 1). The pale yellow powder **2** (103 mg, 82%) was dried at 40 °C under vacuum for 5 h. Further purification was performed with 67 mg of the powder by chromatography (SiO_2, CH_2Cl_2–MeOH:(i-Pr)$_2$NH = 96 : 2 : 2) and obtained 63 mg of pure adduct for the photophysical spectroscopy. (Found C 62.11, H 7.04, N 5.31. Calcd for $C_{52}H_{68}N_4P_2Pt_1$: C 62.07, H 6.81, N 5.57%); IR (cm^{-1}) ν(C≡C): 2090; ^{1}H NMR (600 MHz, CD_3OD, Me_4Si): δ = 9.046 (dd, J = 4.4 and 1.8 Hz, 1 H, Phen-H9), 8.946 (d, J = 2.0 Hz, 1 H, phen-H2), 8.409 (dd, J = 8.2 and 1.8 Hz, 1 H, Phen-H4), 8.116 (d, J = 2.0 Hz, 1 H, Phen-H7), 7.901 (d, J = 9.0 Hz, 1 H, Phen-H6), 7.833 (d, J = 9.0 Hz, 1 H, Phen-H5), 7.712 (dd, J = 8.2 and 4.4 Hz, 1 H, phen-H8), 2.255 (m, 6 H, α-CH_2), 1.748 (m, 6 H, β-CH_2), 1.520 (qt, J = 7.4 and 7.4 Hz, 6 H, γ-CH_2), 1.311 (t, J = 7.4 Hz, 9H, –CH_3).

Acknowledgements

References

1 A. A. Rachford, S. Goeb, R. Ziessel and F. N. Castellano, *Inorg. Chem.*, 2008, **47**, 4348.
2 M. L. Muro, S. Diring, X. Wang, R. Ziessel and F. N. Castellano, *Inorg. Chem.*, 2008, **47**, 6796.
3 F. Guo, Y.–G. Kim, J. R. Reynolds and K. S. Schanze, *Chem. Commun.*, 2006, 1887.
4 K. Haskins-Glusac, I. Ghiviriga, K. A. Abboud and K. S. Schanze, *J. Phys. Chem. B*, 2004, **108**, 4969.
5 P. Du, J. Schneider, F. Li, W. Zhao, U. Patel, F. N. Castellano and R. Eisenberg, *J. Am. Chem. Soc.*, 2008, **130**, 5056.
6 P. Du, J. Schneider, P. Jarosz and R. Eisenberg, *J. Am. Chem. Soc.*, 2006, **128**, 7726.
7 J. Jiang, W. Yang and Y. Cao, *J. Inorg. Organomet. Polym. Mater.*, 2007, **17**, 37.
8 H. Jiang and W. Lin, *J. Am. Chem. Soc.*, 2006, **128**, 11286.
9 Y. Liu, S. Jiang, K. Glusac, D. H. Powell, D. F. Anderson and K. S. Schanze, *J. Am. Chem. Soc.*, 2002, **124**, 12412.
10 E. E. Silverman, T. Cardolaccia, X. Zhao, K. -Y. Kim, K. Haskins-Glusac and K. S. Schanze, *Coord. Chem. Rev.*, 2005, **249**, 1491.
11 A. Harriman and R. Ziessel, *Chem. Commun.*, 1996, 1707.
12 R. Ziessel, M. Hissler, A. El-ghayoury and A. Harriman, *Coord. Chem. Rev.*, 1998, **178–180**, 1251.
13 A. Harriman and R. Ziessel, *Coord. Chem. Rev.*, 1998, **171**, 331.
14 Example for recent work of Ru(II)-Pt(II) heterometallic complexes: (*a*) M. Schwalbe, M. Karnahl, H. Görls, D. Chartrand, F. Laverdiere, G. S. Hanan, S. Tschierlei, B. Dietzek, M. Schmitt, J. Popp, J. G. Vos and S. Rau, *Dalton Trans.*, 2009, 4012; (*b*) Y. Fan, L.-Y. Zhang, F.-R. Dai, L.-X. Shi and Z.-N. Chen, *Inorg. Chem.*, 2008, **47**, 2811; (*c*) S. Zhao, S. M. Arachchige, C. Slebodnick and K. J. Brewer, *Inorg. Chem.*, 2008, **47**, 6144.
15 A. Harriman, M. Hissler, R. Ziessel, A. D. Cian and J. Fisher, *J. Chem. Soc., Dalton Trans.*, 1995, 4067.
16 V. Grosshenny, A. Harriman, M. Hissler and R. Ziessel, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2223.
17 M. Shiotsuka, Y. Yamamoto, S. Okuno, M. Kitou, K. Nozaki and S. Onaka, *Chem. Commun.*, 2002, 590–591.
18 Y. Wang, S. Liu, M. R. Pinto, D. M. Dattelbaum, J. R. Schoonover and K. S. Schanze, *J. Phys. Chem. A*, 2001, **105**, 11118.
19 E. C. Glazer, D. Madge and Y. Tor, *J. Am. Chem. Soc.*, 2005, **127**, 4190.
20 Y. Yamamoto, M. Shiotsuka, S. Okuno and S. Onaka, *Chem. Lett.*, 2004, **33**, 210.
21 Emission spectra at 77 K of all compounds were shown in the ESI†.
22 V. Grosshenny, A. Harriman, F. M. Romero and R. Ziessel, *J. Phys. Chem.*, 1996, **100**, 17472.
23 D. Tzalis and Y. Tor, *J. Am. Chem. Soc.*, 1997, **119**, 852.
24 B. Kauffmann and L. A. Teter, *Inorg. Synth.*, 1963, **7**, 245.