

Stabilization of anti-aromatic and strained five-membered rings with a transition metal

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Anti-aromatic compounds, as well as small cyclic alkynes or carbynes, are particularly challenging synthetic goals. The combination of their destabilizing features hinders attempts to prepare molecules such as pentalyne, an 8 π -electron anti-aromatic bicycle with extremely high ring strain. Here we describe the facile synthesis of osmapentalyne derivatives that are thermally viable, despite containing the smallest angles observed so far at a carbyne carbon. The compounds are characterized using X-ray crystallography, and their computed energies and magnetic properties reveal aromatic character. Hence, the incorporation of the osmium centre not only reduces the ring strain of the parent pentalyne, but also converts its Hückel anti-aromaticity into Craig-type Möbius aromaticity in the metallapentalynes. The concept of aromaticity is thus extended to five-membered rings containing a metal-carbon triple bond. Moreover, these metal-aromatic compounds exhibit unusual optical effects such as near-infrared photoluminescence with particularly large Stokes shifts, long lifetimes and aggregation enhancement.

Aromaticity is a fascinating topic that has long interested both experimentalists and theoreticians because of its ever-increasing diversity^{1–5}. The Hückel aromaticity rule⁶ applies to cyclic circuits of $4n + 2$ mobile electrons, but Möbius topologies favour $4n$ delocalized electron counts^{7–10}. In general, aromatic compounds are substantially more stable thermodynamically—and anti-aromatic compounds less stable—than appropriate non-aromatic reference systems. Accordingly, anti-aromatic compounds (such as pentalyne (**I**), Fig. 1a) are often hard to prepare and isolate because of their unfavourable energies and high reactivity¹¹.

The realization of small cyclic alkynes also challenges synthetic chemists because the angle strain associated with the highly distorted triple bonds^{12–18} must be overcome. Thus, tetramethylcycloheptyne¹⁵ is the smallest isolable carbocyclic alkyne, and benzyne, cyclohexyne and cyclopentyne have only been trapped as reaction intermediates¹⁴ or observed by infrared spectroscopy at low temperatures¹⁶. Not surprisingly, pentalyne **I** has never been reported because the extreme strain in its five-membered cycloalkyne ring further compounds its expected anti-aromatic instability.

The introduction of a metal fragment is an efficient strategy to stabilize cyclic alkynes by reducing ring strain^{19–31}. Two outstanding examples are 1-zirconacyclopent-3-yne¹⁹ and osmabenzynes²³ (the smallest isolated cyclic alkyne and metal carbyne, respectively), which were synthesized recently in the pioneering works by Suzuki and Jia. These two molecules can be regarded as the result of replacement of one sp^3 or sp hybridized carbon atom in cyclopentyne or benzyne, respectively, by a transition metal. We show here that the introduction of a transition metal into pentalyne **I** allows the realization of the smallest cyclic metal carbynes to date (Fig. 1). Moreover, the involvement of transition-metal d orbitals in the π conjugation switches the Hückel anti-aromaticity of pentalyne **I** into the Möbius aromaticity of a metallapentalyne (**II**, Fig. 1a). This significantly enhances the stabilization due to transition-metal substitution.

Results and discussion

Synthesis, characterization and reactivity of osmapentalynes.

Treatment of complex **1** (ref. 32) with methyl propiolate ($\text{HC}\equiv\text{CCOOCH}_3$) at room temperature produced osmapentalyne **2a** (Fig. 1b) in 80% yield in only 5 min. Remarkably, solid **2a** can be stored at room temperature for three months and is even persistent thermally at 120 °C in air for 3 h. Similarly, ethyl and tert-butyl propiolates also react with complex **1** to give the corresponding osmapentalynes in 77% and 50% yields, respectively. A plausible mechanism for the formation of osmapentalynes is proposed in Supplementary Fig. S1. Osmapentalyne **2a** was characterized by high-resolution mass spectrometry (HRMS) and by ¹H, ³¹P and ¹³C NMR spectroscopy. Three strongly down-field ¹H chemical shifts of osmapentalyne **2a** at 14.25, 9.27 and 8.32 ppm suggest that the metallabicycle is aromatic (Fig. 2a). Consistently, the Os \equiv C signal, observed at 324.5 ppm in the ¹³C NMR spectrum, is at an only slightly lower field than the 264.9–316.4 ppm range for osmabenzynes^{23–27}.

X-ray diffraction revealed the key structural features of **2a** (Fig. 1c). It is an essentially planar eight-membered metallabicycle, and the mean deviation from the least-squares plane is 0.0415 Å. The C–C bond lengths (1.377–1.402 Å) are similar to those of benzene (1.396 Å), suggesting aromatic π -conjugation, as represented by resonance structures **2A–2E** in Fig. 2b. Structure **2B** shows cumulative double bonds in a five-membered metallacycle. Similar features have been reported previously, for example, in metallacycloallenes^{20,33} and metallacyclocumulenes^{34,35}. The 1.845 Å Os \equiv C triple bond length in **2a** is slightly longer than those of Os \equiv C triple bonds in acyclic osmium carbynes (1.671–1.841 Å)²⁵ (based on a search of the Cambridge Structural Database, CSD version 5.33, in November 2011). Notably, the 129.5° carbyne carbon bond angle in **2a** is the smallest yet observed, and such distortion must result in considerable strain. Bond angles at carbyne carbons range from 147° to 156° in metallabenzynes^{23–27},

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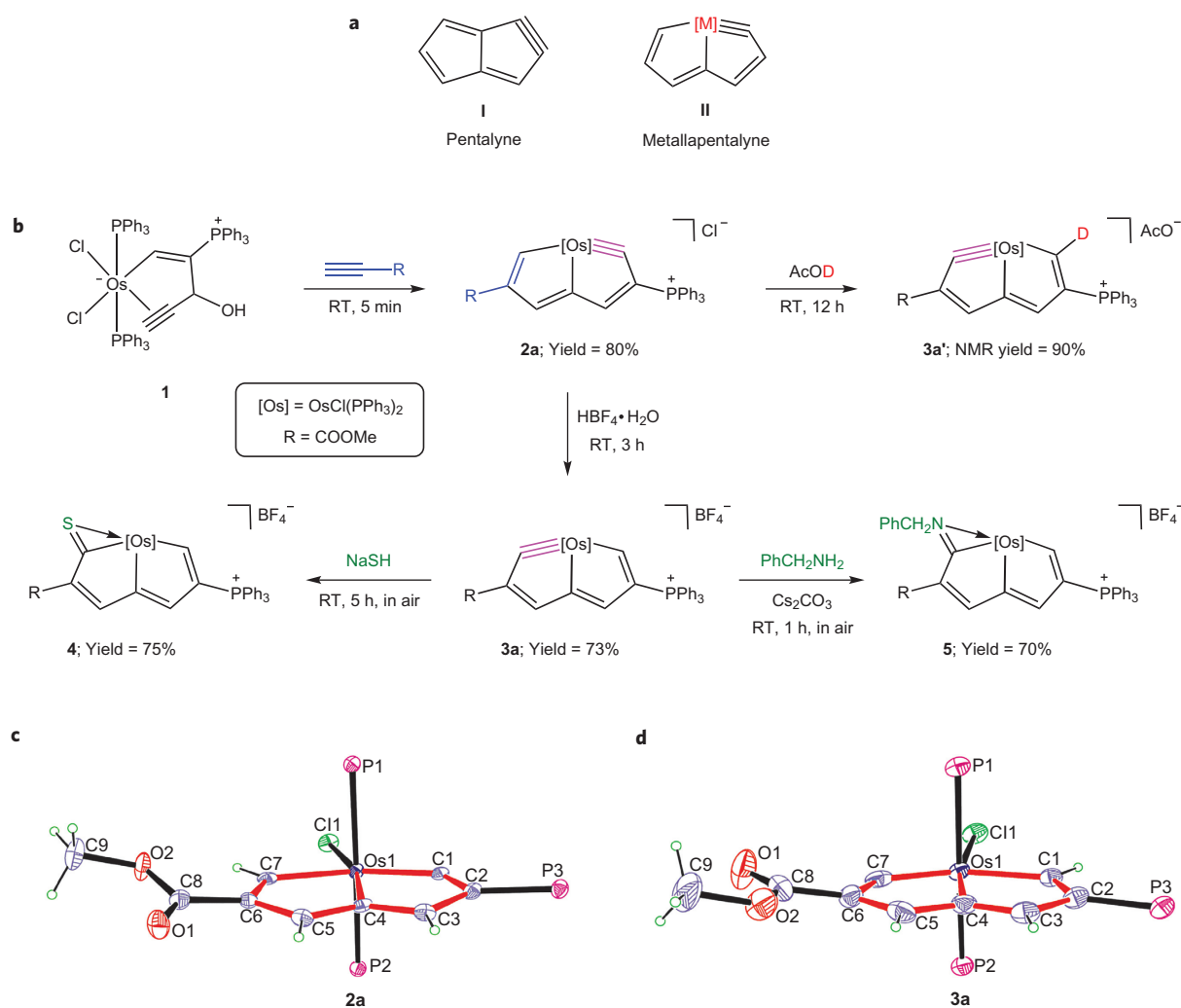


Figure 1 | Synthesis, structure and reactivity of osmapentalynes. **a**, Anti-aromatic pentalyne **I** and aromatic metallapentalyne **II**. [M] = metal fragment. **b**, Synthesis of osmapentalynes **2a** and **3a** and their reactions to deuterated **3a'** (**3a'**) as well as **4** and **5**. The reactions of **2a** with electrophiles (AcOD or HBF_4) shift the metal-carbon triple bond, whereas the reactions of **3a** with sodium hydrosulfide or benzylamine nucleophiles illustrate the electrophilic character of the carbyne carbon in osmapentalynes. **c,d**, X-ray molecular structures for cations of **2a** (**c**) and **3a** (**d**) drawn with 50% probability (the phenyl groups in the PPh_3 moieties are omitted for clarity). RT, room temperature.

the smallest cyclic metal carbynes previously reported, as well as in metallacyclopentynes^{19–22}, the smallest cyclic alkynes.

Treatment of **2a** with $HBF_4 \cdot H_2O$ forms **3a** (Fig. 1b) through a tautomeric shift of the $Os \equiv C$ triple bond to the other five-membered ring. The X-ray structure of **3a** (Fig. 1d) reveals a similar $Os \equiv C$ bond length (1.777 Å) and $Os \equiv C-C$ angle (131.2°), as well as its near planarity (the mean deviation is 0.0218 Å from the least-squares plane). Such tautomeric shifts, which indicate π -conjugation, were also observed for analogous osmapentalynes with ethyl and tert-butyl substituents. Reaction of **2a** with CH_3COOD (AcOD) gave the deuterated osmapentalyne, **3a'** (Fig. 1b). HRMS of **3a** and **3a'** showed molecular ion peaks at 1159.2416 and 1160.2454 (m/z), respectively. Protonation (electrophilic attack) demonstrates the nucleophilic character of the carbyne carbon of the osmapentalyne $Os \equiv C$ triple bond. Metal carbynes are ambiphilic and can also be attacked by nucleophiles^{25,36}. Thus, products **4** and **5** were formed by reacting **3a** with sodium hydrosulfide and benzylamine, respectively (Fig. 1b).

DFT computations on osmapentalynes. Model density functional theory (DFT) computations³⁷ provided estimates of the strain of cyclopentynes and of **2a** due to nonlinear distortion of the carbyne

carbon angles. The 116.0° angles computed at the two carbyne carbon atoms in the parent cyclopentynes (C_5H_6) are much smaller than that at the carbyne carbon in **2a** (129.5°). Accordingly, the metal replacement significantly reduces the ring strain. Indeed, the $24.3 \text{ kcal mol}^{-1}$ computed strain energy of the in-plane π -bond in **2a** based on the chosen cyclic reference molecule is much smaller than the $71.9 \text{ kcal mol}^{-1}$ in cyclopentynes (Supplementary Fig. S2). However, such a strain in **2a** is still larger than that of osmabenzynes ($9.6 \text{ kcal mol}^{-1}$)³⁸. As discussed below, in addition to the reduction in ring strain, the aromaticity induced by metal incorporation into the metallabicyclic further stabilizes **2a** significantly.

DFT computations on **2'**, a simplified model complex in which the PPh_3 ligands of **2a** are replaced by PH_3 , help understand the aromaticity of osmapentalynes. The four occupied π -molecular orbitals of **2'** selected in Fig. 3 (of the six shown in Supplementary Fig. S3) reflect the π -delocalization along the perimeter of the bicyclic system. These four molecular orbitals are derived principally from the orbital interactions between the $p_{z\pi}$ atomic orbitals of the C_7H_5 unit and two of the d orbitals of the Os atom ($5d_{xz}$ and $5d_{yz}$). Accordingly, the eight-membered ring in the model complex **2'** is regarded as a cyclic eight-centre eight-electron (8c–8e)

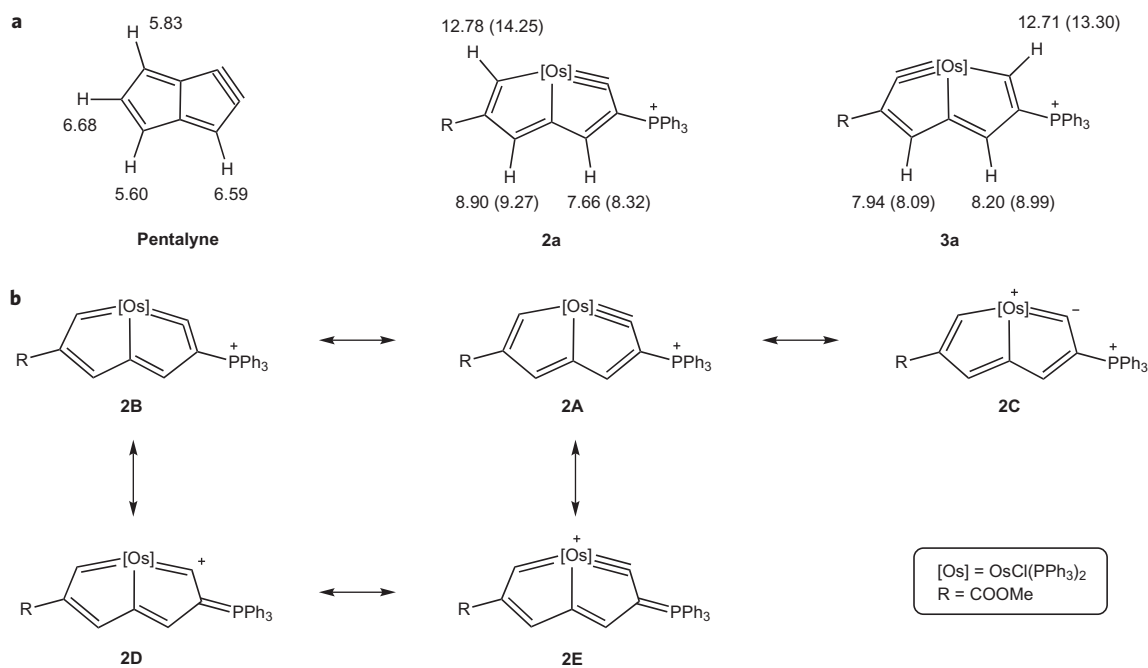


Figure 2 | Aromaticity in osmapentalynes: downfield ^1H chemical shifts and resonance structures. **a**, Computed proton chemical shifts (ppm versus tetramethylsilane) on the rings of the cation moiety of osmapentalynes **2a**, **3a** and pentalyne are compared with the available experimental values (in parentheses). **b**, Five resonance structures of the cation moiety of osmapentalyne **2a**.

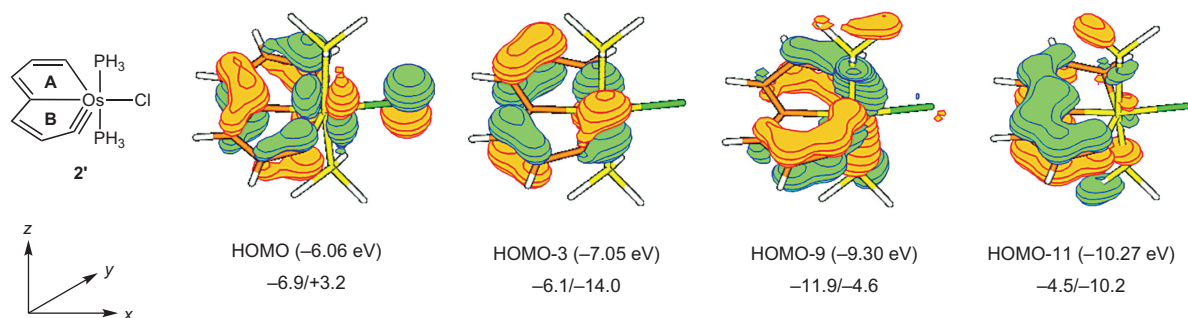


Figure 3 | NICS(0) $_{zz}$ contributions of the four key occupied perimeter molecular orbitals of model complex **2'.** The eigenvalues of the molecular orbitals are given in parentheses. The NICS(0) $_{zz}$ values given before and after the '/' are those computed at the geometrical centres of rings **A** and **B**, respectively. The total diamagnetic contributions of the four π molecular orbitals (-29.4 and -25.6 ppm for rings **A** and **B**, respectively) can be used to evaluate the Craig-type 8c-8e Möbius aromaticity of **2'**. This result contrasts sharply with the 8c-8e anti-aromatic Hückel π conjugation in pentalyne.

Craig-type Möbius aromatic system^{7,9}. This assignment is in line with the resonance structures depicted in Fig. 2b, in which Os-C4 is always a single σ -bond and is further reinforced by the results of canonical molecular orbital (CMO) nucleus-independent chemical shift (NICS)³⁹⁻⁴² computations⁴³. The NICS(0) $_{zz}$ values at the centres of rings **A** and **B** in **2'** are -11.1 and -10.8 ppm, respectively (Supplementary Fig. S3). In general, negative values indicate aromaticity and positive values anti-aromaticity. These NICS(0) $_{zz}$ values are comparable to that of benzene (-14.5 ppm) and in sharp contrast to those of pentalyne ($+45.0$ and $+60.3$ ppm, Supplementary Fig. S4). The net aromaticity of model complex **2'** can be attributed mainly to the total diamagnetic contributions from the four key occupied molecular orbitals (HOMO, HOMO-3, HOMO-9 and HOMO-11, shown in Fig. 3), which have negative CMO-NICS(0) $_{zz}$ value sums of rings **A** and **B**.

Notably, Hoffmann's predictive extension of the fundamental concept of aromaticity to metallabenzene⁴, first realized by Roper⁵, has now been extended to such metallabicycles as osmapentalynes, which have 8c-8e effective $d_{\pi}-p_{\pi}$ Craig-type

conjugation/delocalization of Möbius aromaticity. The osmapentalynes are examples of such rare Möbius aromatic compounds⁹.

Our theoretical analyses verify the aromaticity of the osmapentalynes cations **2a** and **3a**. We first optimized the geometry of **2a** (Supplementary Fig. S5), which is consistent with the X-ray structure. In addition, our computations indicate that **3a** is thermodynamically more stable than **2a** (by 2.3 kcal mol⁻¹ in free energy at 25 °C). The isomerization stabilization energy (ISE) method of Schleyer and Pühlhofer, which is particularly effective for probing the magnitude of aromatic π conjugation for highly strained systems⁴⁴, was applied to compare osmapentalynes with related systems, as shown in Fig. 4. The six ISE reactions presented retained the same total number of *anti* diene units in the reactants and products. The positive values, 8.8 and 6.8 kcal mol⁻¹, respectively, of the pentalene and pentalyne reactions demonstrate and quantify their anti-aromaticity. In sharp contrast, the large and comparable negative energies, -22.8 , -23.3 and -21.2 kcal mol⁻¹, for the next three reactions (approximately two-thirds of the -33.2 kcal mol⁻¹ benzene ISE value⁴⁴) show the extent of the

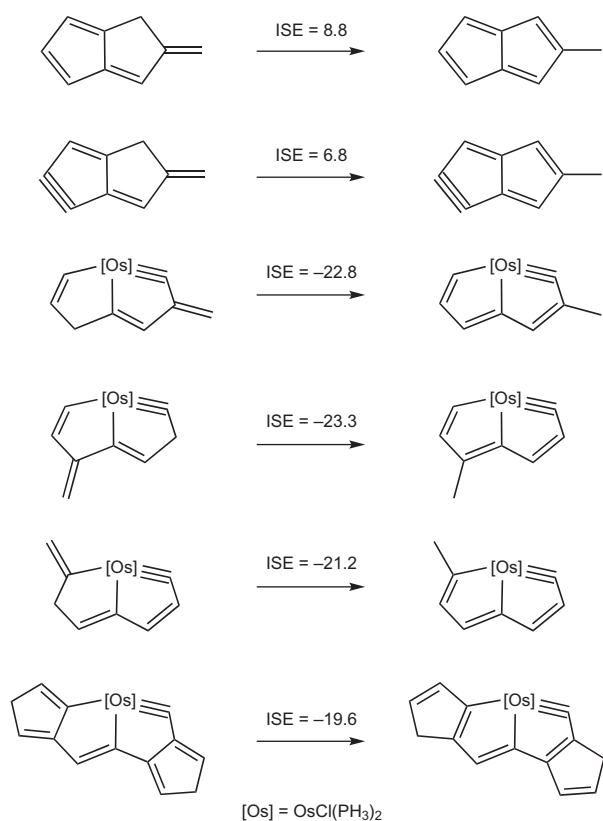


Figure 4 | ISE evaluations of the anti-aromaticity of pentalene and pentalyne and the aromaticity of osmapentalyne models. Note the consistently large negative ISE values of osmapentalyne, roughly two-thirds that of benzene. The energies (in kcal mol⁻¹, computed by the B3LYP functional with LanL2DZ basis set for osmium and 6-311++G(d,p) basis set for carbons and hydrogens) include the zero-point energy corrections.

osmapentalyne aromaticity. In addition, the last reaction in Fig. 4 uses another strain-balanced isomerization method⁴⁵ to evaluate the aromatic stabilization energy. The result for osmapentalyne, -19.6 kcal mol⁻¹, is also about two-thirds that of benzene (-29.0 kcal mol⁻¹)⁴⁵ using the same approach. All the large negative ISE values unambiguously confirm the aromaticity of osmapentalynes.

Photoluminescent properties of osmapentalynes. The efficiency of fused aromatics like naphthalene, anthracene and pyrene as fluorophores⁴⁶ prompted the examination of osmapentalyne photoluminescence. At room temperature, excitation in the 400–500 nm visible region led to near-infrared emission of **2a** in common organic solvents (Fig. 5a). Integration of the coordinated Os atom into the aromatic conjugation caused an unusually large Stokes shift (a 320 nm separation between the excitation and emission wavelengths) comparable to that of lanthanide complexes employing antenna effects in luminescence⁴⁷. The luminescent electronic transition of **2a** was partially forbidden because of the *d* electrons involved in its π system. This was reflected by the long emission lifetimes of **2a** in the range 10⁻⁷ to 10⁻⁶ s (Supplementary Fig. S21), a lifetime level typical of luminescence from ruthenium (II) or osmium (II) coordination complexes⁴⁶. Near-infrared dyes are highly desirable in bioimaging research, with advantages including minimal interfering fluorescence from biological samples, reduced scattering, and enhanced tissue penetration depth. However, most of the organic near-infrared dyes (for example, cyanines) have intrinsically short lifetimes (<1 × 10⁻⁸ s) and small Stokes shifts⁴⁸. The long emission lifetimes and large Stokes shifts of osmapentalynes encourage exploration of their potential application

as novel near-infrared dyes. Sensitivity might be improved vastly by the use of time-gated acquisition methods and the minimization of interference from scattering or autofluorescence.

Unlike the behaviour of most organic aromatics, which display fluorescence quenching in aggregates⁴⁶, the osmapentalyne emission was enhanced by aggregation (Fig. 5a). Most fluorescent aromatics are planar molecules and their emission is usually quenched in their aggregates due to π - π stacking interactions. Such an ‘aggregation quenching’ phenomenon is generally considered to be detrimental in real-world applications. However, the situation is different in osmapentalyne aggregates, because π - π stacking of the fluorophores is precluded sterically by the bulky ligands. Indeed, the opposite aggregation phenomenon occurs in the osmapentalynes. Thus, adding large amounts of water (a poor solvent for osmapentalynes) to ethanol solutions of **2a** resulted in remarkable enhancements of the emission intensity (Fig. 5a). Indeed, the photoluminescence quantum yield of **2a** increased from 0.012 in pure ethanol to 0.046 in a 95% (vol/vol) water-ethanol mixture (Supplementary Fig. S22).

This emission enhancement is attributed to stabilization of the excited states induced by aggregation, in which the intramolecular rotations, vibrations and intermolecular collisions are greatly restricted by the physical constraints⁴⁹. This hypothesis is supported by the longer luminescence lifetimes of **2a** in aggregates (Supplementary Fig. S21). Consistent with the above analysis,

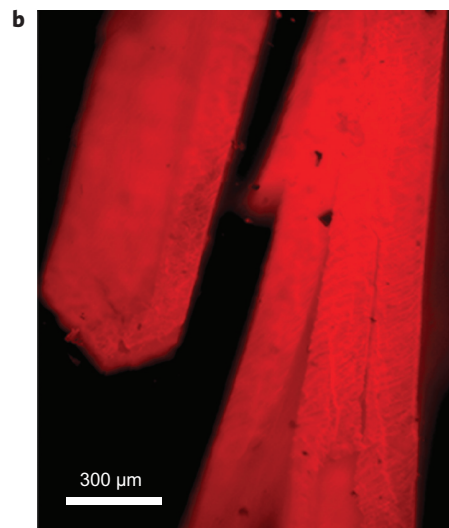
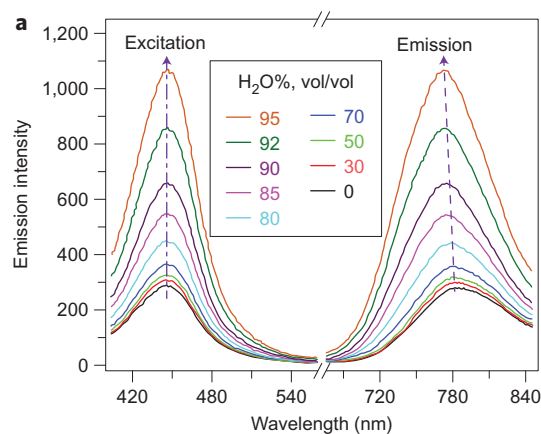


Figure 5 | Photoluminescence of osmapentalyne **2a.** **a**, Excitation and emission spectra of **2a** (1.0 × 10⁻⁴ mol l⁻¹) in ethanol/water solutions of various volume ratios at room temperature. **b**, Fluorescent photomicrograph of the crystals of **2a** excited at 440 nm.

intense red emission could be observed in the crystals of **2a** (Fig. 5b). Similar aggregation-enhanced near-infrared emission behaviour was observed for the other osmapentalynes. Hence, this study illustrates the inherent structure–property relationship between metallaromatics-based luminophores and aggregation-induced emission, which should help guide the fabrication of high-efficiency luminescent materials by taking advantage of crystallization or high-density immobilization of the luminophores.

Conclusions

We have described the synthesis and X-ray crystallography characterization of persistent, highly unusual bicyclic pentalyne systems. Computational analyses show that the incorporation of transition-metal moieties not only relieves considerable strain, but also results in aromatic stabilization of the rarely realized Craig/Möbius type⁵⁰. These new metal–aromatics exhibit unusual aggregation-enhanced near-infrared photoluminescence with unusually large Stokes shifts and long lifetimes. Our findings encourage further efforts to realize novel metal-incorporated aromatic systems with $4n$ mobile electrons as well as the exploitation of their materials science applications as near-infrared luminophores.

Methods

Absorption and fluorescence spectra were recorded on a Hitachi U-3900 ultraviolet–visible spectrophotometer and a Hitachi F-7400 fluorophotometer, respectively. The emission decay times were acquired with a HORIBA Jobin Yvon FluoroMax-4 TCSPC time-resolved fluorophotometer. The electronic structure computations used the Gaussian03 program³⁷. Harmonic frequency calculations were also performed to confirm the nature (for example, minima) of stationary points. X-ray crystal structure information is available at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 820684 (**2a**), CCDC 820685 (**3a**), CCDC 820688 (**4**) and CCDC 897827 (**5**). See Supplementary Information for detailed experimental procedures, and crystallographic, spectroscopic and computational analyses. The synthetic details given here for **2a** and **3a** are representative of all the compounds described. All syntheses were performed at room temperature under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated.

Synthesis of 2a. Compound $\text{HC}\equiv\text{CCOOme}$ (67 μl , 0.80 mmol) was added to a suspension of compound **1** (300 mg, 0.27 mmol) in dichloromethane (15 ml). The mixture was stirred at room temperature for 5 min to give a yellow solution. The solution was evaporated under vacuum to a volume of ~ 2 ml and then purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol = 20:1) to give a yellow solution. Solid yellow **2a** (258 mg, 80%) was collected after solvent evaporation under vacuum.

Synthesis of 3a. A solution of $\text{HBF}_4\cdot\text{H}_2\text{O}$ (85 μl , 0.50 mmol) was added to a solution of compound **2a** (300 mg, 0.25 mmol) in dichloromethane (15 ml). After stirring at room temperature for 3 h, the resulting reddish-brown solution was evaporated under vacuum to a volume of ~ 2 ml, and diethyl ether (20 ml) was then added. The yellow precipitate was collected by filtration, washed with diethyl ether (2×5 ml), and dried under vacuum to give **3a** (227 mg, 73%) as a yellow solid.

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Author contributions

H.X. conceived the project. C.Z., M.L. and X.Z. performed the experiments. S.L. and Y.N. conducted the luminescence study of osmapentalynes. C.Z. and T.W. recorded all NMR data and solved all X-ray structures. H.X., C.Z. and T.W. analysed the experimental data. J.Z. conceived the theoretical work and, with M.-L.L., conducted theoretical computations. J.Z., X.L., Z.C., M.-L.L. and P.v.R.S. analysed and interpreted the computational data. J.Z., H.X., S.L. and C.Z. drafted the paper, with support from Z.C., X.L., T.W. and Z.X., as well as language editing by P.v.R.S. All authors discussed the results and contributed to the preparation of the final manuscript.

Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to J.Z. and H.X.

Competing financial interests

The authors declare no competing financial interests.