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A heterotrimetallic Ir(III), Au(III) and Pt(II) complex incorporating cyclometallating bi- and tridentate ligands: simultaneous emission from different luminescent metal centres leads to broad-band light emission

Rebeca Muñoz-Rodríguez, Elena Buñuel, Noelia Fuentes, J. A. Gareth Williams and Diego J. Cárdenas

Di- and tri-nuclear metal complexes incorporating gold(III), iridium(III) and platinum(II) units linked via a 1,3,5-triethynylbenzene core are reported, together with the corresponding mononuclear complexes as models. The gold(III) and platinum(II) units comprise tridentate, cyclometallating, C=N=C and N=C=C-coordinating ligands respectively, with the Ar-C≡C− directly bound to the metal at the fourth coordination site. The iridium moiety is an Ir(ppy)3(acac) unit bound to the triethylnylbenzene through a phenyl substituent at the 3-position of the acac ligand. The multinuclear compounds are prepared using a modular synthetic strategy from the monometallic complexes. All of the compounds are luminescent in solution at room temperature, and their photophysical properties have been studied. The triplet excited state energies of the mononuclear complexes lie in the order Au > Ir > Pt. Consistent with this order, energy transfer from Au to Ir and from Au to Pt is observed, leading to quenching of the Au emission in the gold-containing multinuclear complexes. Energy transfer from Ir to Pt occurs at a rate that only partially quenches the Ir-based emission. As a result, the dinuclear Ir-Pt and trinuclear Au-Ir-Pt complexes display broad emission across most of the visible region of the spectrum.

Introduction

Luminescent complexes of second and third row d⁶ and d⁸ metal ions have attracted much attention due to their interesting optical properties. These complexes have been used to construct a variety of devices including organic light-emitting diodes (OLEDs), chemical sensors, bioimaging agents, and nonlinear optical systems. The large spin-orbit coupling constant of such metal ions, particularly those from the 3rd row, can lead to efficient phosphorescence from triplet states, even at room temperature, a process rarely possible in all-organic systems. In OLEDs, this allows the otherwise wasted triplet states to be harvested, leading to 4-fold increases in device efficiency compared to fluorescent systems. Meanwhile, in bioimaging, the longer lifetime of luminescence of such metal complexes (typically around a microsecond) allows time-resolved discrimination from background fluorescence (which occurs on the nanosecond timescale), with accompanying increases in sensitivity.

White-light-emitting materials and devices have attracted much interest because of their potential applications in, for instance, solid-state lighting, full-color displays, and backlights. The basic principle for generating white light from an OLED involves combining light output from multiple emission centres of the three primary colors (red, green, and blue). One of the difficulties of such an approach is that energy-transfer between the dopants will tend to favour emission from the red emitter at the expense of the green and blue, essentially a “short-circuiting” of the system. This problem can be overcome by segregating the emitters into different layers, but this adds to device complexity and cost. Single compounds that emit efficiently across the visible region, preferably from triplet states, are therefore of much interest. Cycloometallating ligands have proved to be particularly successful in generating luminescent complexes, owing to their strong ligand fields which ensure that potentially deactivating d-d states are destabilised. Cycloometallated iridium(III) complexes are robust, easy to produce, synthetically versatile, photochemically and thermally stable and display attractive photophysical properties. Indeed, they already feature as green and red emitters in the OLED displays of mass-produced devices. Meanwhile, cycloometallated platinum(II) complexes
are attracting increasing interest, partly due to their potential for white light generation through excimer formation, a process not possible for the pseudo-octahedral complexes of the d® iridium(III) ion. For platinum(II), the use of tridentate cyclometallating ligands, such as phenylbipyridine or dipirydylbenzene, can be advantageous over bidentate ligands, owing to the greater rigidity of their complexes. In contrast to Ir(III) and Pt(II), there are far fewer examples of Au(III) complexes that display appreciable luminescence at room temperature. The lack of luminescence from many Au(III) complexes may be due to the presence of higher-lying but thermally accessible deactivating states (e.g. d-d or LMCT states), and/or to the lower energy of filled metal orbitals in Au(III) complexes compared to Pt(II) analogues. This latter feature results in lower metal character in the excited state and hence to less efficient spin-orbit coupling pathways and low radiative rate constants. The use of strong-field cyclometallating ligands and/or 8-donating alkynyl or N-heterocyclic carbenes can alleviate both issues indeed, quite intense luminescence has recently been reported for a group of cyclometallated Au(III) complexes with 2-phenylpyridine ligands and alkynyl c0-ligands.

As far as multinuclear cyclometallated complexes comprising these elements are concerned, homo-dinuclear platinum(II) complexes have been investigated, often with a view to exploring intramolecular excimeraggregate formation. Energy transfer between covalently-linked iridium centres has been studied in supramolecular Ir,Ru assemblies. In both of these cases, the properties of the individual metal-containing units are largely retained, and the observed phenomena involve face-to-face interactions or energy transfer processes between the discrete units respectively. In contrast, when the metal ions are closer together and bound to a common heterocyclic ring, the properties of the resulting multimetallic assembly differ more profoundly from the mononuclear analogues, with a significant red-shift of the absorption and emission. There are, however, very few heterometallic compounds featuring combinations of Au(III), Pt(II) and Ir(III). Previously, we studied a rigid gold-platinum dinuclear complex constructed on a xanthene scaffold, in which rapid Au to Pt energy transfer was observed. Trinuclear complexes incorporating Ir(III) and Os(II) units assembled around a triptycene or spirobi fluorene core, and related compounds with Pt(II), Ru(II) and Os(II) units linked through a central truxene moiety, have been reported in a series of studies by Ziessel, Ventura and co-workers. The metal units in these supramolecular compounds essentially retain the properties of the individual complexes, and energy transfer is observed between them. Kozhenikov et al. have explored a Pt,Ir trimer, which behaves as a single chromophore whose excited-state properties are very different from those of the constituent units.

In this work, we report on the synthesis and luminescence properties of a unique heterotrimetallic complex 7 (Figure 1) featuring cyclometallated Au(III), Ir(III) and Pt(II) units linked through a 1,3,5-triethylbenzene core. The Au(C=N=C), Ir(N=®N=®C)2 and Pt(N=®N=®C) units selected were chosen on the basis that the analogous mononuclear complexes display blue/green, green and orange/red luminescence respectively. The limited conjugation between meta related positions within a benzene ring might be expected to limit the rate of through-bond energy transfer processes between the metal centres, whilst analysis of through-space processes may be aided by the rigidity of the system, which ensures that the units are kept at a constant separation within the molecule. We were intrigued to explore whether the compound would show multiple emissions from the metal units, to give broad-band emission, or whether fast energy-transfer to the Pt(II) unit would lead to emission from this centre only. Related monometalllic and dimetalllic (Au-Pt, Au-Ir, Ir-Pt) complexes incorporating the triethylbenzene unit are also described, whose properties are important in allowing those of the trinuclear complex to be rationalised.

Results and discussion

Synthesis

The three mononuclear complexes incorporate the same central framework, in which a 1,3,5-triethylbenzene carries trimethylsilyl (TIPS) protecting groups at the termini of two of the three alkynyl units and the third is linked to the metallic unit (Scheme 1). For the gold and platinum complexes, the Ar-C=C=group is directly coordinated to the metal ion, whereas for the iridium complex, it is linked to a coordinating acac unit through an interposed phenyl group. The synthetic route (Scheme 1) involves incorporation of metal complexes on doubly protected alkyne. Thus, treatment of 8 with the previously prepared metal complexes or 10 in the presence of CuI and Et,N, gave the desired mononuclear Au(III) and Pt(II) complexes 1 and 2 respectively. The preparation of the Ir(III) complex 3 was carried out by Pd/Cu-catalysed Sonogashira coupling with a bis-cyclometallated iridium complex carrying a phenylido-substituted acac ligand, 11. A similar procedure has been used recently by others to prepare iridium complexes featuring pendent aryl substituents attached to the acac via a C=C linker.

The preparation of the dinuclear complexes could not be carried out from mononuclear derivatives 1-3, since selective deprotection of just one of the TIPS groups could not be achieved.
Instead, we selected a different mononuclear Au(III) complex, namely $\text{13}$, as a precursor to dinuclear complexes. It incorporates one terminal alkyne and one TIPS-protected alkyne. Its synthesis is shown in Scheme 2 and involves dialkyne $\text{12}$ as starting material. Treatment of $\text{12}$ with the bis-cyclometallated gold precursor $\text{9}$ gave the Au(III) complex $\text{13}$, which was then reacted with the cyclometallated platinum precursor $\text{10}$ under similar conditions to give the heterodinuclear Au-Pt complex $\text{4}$.

Unfortunately, the synthesis of heterodinuclear compounds containing the Ir(III) unit could not be carried out from $\text{13}$, because $\text{13}$ undergoes dimerization under the reaction conditions. Therefore, a different strategy was devised, using a mononuclear Ir(III) complex $\text{14}$ that carries two terminal alkynes, and is obtained by desilylation of $\text{3}$ with $(n-\text{Bu})_4\text{NF}$ (Scheme 3).

Treatment of $\text{14}$ with the Au precursor complex $\text{9}$ (0.59 equiv) in the presence of CuI and Et$_3$N gave the dinuclear Au-Ir complex $\text{5}$. The same route was used to obtain a dinuclear Ir-Pt complex, but the initially formed product proved difficult to isolate and purify. Consequently, an excess of iodobenzene and catalytic Pd(PPh$_3$)$_2$Cl$_2$ were added at the end of the reaction in order to arylate the free alkyne, to give the Ir-Pt complex $\text{6}$, which could be isolated and purified more readily.

Finally, the heterotrinuclear Au-Ir-Pt complex $\text{7}$ was synthesized from $\text{5}$ by treatment with the precursor Pt complex $\text{10}$ in the presence of CuI and Et$_3$N, as shown in Scheme 4.

**Photophysical properties**

Photophysical data for the complexes $\text{1}$–$\text{7}$ are compiled in Tables 1 and 2, and selected absorption and photoluminescence spectra are shown in Figures 2–5.
(i) Mononuclear complexes.

We shall first consider the mononuclear complexes 1–3. The absorption spectrum of the mononuclear Au(III) complex 1 (Fig. 2a) displays a vibronically structured band around 400 nm, typical of cyclometallated Au(III) complexes with C=N-C-coordinating ligands, corresponding to predominantly spin-allowed intraligand (IL) transitions with a small participation of the metal.32 This complex emits weakly in solution at room temperature, displaying a structured band, \( \lambda_{0,0} = 484 \) nm (Fig. 2a), assigned to the \(^3\)IL transition with a small participation of the metal; \( \Phi_{\text{lum}} = 4.4 \times 10^{-4}, \tau = 120 \) ns. Assuming, nevertheless, that the triplet state is formed with approximately unitary efficiency, the radiative \( k_r \) and non-radiative \( \Sigma \kappa_{nr} \) decay constants can be estimated on the basis that \( k_r = \Phi_{\text{lum}}/\tau \) and \( \Sigma \kappa_{nr} = \tau^{-1}-k_r \). The rather small value of \( k_r \) of 3700 s\(^{-1}\) thus obtained is consistent with the relatively small participation of the metal in the excited state, limiting the extent to which it can promote phosphorescence from the triplet state and allow it to compete with non-radiative decay. In a frozen glass at 77 K, under which conditions the non-radiative decay processes are inhibited, the lifetime increases greatly to 274 \( \mu \)s, a long value that is again indicative of a small metal contribution.

The absorption and emission properties of the mononuclear Pt(II) complex 2 are typical of Pt(II) complexes with N=N-C-coordinating ligands based on phenylbipyridine (phbpy). The absorption spectrum features moderately intense bands in the 400–500 nm region associated with charge-transfer transitions, and the complex displays a structureless emission band at room temperature, \( \lambda_{\text{max}} = 586 \) nm, \( \Phi_{\text{lum}} = 7.0 \times 10^{-2}, \tau = 570 \) ns (Fig. 2b). These values are similar to those reported previously for Pt(phbpy)(C≡C-Ph).39b

Finally, the mononuclear Ir(III) complex 3 displays an absorption spectrum characteristic of cyclometallated Ir(III) complexes with ppy ligands, of the type Ir(N=C)\(_2\)(O^O), including a set of bands that extend into the visible region corresponding to metal-to-ligand charge-transfer transitions.33

This complex emits brightly in solution at room temperature, with a structureless emission band (Fig. 2c) emanating from the \(^3\)MLCT state; \( \lambda_{\text{max}} = 523 \) nm, \( \Phi_{\text{lum}} = 0.31, \tau = 880 \) ns. These data are similar to those of the structurally similar complex of the form \( \text{(ppy)}_2\text{Ir(acac)}\text{C}_6\text{H}_4\text{(C≡C-tolyl)} \), referred to above.30

Figure 3a shows the emission spectra of the three mononuclear complexes on the same scale for convenience, together with the spectra at 77 K. Owing to the broadness of the Ir(III) and Pt(II) spectra, which do not show a clear 0–0 band at room temperature, the 77 K data have been used to generate an energy level diagram for the lowest triplet states of the
complexes (Fig 3b). It is clear that energy transfer from the Au to the Ir and Pt unit, and from the Ir to the Pt unit, could be anticipated in the multinuclear systems, which are discussed in the following sections.

The excitation spectrum incorporates the structured bands in the 360–430 nm region that are characteristic of the Au complex. These data suggest that excitation of the Au unit is followed by rapid energy transfer to the Pt unit, at a rate that is sufficiently fast that emission from the Au unit becomes undetectable under these conditions. The rate of the energy transfer process is considered in more detail in section (iv) below. The luminescence quantum yield is of a similar magnitude, though somewhat reduced, in 4 compared to the mononuclear Pt complex 2. Normally, if fast energy transfer occurs, \( \Phi \) should be determined largely by the emitting unit and a similar value expected. Given the rather large uncertainty on quantum yield measurements (±20%), there is a danger in over-interpreting the small difference. It is possible that the excited state becomes somewhat more extended in 4 compared to 2 through the effect of the Au ion, such that the net Pt character in the excited state is slightly diminished and hence the radiative rate constant \( k_r \) reduced, as observed (Table 2). At 77 K, for \( \lambda_{ex} < 430 \) nm, a very weak band assignable to residual Au emission is detectable (see Supporting Information Fig 5). For longer excitation wavelengths, no Au component to the emission is observed, consistent with the fact that, of the mononuclear Au and Pt complexes 1 and 2, only the Pt complex 2 absorbs at such wavelengths.

Similar observations are made for the dinuclear Au-Ir complex 5. Its absorption spectrum is again similar to that simulated by addition of the spectra of the two constituent mononuclear complexes (see Supporting Information). The emission spectrum at room temperature shows a single band similar in energy and profile to that of 3 (Fig. 4b), and the luminescence lifetime is very similar to the value for 3 (Table 2). These data again suggest that those photons absorbed by the Au unit are transferred to the Ir unit, at a rate sufficient to render the weak Au emission undetectable. The quantum yield is of the same order of magnitude but somewhat reduced compared to 3, apparently due to a lower \( k_r \) value although it is difficult to rationalise such an effect in this instance. At 77 K for \( \lambda_{ex} < 430 \) nm, a very weak band assignable to Au emission is detectable (see Supporting Information Fig 6).

The absorption spectrum of the dinuclear Ir-Pt complex 6 also matches well with that simulated by addition of the spectra of its constituent mononuclear complexes 2 and 3 (see Supporting Information). However, in this case, the emission spectrum at room temperature clearly shows two components: a broad structureless band with \( \lambda_{max} = 577 \) nm accompanied by a weaker yet distinct shoulder at 520 nm (Fig. 4c). They can be attributed to emission from the Pt and Ir moieties respectively. The emission of the Pt unit can be monitored independently of the Ir unit since the Pt emission extends out to longer wavelengths (Fig. 2). For example, at 700 nm, the luminescence decay follows monoeXponential kinetics giving a lifetime of 570 ns, the same as that recorded for Pt complex 2. The emission of the Ir unit cannot be monitored independently of the Pt unit, since it overlaps with the emission of the Pt unit. The luminescence decay monitored in the shorter-wavelength region of the spectrum (e.g. \( \lambda_{em} = 520 \) nm) displays biexponential kinetics, with components of 560 ns and 25 ns...
corresponding to the Pt and Ir units respectively (Table 2). It may be noted that the lifetime associated with the Ir emission band is much shorter than that of the mononuclear Ir complex 3 (880 ns), indicative of energy transfer from the Ir unit to the Pt component, but at a rate (see section (iv) below) that is not sufficient to completely quench the emission from the Ir component. The relative contribution of the shoulder due to the Ir unit in the emission spectrum is essentially independent of the excitation wavelength. At 77 K, the high-energy band shifts slightly to the blue, whilst the main lower-energy band becomes vibrationally resolved showing three main components (see Supporting Information Fig 7). This trend upon cooling is fully consistent with the spectra of the two mononuclear units at 77 K (Fig 3a, Table 2).

At 77 K, the high-energy band shifts slightly to the blue, whilst the main lower-energy band becomes vibrationally resolved showing three main components (see Supporting Information) mononuclear Au, Pt and Ir complexes at 77 K (Fig 3a, Table 2).

The absorption spectrum of the trinuclear complex 7 resembles that of 6 (dinuclear Ir-Pt derivative) showing two components: a broad band centred at 577 nm attributable to emission from the Pt unit, and a weaker, high-energy shoulder which can be assigned to residual Ir emission (Fig. 5a).

### Table 1 UV-visible absorption data for the complexes 1–7[a]

<table>
<thead>
<tr>
<th>Complex</th>
<th>Absorption λ\text{max} / nm (ε / M⁻¹cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Au</td>
<td>256 (108500), 262sh (98300), 312 (20600), 320 (19400), 367sh (4590), 393 (6330), 413 (6140)</td>
</tr>
<tr>
<td>2 Pt</td>
<td>268 (61200), 280 (42500), 338 (15400), 367 (11300), 430 (5050), 462sh (4160)</td>
</tr>
<tr>
<td>3 Ir</td>
<td>259 (122000), 270 (131400), 287 (76700), 306sh (63000), 339 (22400), 407 (5560), 458 (4920)</td>
</tr>
<tr>
<td>4 Au-Pt</td>
<td>261 (93400), 321 (29900), 372 (15300), 415 (9400), 443 (5150)</td>
</tr>
<tr>
<td>5 Au-Ir</td>
<td>262 (108400), 306sh (62300), 364sh (13600), 381 (11000), 411 (9020), 456 (3390)</td>
</tr>
<tr>
<td>6 Ir-Pt</td>
<td>288 (124500), 337 (47500), 368sh (23800), 408sh (11100), 455 (9110)</td>
</tr>
<tr>
<td>7 Au-Ir-Pt</td>
<td>264 (148900), 342sh (37700), 368 (24900), 413 (14000), 450 (7820)</td>
</tr>
</tbody>
</table>

[a] Absorption spectra were recorded for solutions of concentrations in the range 2 × 10⁻¹ to 1 × 10⁻¹ M, over which the absorbance was confirmed to vary linearly with concentration.

However, under these conditions, only one lifetime can be resolved, of 6 µs, with no significant dependence on the wavelength at which the emission is monitored. The lifetime at 500 nm is not significantly shorter than at longer wavelengths, as might have been expected on the basis of the behaviour at room temperature. It is notable, however, that at 77 K the Pt and Ir mononuclear complexes (2 and 3) both have lifetimes of around 5 or 6 µs. Apparently, then, the Ir→Pt energy transfer rate in 6 is slowed down under these conditions, and the two units behave essentially independently.

### Trinuclear complex

The absorption spectrum of the trinuclear complex 7 is similar to that simulated by addition of the spectra of the three mononuclear Au, Pt and Ir complexes 1, 2 and 3 (see Supporting Information). This observation is consistent with the behaviour of the binuclear complexes, and is indicative of rather minimal ground-state interactions between the three units. The emission spectrum of 7 resembles that of 6 (dinuclear Ir-Pt derivative) showing two components: a broad band centred at 577 nm attributable to emission from the Pt unit, and a weaker, high-energy shoulder which can be assigned to residual Ir emission (Fig. 5a).
No higher-energy emission attributable to the Au component is detectable. The decay in the shorter-wavelength region (λ_{em} = 520 nm was selected) displays biexponential kinetics, with components of 670 ns and 42 ns respectively, attributable to emission from the Pt and Ir units. The data support the expectation, based on the behaviour of the dinuclear complexes, that energy absorbed by the Au unit will be transferred to the Pt unit and/or to the Ir unit, and that the excited state of the Ir unit will be predominantly deactivated by energy transfer to the Pt unit, which has the lowest excited state energy (Fig. 3). As in 6, the rate of this energy transfer is apparently not fast enough to lead to the complete disappearance of the emission from the Ir unit. Again, the proportion of Ir-based emission in the spectrum is approximately independent of the excitation wavelength employed.

(iv) Energy transfer.

The observation of dual emission in 6 and in 7, with bands attributable to the Ir and Pt components appearing simultaneously, allows the rate of energy transfer to be considered in more detail. We will consider the Ir-Pt dinuclear complex 6. The rate of energy transfer, k^{ET}, from Ir to Pt can be estimated on the basis of the extent to which the lifetime of the Ir emission component is shortened compared to its value in the mononuclear Ir complex 3, as in equation [1]:

$$k^{ET} = \frac{\tau_{Ir} - 1}{\tau_{Ir} - 1}$$

[1]

where \(\tau_{Ir}\) is the lifetime of the short component of the emission detected at 520 nm in 6, and \(\tau_{Ir}\) is the luminescence lifetime of 3. This approach assumes that, apart from the introduction of energy transfer, the radiative and non-radiative decay processes open to the Ir unit are the same in 6 as in 3. Although this assumption is unlikely to be strictly correct, it is probably valid to a first approximation. It gives a value of \(k^{ET}\) = 4 × 10^7 s^{-1}.

An estimate of the rate of energy transfer through the Förster (through-space dipole–dipole) mechanism can be made, based on the absorption and emission properties of the mononuclear Pt and Ir complexes respectively. The Förster radius \(R_0\) is given by equation [2]:

$$R_0 = 8.79 \times 10^{23} \left( \frac{k^2 n^2 Q_D Q_a}{\lambda} \right)$$

[2]

where \(Q_D\) is the quantum yield of the donor (the Ir unit), \(n\) is the refractive index (1.44 for CH\(_2\)Cl\(_2\)), and \(k^2\) is a factor that takes into account the orientational dependence of the dipoles of donor and acceptor; a value of 2/3 applies to random averaging in intermolecular energy transfer, and will be used here. The overlap integral \(J(\lambda)\) is given by equation [3]:

$$J(\lambda) = \int_0^\infty F_D(\lambda)e_a(\lambda)\lambda^2d\lambda$$

[3]
Table 2 Photophysical data for the mono-, di- and tri-nuclear complexes in deoxygenated CH₂Cl₂ at 298 K, except where indicated otherwise.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Emission ( \lambda_{\text{max}} )/ nm</th>
<th>( \tau )/ ns[^a]</th>
<th>( \Phi_{\text{num}} )[^b]</th>
<th>( k_{\text{ET}} )/ ( 10^3 ) s(^{-1})</th>
<th>( \sum k_{\text{nr}} )/ ( 10^5 ) s(^{-1})</th>
<th>Emission at 77 K[^d]</th>
<th>( \lambda_{\text{max}} )/nm</th>
<th>( \tau )/ ( \mu )s[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>484, 516</td>
<td>120</td>
<td>0.044[^c]</td>
<td>3.7</td>
<td>83</td>
<td>476,511, 546, 583</td>
<td>274</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>555, 591sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>586</td>
<td>570</td>
<td>7.0[^f]</td>
<td>123</td>
<td>16</td>
<td>537, 575, 623, 683</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>523</td>
<td>880</td>
<td>31[^e]</td>
<td>354</td>
<td>7.9</td>
<td>499, 534, 576</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>588</td>
<td>520</td>
<td>4.5[^e]</td>
<td>86</td>
<td>18</td>
<td>477, 537, 577, 628</td>
<td>208 @ 478 nm</td>
<td></td>
</tr>
<tr>
<td>Au-Pt</td>
<td>523</td>
<td>860</td>
<td>14[^e]</td>
<td>163</td>
<td>10</td>
<td>478, 500, 536, 680</td>
<td>211 @ 475 nm</td>
<td></td>
</tr>
<tr>
<td>Au-Ir</td>
<td>520sh, 577</td>
<td>570 @ 700 nm</td>
<td>5.1[^f]</td>
<td>91</td>
<td>17</td>
<td>500, 536, 573, 625</td>
<td>6.0 @ 535 nm</td>
<td></td>
</tr>
<tr>
<td>Ir-Pt</td>
<td>520sh, 577</td>
<td>580 @ 700 nm</td>
<td>7.2[^e]</td>
<td>107</td>
<td>14</td>
<td>483, 504, 537, 567</td>
<td>200 @ 480 nm</td>
<td></td>
</tr>
<tr>
<td>Au-Ir-Pt</td>
<td>520sh, 577</td>
<td>580 @ 700 nm</td>
<td>7.2[^e]</td>
<td>107</td>
<td>14</td>
<td>483, 504, 537, 567</td>
<td>200 @ 480 nm</td>
<td></td>
</tr>
</tbody>
</table>

\[^a\] \( \lambda_{\text{ex}} = 374 \) nm. The symbol @ indicates the emission wavelength (\( \lambda_{\text{em}} \)) at which the lifetime was measured; when no \( \lambda_{\text{ex}} \) is indicated, the lifetime was found to be invariant (within the error) across the spectrum.  

\[^b\] Quantum yield measured using Ru(bpy)₃Cl₂ in water as the standard. The concentrations of solutions were such that the optical density at the excitation wavelength employed was 0.1 or less. 

\[^c\] \( k_{\text{ET}} \) and \( \Sigma k_{\text{nr}} \) are the radiative and non-radiative decay rate constants, estimated by assuming that the emissive state is formed with unitary efficiency, such that \( k_{\text{ET}} = \Phi_{\text{num}} / \tau \) and \( \Sigma k_{\text{nr}} = \tau^{-1} - k_{\text{ET}} \). 

\[^d\] Data at 77 K recorded in diethyl ether / isopentane / ethanol (2:2:1 by volume). 

\[^e\] \( \lambda_{\text{ex}} = 415 \) nm. 

\[^f\] \( \lambda_{\text{ex}} = 430 \) nm. 

\[^g\] \( \lambda_{\text{ex}} = 460 \) nm.

where \( F_\text{al}(\lambda) \) is the corrected emission spectrum of the energy donor (Ir complex 3) with its integrated area normalised to unity, and \( \alpha_\text{al}(\lambda) \) is the molar absorptivity of the acceptor unit (Pt complex 2), with \( \lambda \) being the wavelength in cm. The overlap integral so calculated has a value of \( 2.13 \times 10^{-15} \) M\(^{-1}\)cm\(^3\), from which a Förster radius of 21.4 Å is obtained. From a simple molecular model, the distance, \( r \), between the Pt and Ir metal centres in 6 is measured to be around 18.4 Å. Using this value in conjunction with the Förster radius, the rate of Förster energy transfer is calculated through equation [4], where \( \tau_D \) is the lifetime of the Ir complex 3.

\[ k_{\text{ET}} = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6 \]  

[4]

A value of \( k_{\text{ET}} = 2.8 \times 10^6 \) s\(^{-1}\) is obtained. Although such a value would certainly introduce a significant deactivation of the iridium-based excited state, being of a similar magnitude to that of the luminescence decay rate constant of 3 (= \( 1.1 \times 10^8 \) s\(^{-1}\)), it is significantly less than the \( k_{\text{ET}} \) value of \( 4 \times 10^7 \) s\(^{-1}\) estimated above based on the change in the lifetime. A significant Dexter contribution to the energy transfer rate is therefore highly likely, through the conjugated \( x \) system of the C=C bonds and the central aryl ring. It may be noted that similar conclusions regarding the importance of triplet-triplet Dexter energy transfer have been reported in other recent studies of multmetallic systems incorporating triplet-emitting metal centres, such as Ru(III), Os(II) and Ir(III), assembled around cores which do not facilitate good conjugation in the ground state.\(^{26}\) The absence of detectable Au emission makes it difficult to determine experimental Au→Pt and Au→Ir energy transfer rate constants for 4 and 5 respectively. Förster radii of 8.35 Å and 8.45 Å respectively are calculated using equations [2] and [3], which – in conjunction with intermetallic distances, \( r \), of 10.5 Å and 18.4 Å respectively – yield \( k_{\text{ET}} \) values of \( 2.1 \times 10^6 \) s\(^{-1}\) and \( 7.8 \times 10^5 \) s\(^{-1}\). Again, these values are probably too small to account for the absence of detectable emission from the Au unit, although it must be noted that the quantum yield of the mononuclear Au complex 1 is two orders of magnitude lower than for the Pt and Ir analogues and for the multinuclear compounds, and so some residual Au emission in 4, 5 and 7 could simply be obscured by the much higher intensity associated with the other metal centres.

**Experimental**

**Information:** NMR spectra were recorded on Bruker AC-300 MHz spectrometer. Chemical shifts are given in ppm. The spectra were calibrated to the residual \(^1\)H and \(^13\)C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), double triplet (dt), triple doublet (td), double double doblet (ddd) and multiplet (m). Absorption spectra were measured on a Biotek Instruments XS spectrometer, using quartz cuvettes of 1 cm pathlength. Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube; the spectra shown are corrected for the wavelength dependence of the detector, and the
High-resolution mass spectrometry was performed on a QSTAR (Applied Biosystems) for ESI and ULTRAFLEX III (MALDI-TOF) (Bruker) for MALDI.

**Synthesis of compounds 1-7:**

**Compound 1:** A Schlenk was charged with 9 (72 mg, 0.125 mmol), 10 (87 mg, 0.188 mmol), Et3N (0.6 mL) and Cul (6 mg, 0.029 mmol), followed by addition of anhydrous CH2Cl2 (10 mL). Then Ar was bubbled into the mixture for 3 min, the mixture was stirred at 40 °C for 24 hours and finally concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with hexane-CH2Cl2 (3:1) as eluent to give 1 (120 mg, 96%) as a yellow solid. 1H NMR (300 MHz, CDCl3): δ = 7.84 (d, J = 1.4 Hz, 2H), 7.76 (t, J = 8.0 Hz, 1H), 7.69-7.65 (m, 2H), 7.49-7.46 (m, 1H), 7.42 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.03 (dd, J = 7.9, 1.4 Hz, 2H), 2.68-2.58 (m, 4H), 1.73-1.56 (m, 4H), 1.47-1.31 (m, 4H), 1.15 (s, 4H), 0.94 (t, J = 7.3 Hz, 6H). 13C NMR (75 MHz, CDCl3, DEPT 135): δ = 166.9 (C), 165.2 (C), 147.6 (C), 146.6 (C), 142.1 (CH), 136.9 (CH), 135.3 (CH3), 133.3 (CH), 127.4 (C), 126.9 (CH2), 125.2 (CH), 123.8 (C), 116.0 (CH), 106.1 (C), 99.8 (C), 94.3 (C), 91.4 (C), 36.2 (CH2), 33.5 (CH), 22.6 (CH), 18.8 (CH), 14.1 (CH2), 11.5 (CH). HRMS MALDI: Caled for C28H32AuNSi2[M+H]+: 1000.4945; found 1000.4929.

**Compound 2:** Anhydrous CH2Cl2 (7 mL) was added to a Schlenk charged with 10 (42 mg, 0.082 mmol), 8 (57 mg, 0.123 mmol), Et3N (0.4 mL) and Cul (4 mg, 0.019 mmol). Then Ar was bubbled into the mixture for 3 min and the mixture was stirred at 40 °C for 48 h. The resulting mixture was then concentrated under reduced pressure and was purified by flash column chromatography on neutral Al2O3 with CH2Cl2 as eluent to give 2 (60 mg, 77%) as an orange solid. 1H NMR (300 MHz, CDCl3): δ = 9.09 (d, J = 5.0 Hz, 1H), 8.03 (t, J = 7.0 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.78 (t, J = 8.0 Hz, 1H), 7.68-7.47 (m, 6H), 7.37 (s, 1H), 7.30 (d, J = 7.9 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 2.61 (t, J = 7.7 Hz, 2H), 1.74-1.57 (m, 2H), 1.48-1.34 (m, 2H), 1.16 (s, 4H), 0.95 (t, J = 7.3 Hz, 3H). 13C NMR (75 MHz, CDCl3, DEPT 135): δ = 165.8 (C), 158.6 (C), 154.9 (C), 137.7 (CH), 134.8 (CH), 133.6 (CH), 133.0 (CH), 132.3 (CH), 129.2 (CH), 124.6 (C), 124.37 (C), 124.3 (C), 122.2 (CH), 121.2 (CH), 121.1 (C), 119.1 (CH), 115.7 (C), 105.6 (C), 92.8 (C), 90.9 (C), 87.9 (C), 29.5 (CH3), 18.8 (CH2), 11.7 (CH). HRMS MALDI: Caled for C23H19N2O3Si2[M+H]+: 1136.4678; found 1136.4727.

**Compound 13:** Anhydrous CH2Cl2 (7 mL) was added to a Schlenk charged with 9 (200 mg, 0.348 mmol), 12 (89 mg, 0.290 mmol), Et3N (1.2 mL) and Cul (14 mg, 0.078 mmol). The resulting mixture was then concentrated under reduced pressure and was purified by flash column chromatography on silica gel with hexane-CH2Cl2 (3:1) as eluent to give 13 (127 mg, 52%) as a yellow solid. 1H NMR (300 MHz, CDCl3): δ = 7.86 (s, 2H), 7.79 (t, J = 7.9 Hz, 1H), 7.69 (d, J = 7.7 Hz, 2H), 7.51 (s, 1H), 7.46 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 7.7 Hz, 2H), 3.08 (s, 1H), 2.65 (t, J = 7.7 Hz, 4H), 1.73-1.57 (m, 4H), 1.48-1.32 (m, 4H), 1.14 (s, 2H), 0.95 (t, J = 7.3 Hz, 6H). 13C NMR (75 MHz, CDCl3, DEPT 135): δ = 167.0 (C), 165.1 (C), 147.5 (C), 146.5 (C), 142.1 (CH), 136.8 (CH), 135.6 (CH), 135.1 (CH), 133.7 (CH), 127.6 (C), 126.9 (CH2), 125.2 (CH), 124.0 (C), 122.5 (C), 116.0 (CH), 105.9 (C), 99.5 (C), 94.8 (C), 91.7 (C), 82.8 (C), 77.8 (C), 36.2 (CH2), 33.5 (CH2), 22.6 (CH), 18.8 (CH2), 14.1 (CH), 11.5 (CH). HRMS MALDI: Caled for C28H19AuNSi2[M+H]+: 844.3607; found 844.3609.

**Compound 4:** A Schlenk was charged with 10 (34 mg, 0.065 mmol), 13 (50 mg, 0.059 mmol), Et3N (0.4 mL), Cul (2 mg, 0.010 mmol) and anhydrous CH2Cl2 (7 mL). Then Ar was bubbled into the mixture for 3 min and the mixture was stirred at 40 °C for 48 h. The mixture was then concentrated in vacuo and was purified by flash column chromatography on neutral Al2O3 with hexane-CH2Cl2 (1:3). The obtained solid was sonicated with a hot mixture Hexane-CH2Cl2 (10:1). The compound was filtered off and washed with hot hexane to give 4 (60 mg, 77%) as an orange solid. 1H RMN (300 MHz, CDCl3): δ = 9.17 (d, J = 5.2 Hz, 1H), 8.05 (t, J = 7.8 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.87-7.76 (m, 4H), 7.74-7.66 (m, 2H), 7.64-7.45 (m, 7H), 7.41 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 7.9 Hz, 1H), 7.08 (dd, J = 7.9, 1.7 Hz, 2H), 6.92 (d, J = 6.2 Hz, 1H), 2.73-2.56 (m, 6H), 1.75-1.57 (m, 6H), 1.48-1.30 (m, 6H), 1.01-0.85 (m, 9H). 13C NMR (75 MHz, CDCl3, DEPT 135): δ = 167.2 (C), 165.8 (C), 165.2 (C), 158.5 (C), 154.9 (C), 151.8 (CH), 147.7 (C), 147.2 (C), 144.9 (C), 142.6 (C), 139.3 (CH), 138.8 (CH), 135.4 (CH), 131.7 (CH), 129.9 (C), 128.1 (CH), 124.9 (CH), 124.3 (CH), 123.9 (C), 123.2 (CH), 118.7 (CH), 117.9 (CH), 110.1 (C), 106.8 (C), 104.4 (C), 91.2 (C), 36.3 (CH3), 34.0 (CH2), 22.9 (CH), 18.9 (CH2), 14.2 (CH), 11.8 (CH). HRMS MALDI: Caled for C50H48N2P2Si2[M+H]+: 944.4331; found 944.4370.
Compound 14: A solution 1 M of tetra-n-butylammonium fluoride (0.2 mL, 0.185 mmol) in THF was added to a solution of 3 (70 mg, 0.062 mmol) in anhydrous THF (7 mL) under argon at -78 °C. The mixture was stirred while allowing to warm to room temperature (3 h). The solvent was evaporated and the residue was purified by flash chromatography on neutral Al2O3 with hexane-CH2Cl2 (2:3). Finally the obtained solid was washed with hot hexane afforded 14 (38 mg, 74%) as a yellow solid. 1H NMR (300 MHz, CDCl3): δ = 8.65 (dd, J = 5.8, 1.8 Hz, 2H), 7.93 (d, J = 7.8 Hz, 2H), 7.88-7.79 (m, 2H), 7.66-7.58 (m, 4H), 7.58-7.49 (m, 3H), 7.28 (dd, J = 7.3, 5.8, 1.5 Hz, 2H), 7.22-7.14 (m, 2H), 6.87 (td, J = 7.5, 1.2 Hz, 2H), 6.70 (td, J = 7.4, 1.4 Hz, 2H), 6.26 (dd, J = 7.6, 0.8 Hz, 2H), 3.20 (s, 2H), 1.56 (s, 6H). 13C NMR (75 MHz, CDCl3, DEPT 135): δ = 183.9 (C), 168.7 (C), 148.6 (CH), 148.1 (C), 145.5 (C), 144.4 (C), 137.7 (CH), 135.5 (CH), 135.3 (CH), 133.6 (CH), 133.0 (CH), 132.4 (CH), 129.2 (CH), 124.7 (C), 124.4 (CH), 123.4 (C), 122.2 (CH), 121.2 (CH), 120.9 (C), 119.1 (C), 115.7 (C), 91.3 (C), 87.6 (C), 82.0 (C), 78.9 (CH), 29.5 (CH2), 12.9 (CH3). HRMS MALDI: Calcd for C34H33IrN2O2Pt+ [M]+ 1381.3450; found 1381.3400.

Compound 5: Anhydrous CH2Cl2 (5 mL) was added to Schlenk charged with 9 (30 mg, 0.052 mmol), 14 (73 mg, 0.088 mmol), Et3N (0.5 mL) and CuI (3 mg, 0.014 mmol). The resulting mixture was bubbled with Ar for 3 min and then was stirred at 0 ºC for 3 h. The reaction mixture was then sonicated with a hot mixture of hexane-CH2Cl2 (2:3) followed by crystallization by the slow diffusion method. The obtained solid was washed with hot hexane afforded 5 (63 mg, 15%) as an orange solid (30 mg, 42%). 1H NMR (300 MHz, CDCl3): δ = 8.66 (d, J = 5.7 Hz, 2H), 7.93 (d, J = 7.9 Hz, 2H), 7.89-7.79 (m, 5H), 7.75 (t, J = 1.5 Hz, 1H), 7.69 (t, J = 1.5 Hz, 1H), 7.64-7.49 (m, 7H), 7.42 (d, J = 8.0 Hz, 2H), 7.29 (ddd, J = 7.2, 5.8, 1.4 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.10 (ddd, J = 7.9, 1.7 Hz, 2H), 6.86 (td, J = 7.5, 1.1 Hz, 2H), 6.70 (td, J = 7.4, 1.3 Hz, 2H), 6.26 (d, J = 7.6 Hz, 2H), 3.20 (s, 1H), 2.73-2.60 (m, 4H), 1.74-1.59 (m, 4H), 1.55 (s, 6H), 1.60 (m, 6H), 0.96 (s, J = 7.3 Hz, 6H). 13C NMR (75 MHz, CDCl3, DEPT 135): δ = 183.9 (C), 168.7 (C), 167.0 (C), 165.2 (C), 148.6 (CH), 148.1 (C), 147.8 (C), 147.0 (C), 145.5 (C), 144.1 (C), 142.6 (CH), 137.7 (CH), 136.8 (CH), 135.3 (CH), 135.2 (CH), 133.5 (CH), 133.4 (CH), 132.9 (CH), 132.3 (CH), 129.2 (CH), 128.0 (C), 127.2 (CH), 125.6 (CH), 124.3 (CH), 124.2 (C), 122.9 (CH), 122.2 (CH), 121.2 (C), 121.1 (CH), 119.0 (CH), 116.6 (CH), 115.7 (C), 99.6 (C), 95.5 (C), 88.3 (C), 82.7 (C), 78.2 (CH), 36.4 (CH2), 33.9 (CH3), 29.5 (CH2), 14.2 (CH3). HRMS MALDI: Calcd for C35H28AurN3O2 Pt+ [M]+ 1842.4870; found 1842.4845.

Photophysical measurements. Absorption spectra were measured using a Bio Tek Instruments X8 spectrometer, using quartz cuvettes of 1 cm path length. Steady-state luminescence spectra were measured using a Jobin Yvon Fluoromax-2 spectrophotometer, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube; the spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Samples for emission measurements were contained within quartz cuvettes of 1 cm path length modified with appropriate glassware to allow connection to a high-vacuum line. Degassing was achieved via a minimum of three freeze-pump-thaw cycles whilst connected to the vacuum manifold; final vapour pressure at 77 K was < 5 x 10⁻² mbar, as monitored using a Pirani gauge. Luminescence quantum yields were determined.
using [Ru(bpy)₃]Cl₂ in degassed aqueous solution as the standard (Φₓₓₓₓ = 0.042); estimated uncertainty in Φₓₓₓₓ is ± 20% or better. The luminescence lifetimes of the complexes were measured by time-correlated single-photon counting, following excitation at 374.0 nm with an EPL-375 pulsed-diode laser. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator. The estimated uncertainty in the quoted lifetimes is ± 10% or better. Low-temperature measurements were made using a home-built quartz dewar with the sample contained within 4 mm o.d. quartz tubes immersed in liquid nitrogen. For lifetimes exceeding 10 μs, a pulsed xenon flashlamp was used as the excitation source (an appropriate wavelength being selected using a monochromator), in conjunction with the same R928 detector used in multichannel scaling mode.

Conclusions

In summary, we demonstrate how the 1,3,5-triethynylbenzene unit can be successfully used to link together three different metal centres using a modular synthetic approach. This linking core offers only minimal conjugation, such that the properties of the individual metal complexes are to a large extent retained in the supramolecular di- and tri-nuclear systems. For example, the absorption spectra of the multinuclear complexes in the longer-wavelength region, where the metal-based units absorb, match well with the spectra simulated by addition of the spectra of the mononuclear metal complexes. In the multinuclear complexes containing both Ir(III) and Pt(II) units, emission attributable to both moieties is observed, but the intensity and lifetime of the higher-energy Ir(III)-based emission are greatly reduced compared to the mononuclear iridium complex, attributable to energy transfer from the Ir unit to the Pt unit. The overlap of the emission spectrum of the former with the absorption spectrum of the latter is quite limited, and the calculated Förster rate constant is not sufficient to fully account for the the experimentally observed energy transfer rate, suggesting a significant through-bond Dexter component to the process. No detectable Au-based emission is observed at room temperature in the gold-containing multinuclear complexes 4, 5 and 7, indicative of energy transfer from the Au unit to the Ir and Pt units, as expected on the basis of the order of the excited state energies of the individual components. The simultaneous emission from both the Ir and Pt units in 6 and in 7 leads to broad-band emission covering much of the visible region of the spectrum, and CIE coordinates of x = 0.50, y = 0.49 for 7. It is clear, however, that in order to obtain an efficient white light emitter, the molecular design would need to be modified in such a way as to (i) further slow the rate of Ir→Pt energy transfer, and (ii) incorporate a more efficient blue emitter than the N=C−N-coordinated Au unit, whose quantum yield is very low.

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Notes and references

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34 The approach used follows the standard treatment, as described in, for example: J. R. Lakowicz, Principles of Fluorescence Spectroscopy, 3rd edition, Chapter 13, Springer, New York, 2006.