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Synthesis and Application of Ruthenium(II) Alkenyl Complexes with Perylene Fluorophores for the Detection of Toxic Vapours and Gases

José García-Calvo,[a] Jonathan A. Robson,[b] Tomás Torroba,*[a] and James D. E. T. Wilton-Ely*[b]

Abstract: A series of new ruthenium(II) vinyl complexes has been prepared incorporating perylenemonoimide (PMI) units. This fluorogenic moiety was functionalised with terminal alkyne or pyridyl groups, allowing attachment to the metal either as a vinyl ligand or through the pyridyl nitrogen. The inherent low solubility of the perylene compounds was improved through the design of poly-PEGylated (PEG = polyethylene glycol) units bearing a terminal alkyne or a pyridyl group. By absorbing the compounds on silica, vapours and gases could be detected in the solid state. The reaction of the complexes [Ru(CH=CH-Per^{Im})Cl(CO)(py-3PEG)(PPh$_3$)$_2$] and [Ru(CH=CH-3PEG)Cl(CO)(py-Per^{Im})(PPh$_3$)$_2$] with carbon monoxide, isonitrile or cyanide was found to result in modulation of the fluorescence behaviour. The complexes were observed to display solvatochromic effects and the interaction of the complexes with a wide range of other species was also studied. The study suggests that such complexes have potential for the detection of gases or vapours that are toxic to humans.

Introduction

The growth in interest in vinyl complexes of the heavier congeners of group 8 started around 30 years ago[1–9] and, since then, these versatile complexes have attracted much attention. Although other approaches are known, the most widely used route to ruthenium vinyl complexes, such as the 5-coordinate compounds [Ru(CR=CHR′)Cl(CO)(PR$_3$)$_2$] (R = Ph, *i*Pr), is through the hydrometallation of alkynes by the compounds [RuHCl(CO)(PPh$_3$)$_3$][1a] and [RuHCl(CO)(P*i*Pr$_3$)$_2$].[3a] Harris and Hill reported a modification of this approach to yield triphenylphosphine derivatives, which avoided contamination with tris(phosphine) side products by using [RuHCl(CO)(BSD)(PPh$_3$)$_2$] as the precursor.[10a] The labile 2,1,3-benzoselenadiazole (BSD) ligand permitted insertion of alkynes into the Ru–H bond to yield the coordinatively-saturated products [Ru(CR=CHR′)Cl(CO)(BSD)(PPh$_3$)$_2$] (R, R′ = H or alkyl/aryl substituents).[10a] Our work has focused on the analogous 2,1,3-benzothiadiazole (BTD) complexes, including osmium examples,[10b] which use the cheaper BTD heterocycle. Through the lability of the chloride and phosphine ligands (and BTD/BSD, if present), mono-,[11,12] bi-[13,14,15] and tridentate[16] donors can be coordinated to these vinyl compounds. This provides ample demonstration of the reactivity at the metal centre, however, the installation of the vinyl ligand through facile reaction with terminal alkynes (also internal alkynes under more forcing conditions) allows the incorporation of further functionality that can be influenced by the metal centre.[17] Our recent work has demonstrated the potential of this approach through the selective detection of very low concentrations of carbon monoxide both in air[12a,b] and in cells,[12c,d] following work by others in the area.[12e–t] Among other features, this contribution provides an illustration of the versatility of such ruthenium vinyl complexes to install a fluorophore either through coordination to the metal centre or as the substituent of the vinyl itself.

Perylenemonoimide (PMI) compounds have been demonstrated to be effective fluorescent signalling units for use in fluorogenic sensors.[18] They possess many advantages with respect to other more classical and widely-used fluorescent molecules, such as BODIPY (boron dipyrromethene) derivatives. For example, they display excitation/emission wavelengths in the visible and near-IR regions of the spectrum, which offer substantial advantages in terms of biological imaging. As well as excellent thermal and photo-stability, PMI compounds are tolerant towards a wide range of different reagents and are easily functionalised, for example by bromination followed by Suzuki coupling.[19] All the above characteristics are exploited here to allow the incorporation of PMI units into divalent ruthenium vinyl complexes for application in the detection of a range of analytes. The use of silica supports in this work provides an illustration of the application of these inorganic materials as an inexpensive and efficient method for enhancing the application of colorimetric or fluorogenic chemosensors.[12,19]

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[a] Dr. J. García-Calvo, Prof. Dr. T. Torroba
Department of Chemistry, Faculty of Science
University of Burgos, 09001 Burgos, (Spain)
E-mail: ttorroba@ubu.es

[b] Dr. J. A. Robson, Prof. Dr. J. D. E. T. Wilton-Ely
Department of Chemistry, Imperial College London
Molecular Sciences Research Hub, White City Campus
London, W12 0BZ (UK)
E-mail: j.wilton-ely@imperial.ac.uk

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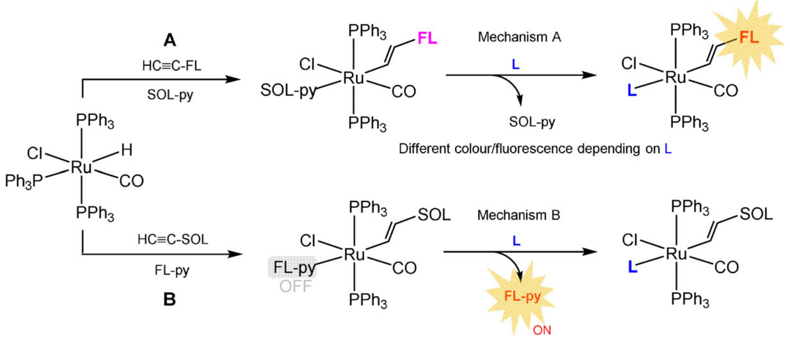
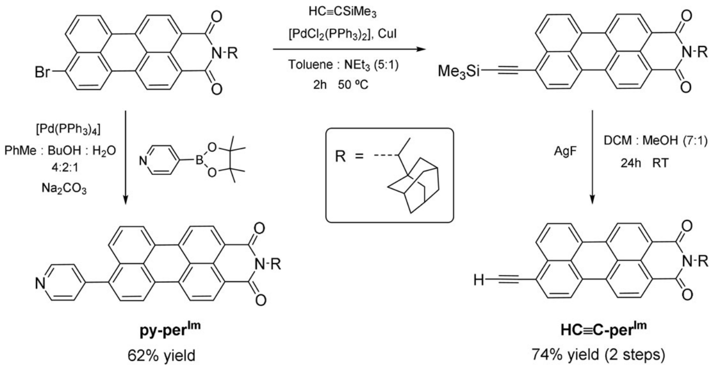


Scheme 1. Two approaches to functionalising ruthenium vinyl complexes with fluorogenic units. FL = fluorophore, SOL = solubilizing unit.

Results and Discussion

Two different approaches were used to incorporate fluorescent units into ruthenium vinyl complexes.[12] The two designs are shown in Scheme 1 and involve the fluorophore as either the vinyl substituent or the ligand directly attached to the metal centre.

The benefits of mechanism **A** include the fact that the fluorophore is retained within the metal complex, ensuring that the metal complex is located where fluorescence is observed. The fluorogenic response originates from the electronic changes caused by displacement of the ligand *trans* to the vinyl group by the analyte (L). This also leads to a modulation of the colour observed in many cases. However, mechanism **B** can often result in a greater fluorescence revival as the fluorophore is completely detached from the metal centre, allowing the quenching (heavy atom effect[20]) to be fully removed, resulting in a turn-ON fluorescence response.[21] A possible disadvantage of mechanism **B** is that premature displacement of the fluorophore is more likely and that, once displacement occurs, the fluorophore and the metal complex may not remain co-localised. However, this design does allow the facile addition of other functional units (e.g., to enhance solubility or cellular targeting) to the vinyl ligand through use of a functionalised terminal alkyne.



Scheme 2. Synthesis of new perylene monoimide derivatives.

Synthesis of fluorophores and solubilizing units

To explore both sensing mechanisms shown in Scheme 1, two new PMI derivatives, **py-per**^{Im} and **HC≡C-per**^{Im}, were prepared with pyridyl and ethynyl functionality. This was achieved starting from the 9-bromo derivative, as shown in Scheme 2.

The synthesised compounds, **py-per**^{Im} and **HC≡C-per**^{Im}, were fully characterised using ^{1}H and $^{13}C\{^{1}H\}$ NMR and infrared spectroscopies and mass spectrometry. Both compounds possess an imide group with a bulky aliphatic group (1-adamantyl-ethylamine) to increase solubility and were synthesised using palladium-catalysed C–C coupling approaches. A Suzuki reaction was used to prepare **py-per**^{Im} while **HC≡C-per**^{Im} was obtained as the product of a Sonogashira coupling after a deprotection step. Both compounds were purified using column chromatography (silica gel) and were obtained as red solids in good yields (further details in Supporting Information).

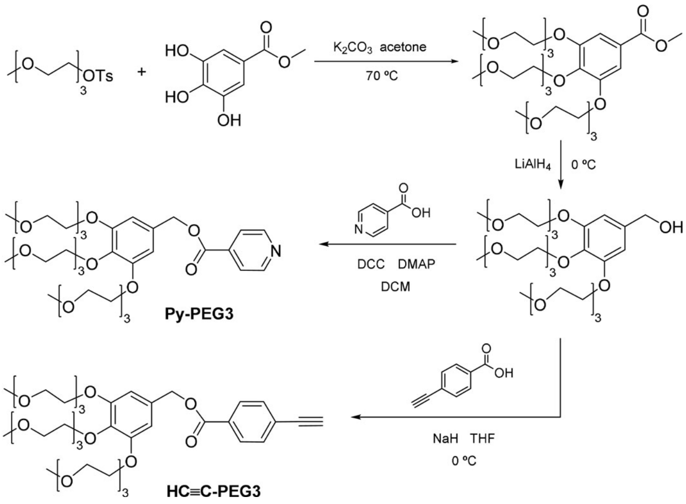
Perylenemonoimide compounds often suffer from poor solubility and it was considered likely that this characteristic would also be imparted to their metal complexes. It was therefore decided to devise a solubilizing unit that could be used with both designs shown in Scheme 1. This led to the synthesis of a structure with three polyethylene glycol chains and this was used to generate two new pyridyl (**py-PEG3**) and alkynyl (**HC≡C-PEG3**) derivatives (Scheme 3).

These solubilizing units, **py-PEG3** and **HC≡C-PEG3**, were fully characterised by ^{1}H, $^{13}C\{^{1}H\}$ NMR and infrared spectroscopies and mass spectrometry. Both **py-PEG3** and **HC≡C-PEG3**, were obtained as pale yellow oils after purification by column chromatography in DCM/MeOH mixtures. Characteristic signals were observed, such as the 5.26 ppm singlet attributed to the terminal alkyne in the ^{1}H NMR spectrum (see Supporting Information).

With the perylenemonoimide fluorophores and the complementary PEGylated solubilizing units prepared, the focus moved to the synthesis of the ruthenium vinyl complexes.

Ruthenium vinyl complexes

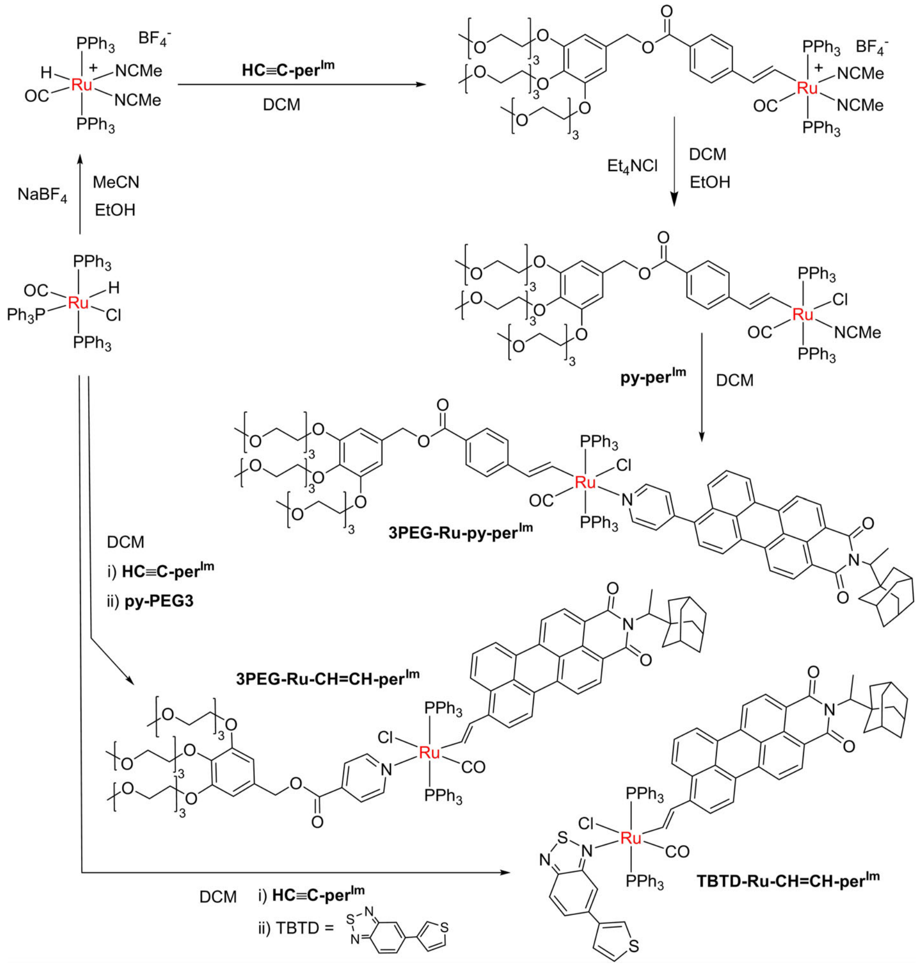
Two approaches were employed to synthesise the new ruthenium vinyl complexes reported in this contribution. The most straightforward method utilises the 5-coordinate triphenyl-



Scheme 3. Synthesis of PEGylated units suitable for use in aqueous and polar solvents.

phosphine compounds first reported by Santos and co-workers,[1a] $[Ru(CH{=}CHR)Cl(CO)(PPh_3)_2]$, which are formed by the hydrometallation of alkynes by the commercially-available tris(phosphine) compound, $[RuHCl(CO)(PPh_3)_3]$. The second approach takes this hydride compound and converts it to the cationic bis(acetonitrile) adduct, $[RuH(CO)(NCMe)_2(PPh_3)_2]^+$,[2e,22] which reacts with alkynes to form $[Ru(CH{=}CHR)(CO)(NCMe)_2(PPh_3)_2]^+$[2e] before halide addition yields the neutral compound $[Ru(CH{=}CHR)Cl(CO)(NCMe)(PPh_3)_2]$, in which the labile acetonitrile ligand can be readily substituted.

Reaction of $[RuHCl(CO)(PPh_3)_3]$ with **HC≡C-per^{Im}** in dichloromethane solution generated the 5-coordinate $[Ru(CH{=}CH\text{-}per^{Im})Cl(CO)(PPh_3)_2]$ in situ. Addition of **py-PEG3** led to formation of the dark blue complex $[Ru(CH{=}CH\text{-}per^{Im})Cl(CO)(py\text{-}PEG3)(PPh_3)_2]$ (**3PEG-Ru-CH=CH-per^{Im}**) in 84 % yield (Scheme 4). A singlet in the $^{31}P\{^1H\}$ NMR spectrum at 26.2 ppm indicated the presence of mutually *trans* phosphine ligands. In the ^1H NMR spectrum, the retention of the vinyl ligand was confirmed by characteristic doublets ($J_{HH}=16.3$ Hz) for the Hα and Hβ protons at 9.59 and 6.96 ppm, respectively. Typical resonances for the perylene unit were observed between 8.02–8.39 ppm (aromatic) and 1.63–1.98 ppm (adamantyl), with a diagnostic resonance at 5.09 ppm for the CH(Me)Ad proton. Pyridyl resonances were observed at 7.66 and 8.74 ppm, confirming the presence of the water-solubilizing unit. The carbonyl groups were clearly visible in the $^{13}C\{^1H\}$ NMR spectrum at



Scheme 4. Synthesis of ruthenium vinyl complexes.

203.6 ppm (RuCO), and between 166.0–164.6 ppm (amide and ester groups). The carbon monoxide ligand bonded to the metal gave rise to an absorption at 1926 cm^{-1} while the ester and amide carbonyls contributed to a broader resonance at 1734 cm^{-1}. The overall composition was confirmed by mass spectrometry data and good agreement between calculated and measured elemental analysis values.

The bis(acetonitrile) cation, [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]BF$_4$ reacted with **HC≡C-per^{Im}** in dichloromethane solution to initially yield [Ru(CH=CH-PEG3)(CO)(NCMe)$_2$(PPh$_3$)$_2$]BF$_4$, before addition of [NEt$_4$]Cl gave the neutral [Ru(CH=CH-PEG3)Cl(CO)(NCMe)(PPh$_3$)$_2$] (Scheme 4). The labile acetonitrile ligand was readily displaced by **py-per^{Im}** to yield the red complex, [Ru(CH=CH-PEG3)Cl(CO)(py-per^{Im})(PPh$_3$)$_2$] (**3PEG-Ru-py-per^{Im}**) in 65% overall yield. The purity of the product was indicated by the presence of only one singlet at 26.7 ppm in the ^{31}P{^{1}H} NMR spectrum, while the vinyl ligand gave rise to two doublets (J_{HH} = 16.8 Hz) at 9.35 and 6.00 ppm for the Hα and Hβ protons, with the lower field resonance displaying broadening due to coupling with the mutually *trans* phosphines. The presence of the coordinated py-per^{Im} unit was indicated by pyridyl resonances at 7.85 and 8.76 ppm as well as a diagnostic quartet at 5.10 ppm for the C*H*(Me)Ad proton. Good agreement between calculated and determined elemental analysis values confirmed the overall composition along with MALDI mass spectrometry data (Supporting Information).

There is considerable interest in ratiometric probes in which two fluorophores are combined within the same molecule.[23] This allows detection of an analyte through two different emission responses. Previously, we have used the 5-(3-thienyl)-2,1,3-benzothiadiazole (TBTD) fluorophore (λ_{exc} = 355 nm, λ_{em} = 500 nm) to detect carbon monoxide in cells and in a mouse model of inflammation.[12c,d] This fluorophore could also be excited under two-photon conditions[12c] at 715 nm to allow detection of endogenous CO at extremely low probe concentrations. It was therefore decided to explore the installation of both the perylenemonoimide (PMI) and TBTD fluorophores within the same complex. Treatment of [RuHCl(CO)(PPh$_3$)$_3$] with **HC≡C-per^{Im}** in dichloromethane led to in situ generation of [Ru(CH=CH-per^{Im})Cl(CO)(PPh$_3$)$_n$] (n = 2 or 3) before addition of the TBTD ligand, which provided the dark blue compound [Ru(CH=CH-per^{Im})Cl(CO)(TBTD)(PPh$_3$)$_2$] (**TBTD-Ru-CH=CH-per^{Im}**) in 71% overall yield. The ^{1}H NMR spectrum was again the most diagnostic characterisation method, displaying clear resonances for the CH=CH-per^{Im} unit at 9.41 (Hα), 6.94 (Hβ) and 5.08 (CH(Me)adamantyl) ppm as well as features between 1.5–2.0 ppm for the adamantyl unit. In the same spectrum, the TBTD ligand gave rise to resonances at 7.63, 7.74 and 7.86 ppm. The overall composition was supported by MALDI data and satisfactory elemental analysis values for the dichloromethane solvate. Substantial effort was invested in attempts to grow single crystals of all ruthenium complexes suitable for a structural determination, but without success. The difficulty in obtaining structural data on PMI derivatives has been remarked upon previously.[18] However, the presence of characteristic features in the NMR and IR spectra and the many established examples of ruthenium vinyl complexes of this type ensure that there is little doubt as to the composition of these complexes.

Photophysical characterisation

The absorbance and fluorescence properties of the synthesised compounds were investigated in solution (Table 1). All of the PMI derivatives displayed high molar extinction coefficients and around three times greater quenching of the fluorescence for the complexes compared to the ligands **HC≡C-per^{Im}** and **py-per^{Im}**. It was also found that the fluorescence lifetime decay values increased by 0.12 ns in the complexes over those measured for the ligands.

Table 1. Photophysical parameters of the different PMI derivatives synthesised.

Compound	log ε (λ_{max})	Φ [%] (±2%)	τ [ns]	χ
	(CHCl$_3$)	(CH$_2$Cl$_2$)	(CH$_2$Cl$_2$)	
HC≡C-per^{Im}	4.7 (500 nm)	90	4.62	1.085
py-per^{Im}	4.5 (500 nm)	91	4.45	1.116
3PEG-Ru-CH=CH-per^{Im}	4.7 (575 nm)	38	4.74	1.078
3PEG-Ru-py-per^{Im}	4.7 (500 nm)	29	4.57	1.098

The absorption and fluorescence studies also showed that **3PEG-Ru-CH=CH-per^{Im}** displayed a remarkable bathochromic shift with polarity. It was also noted that the absorption bands were broader than in the free perylenemonoimides, partly overlapping with the emission bands. The absorption and fluorescence of **3PEG-Ru-py-per^{Im}** was found to depend on the solvent in the same way as its perylenemonoimide precursor **py-per^{Im}**. Complexation to a metal served to increase its solubility, rendering it slightly soluble in organic:water mixtures, however, the fluorescence was found to be quenched under these conditions.

In general, it was found that there was little difference in the absorption and fluorescence behaviour of **3PEG-Ru-CH=CH-per^{Im}** and **TBTD-Ru-CH=CH-per^{Im}**. The only exception to this was the observation of an absorption in the region 300–400 nm, attributed to the absorption of the TBTD fluorophore (Figure S4.2 in Supporting Information).

After this initial evaluation of the photophysical parameters, a solvatochromic (Figures S2.16, S2.21, S2.26 and S2.31 in the Supporting Information) and solubility study led to acetone being chosen as the optimal solvent for testing the response to other analytes (Supporting Information).

The coordinated PMI complexes were screened against a series of 16 different cations (Section S4.4 in Supporting Information). For **3PEG-Ru-CH=CH-per^{Im}**, little change was observed apart from in the presence of Cu^{2+} when irradiated with UV light (Figure S4.12 in ESI). The effect of different pH conditions was also investigated with this PMI compound, which revealed little change until a highly basic aqueous solution (pH 12.3) was reached, likely due to chemical modification of the complex itself (Figure S4.13. in ESI). For **3PEG-Ru-py-per^{Im}** there was no significant change in the fluorescence properties except with Au^{3+} cations (Figure S4.14), which could be a result of the acidity of the HAuCl$_4$ used.

Eleven different anions were screened for interactions with the perylene moiety in the complexes. In almost all cases, little significant change was observed. An exception was a colour change to pale blue and the observation of a red emission for **3PEG-Ru-CH=CH-per^{lm}** with cyanide ions (Figure S4.15). This was attributed to the π-acid cyanide forming a complex with the ruthenium compound in a similar way to that found with carbon monoxide.[12] This result led to an investigation of the sensing potential of the complexes with a series of π-acid analytes. It was of particular interest to explore the detection of toxic substances found as gases or vapours as the risk of exposure is particularly great. The detection of carbon monoxide (CO), cyanide (CN$^-$) and a representative isonitrile (*t*BuNC) was studied. Accordingly, it was found that 5 μM solutions of the probes **3PEG-Ru-CH=CH-per^{lm}** and **3PEG-Ru-py-per^{lm}** displayed spectroscopic changes in presence of these analytes (Figure 1 and Figure 2).

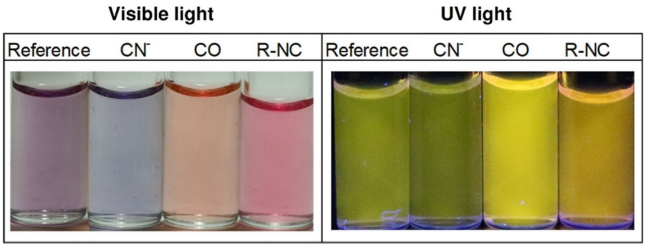


Figure 1. Colour (left) and fluorescence (right) responses of **3PEG-Ru-CH=CH-per^{lm}** (5 μM) to NBu$_4$CN (50 μM), CO (bubbled for 2 min) and *t*BuNC (50 μM) in acetone solution. Reference = acetone solution of the original complex.

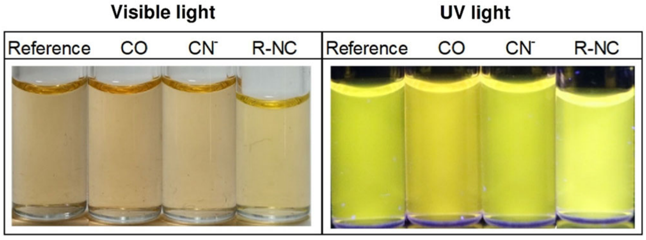


Figure 2. Colour (left) and fluorescence (right) responses of **3PEG-Ru-py-per^{lm}** (5 μM) to NBu$_4$CN (50 μM), CO (bubbled for 2 minutes) and *t*BuNC (50 μM) in acetone solution. Reference = acetone solution of the original complex.

In contrast, acetone solutions of **3PEG-Ru-py-per^{lm}** produces an increase in fluorescence for all three analytes ([NBu$_4$]CN, CO and *t*BuNC), with little differentiation between them. The significant colour and fluorescence changes displayed by **3PEG-Ru-CH=CH-per^{lm}** depending on the analyte are reflected in the quantitative data shown in Figure 3.

Using the absorbance and fluorescence data, several titrations were carried out, which allowed calculations to be performed to determine the limit of detection (LOD) in solution for cyanide and *t*BuNC.[24] A limit of detection of 0.29 μM (7.55 μg L^{-1}) was recorded for cyanide with probe **3PEG-Ru-CH=CH-per^{lm}** while the corresponding value for **3PEG-Ru-py-per^{lm}** was 0.41 μM (10.7 μg L^{-1}). For the isonitrile *t*BuNC, the LOD was measured to be 0.29 μM (24.1 μg L^{-1}) for **3PEG-Ru-CH=CH-per^{lm}** and 0.12 μM (10 μg L^{-1}) for **3PEG-Ru-py-per^{lm}**. Across all experiments, the results showed a very high sensitivity for both cyanide and isocyanide as analytes (Section S4.5 in Supporting Information).

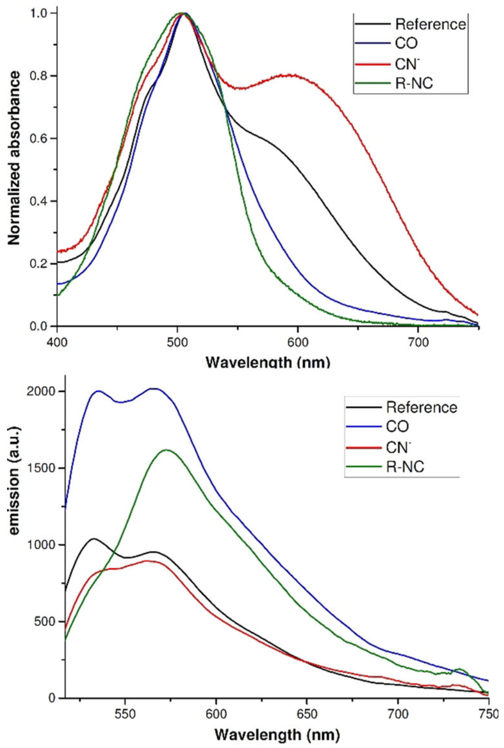


Figure 3. Absorbance (top) and fluorescence (bottom) spectra of **3PEG-Ru-CH=CH-per^{lm}** (5 μM) with [NBu$_4$]CN (50 μM), CO (bubbled for 2 min) and *t*BuNC (50 μM) in acetone solution.

Silica immobilisation of the complexes

Detection of analytes, such as cyanide, in solution is important due to its common occurrence as an environmental pollutant in ground water.[25] Such applications, where measurement is often undertaken by non-specialists, are served best by simple, low-cost and easily-used systems, such as colorimetric methods.[23] The use of colour strips has been investigated in our earlier work on carbon monoxide detection and this approach proved successful,[12a,b] whether analysis was performed by the naked eye or by an optoelectronic device.[26] With this in mind, the compounds **3PEG-Ru-CH=CH-per^{lm}** and **3PEG-Ru-py-per^{lm}** were immobilised on a silica support backed by an aluminium sheet (TLC, silica gel 60, Merck). The absorption was performed by dissolving the compound (2 mg) in toluene (25 mL) and then submerging the TLC plates (5 × 5 cm) in the solution overnight at 60 °C. The solution became colourless and successful immobilisation of the compound on the silica was confirmed by the bright colours observed for the plates (Figure 4).

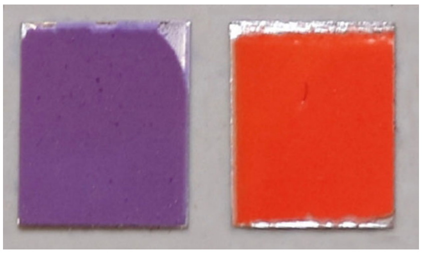


Figure 4. Image of the TLC plates with absorbed **3PEG-Ru-CH=CH-per**^{lm} (left) and **3PEG-Ru-py-per**^{lm} (right).

In a similar way to the behaviour observed in solution, the immobilised complexes gave rise to fluorescence changes after short periods in an atmosphere with CO gas or when isonitrile or BrCN vapours were present. Using the apparatus shown in Figure 5, these gases/vapours were found to lead to distinct changes in colour/fluorescence for each analyte without the need for any solvent.

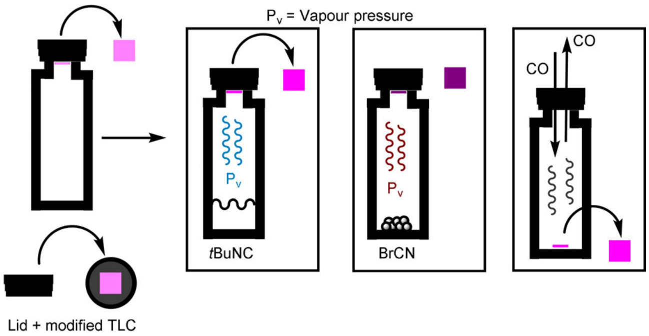


Figure 5. Representation of the method employed to expose the modified TLCs to different vapours or gas.

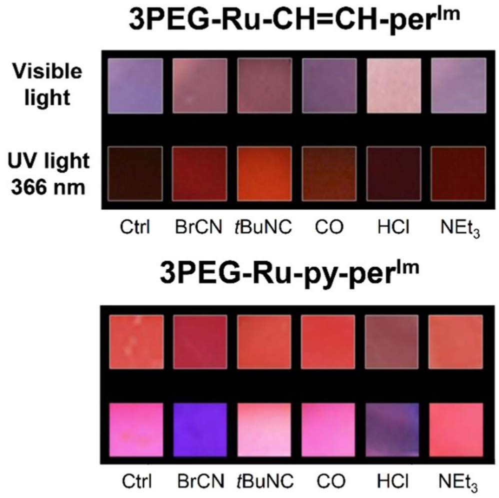


Figure 6. Qualitative response of the TLC plates modified with **3PEG-Ru-CH=CH-per**^{lm} (top) and **3PEG-Ru-py-per**^{lm} (bottom) in the presence of different vapours/gases with measurement after 6 hours.

The experiments were performed for both the modified TLC plates based on **3PEG-Ru-CH=CH-per**^{lm} and **3PEG-Ru-py-per**^{lm} (See Section S4.5 in Supporting Information). In order to measure the colour changes on reaction with the analyte, the immobilised compounds were exposed to a constant stream of CO to saturate the chamber and the changes were then studied over time. In a similar process, the TLC plates were placed in sealed 15 mL vials with 20 μL of *t*BuNC or 5 mg of BrCN at room temperature. The response observed depended on the vapour pressure of the compound and the interaction with the supported probe, as can be seen in Figure 6.

At constant vapour pressure, the changes of colour and fluorescence of the immobilised compounds were found to depend on time. When studying the response to *t*BuNC, it was enough to wait for only 30 minutes to observe a significant increase in fluorescence, with both probes reaching the saturation point after 2–3 hours (Figure 7).

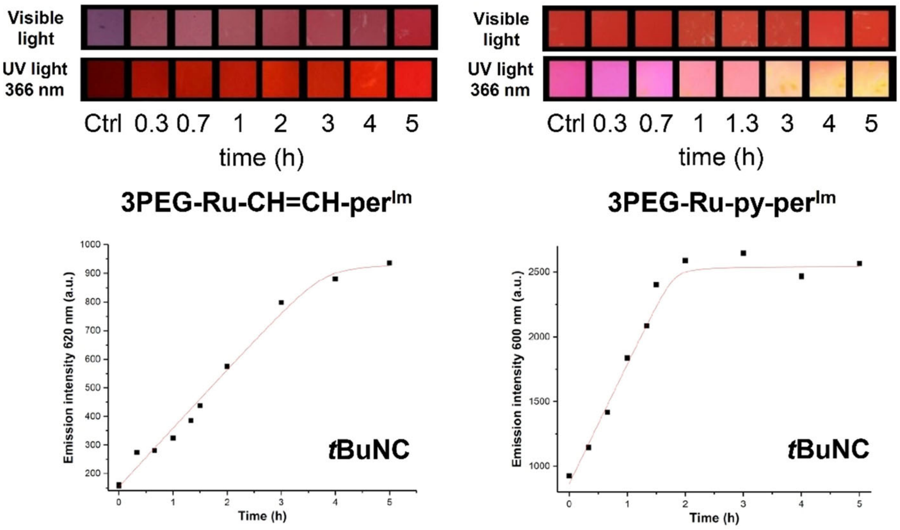


Figure 7. Colour and fluorescence responses of immobilised **3PEG-Ru-CH=CH-per**^{lm} (left) and **3PEG-Ru-py-per**^{lm} (right) to *t*BuNC vapour over time, based on the emission at 620 nm ($\lambda_{exc} = 515$ nm).

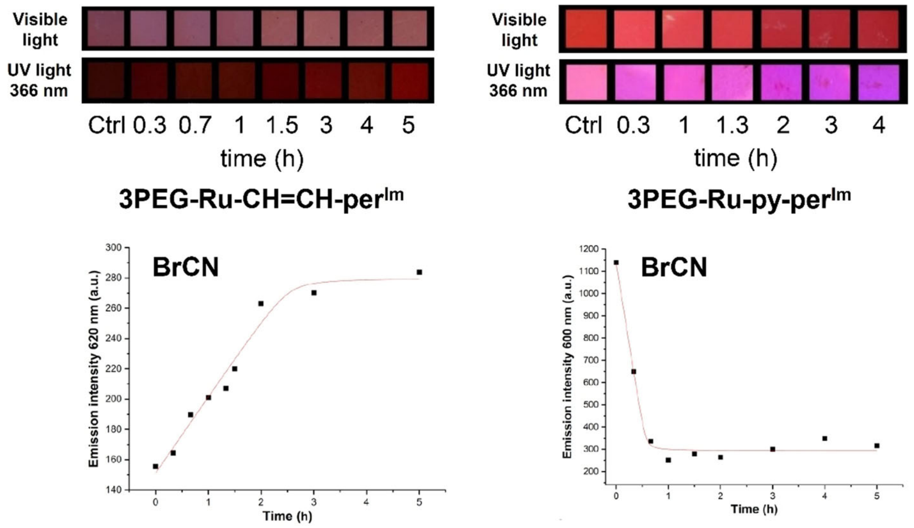


Figure 8. Colour and fluorescence responses of immobilised **3PEG-Ru-CH=CH-per^{Im}** (left) and **3PEG-Ru-py-per^{Im}** (right) to BrCN vapour over time, based on the emission at 620 nm (λ_{exc} = 515 nm).

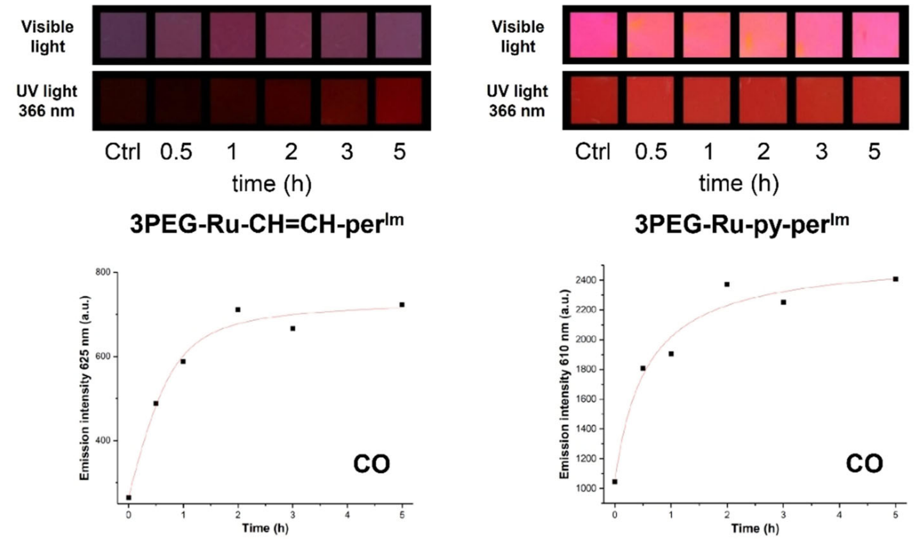


Figure 9. Colour and fluorescence responses of immobilised **3PEG-Ru-CH=CH-per^{Im}** (left) and **3PEG-Ru-py-per^{Im}** (right) to a stream of CO over time, based on the emission at 625 nm (λ_{exc} = 515 nm).

In contrast, the response was completely different when evaluating the reaction with BrCN, which produced only a small increase in fluorescence for the supported probe **3PEG-Ru-CH=CH-per^{Im}**, reaching a maximum after 2–3 hours (Figure 8, left). However, in contact with BrCN vapour, the fluorescence of immobilised **3PEG-Ru-py-per^{Im}** was almost totally quenched after one hour (Figure 8, right).

The behaviour of the immobilised probes with CO was found to be very similar to those obtained in solution, with the fluorescence increasing rapidly in the presence of a constant stream of CO (saturated atmosphere). Saturation occurs in less than 30 minutes and the response is similar to that observed with *t*BuNC vapour, although with a smaller increase in fluorescence for both of the immobilised systems (Figure 9 and Figures 1 and 2).

Conclusions

The first fluorescent ruthenium(II) vinyl complexes based on the perylenemonoimide (PMI) fluorophore have been synthesised and characterised and their photophysical properties investigated. While one ruthenium example based on a perylenebisimide design has been reported (as a photosensitizer for photodynamic therapy),[19f] these solvatochromic compounds represent the first examples of ruthenium with PMI-based ligands. Using the inherent versatility of these compounds, both the vinyl substituent and the coordination site at the metal centre were used to introduce the PMI fluorophore. To increase the solubility and stability of the complexes in solution, two new water-solubilizing moieties were designed and introduced through either the vinyl ligand or a pyridyl unit. The two designs allowed sensing mechanisms based on a) modulation of the fluorescence of the retained fluorophore through ligand substitution (**3PEG-Ru-CH═CH-per**^{lm}) and b) displacement of the fluorophore to be investigated (**3PEG-Ru-py-per**^{lm}). In acetone solution, the compounds displayed a particular affinity for the π-acid species investigated. This led to preliminary studies in which the probes proved effective for the detection of several toxic analytes (isonitrile, cyanide and carbon monoxide), not only in solution but supported on silica. In particular, the probes showed very low limits of detection (LOD) for cyanide (0.29 μM) and tertiarybutylisonitrile (0.12 μM) in solution and sensitive detection of these analytes as vapours in less than an hour when the probes were immobilized on silica.

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Conflict of interest

The authors declare no conflict of interest.

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[24] The calculation was performed using the software “R” v2.7 and following the procedure described in ref. [19b]. A least-square regression was carried out before the LODs were calculated by taking into account 5% or less probability of false positives/negatives. The number was always within the range of the performed measurements without considering the value at 0.

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FULL PAPER

Organometallic Chemistry

*J. García-Calvo, J. A. Robson, T. Torroba,**
*J. D. E. T. Wilton-Ely**

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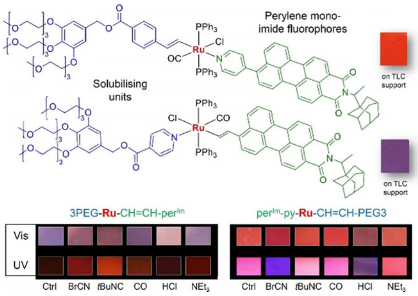
Synthesis and Application of Ruthenium(II) Alkenyl Complexes with Perylene Fluorophores for the Detection of Toxic Vapours and Gases



Sensors: The first reported examples of ruthenium(II) vinyl complexes bearing perylenemonoimide units are able to detect carbon monoxide, isonitriles or cyanide through fluorescence changes (see figure).