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ARTICLE TYPE

Rh-catalysed direct cyclisation of 1,4-naphthoquinone and 9,10-phenanthraquinone with alkyne: a facile access to 1,8-dioxapyrenes and 1,12-dioxaperylenes as orange and red-emitting luminophores†

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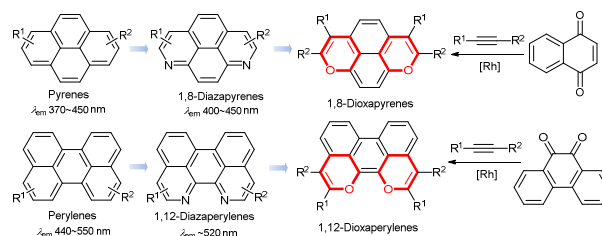
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Rh-catalysed direct cyclisation of 1,4-naphthoquinones and 9,10-phenanthraquinones with alkynes has been accomplished for the first time through C–H activation strategy to forge 1,8-dioxapyrenes and 1,12-dioxaperylenes. Starting from readily available substrates, a variety of dipyran-containing PAHs are obtained in one step and exhibit orange/red-emitting performance, large Stokes shifts and highly thermal stability.

The design and construction of high performance RGB (red, green, blue) light-emitting materials have been one of the most important prerequisites to meet requirements for organic light-emitting devices (OLEDs) in full-color displays and white-light lighting.¹ Currently, the development of red-emitting materials lags far behind the green and blue components in both color purity and efficiency.² Pyrene and perylene are two kinds of important polycyclic aromatic hydrocarbons (PAHs) with extended π -conjugated structures and have often been chosen as chromophores for the construction of fluorescent probes, sensors and OLEDs.³ 1,8-Diazapyrenes and 1,12-diazaperylenes, as diaza-analogs of pyrene and perylene, have also been extensively studied in nucleic acid intercalators and nonlinear optical materials.⁴ However, emission wavelengths of pyrene, perylene and their diaza-analogs are relatively short and usually confined to the blue or green light region (Scheme 1).^{3,4} Common red-emitting materials usually have strong charge-transfer character, such as pyran-containing dyes,⁵ or extended π -conjugated structure, such as porphyrins.⁶ We conceive that incorporation of pyrans into large π -conjugated structure could also be an effective construction strategy for red light materials, which means that 1,8-dioxapyrenes and 1,12-dioxaperylenes, as dioxa-analogs of pyrene and perylene, might possess red-emitting property owing to their dipyran-containing extended π -conjugation.

Relative to pyrene, perylene and their diaza-analogs, the reports about dioxapyrenes and dioxaperylenes are scarce.⁷ Derivatives of 1,8-dioxapyrene have been known since the 1990s, an eight-step synthesis and the NMR characterization were

reported in 1993,^{7a} and a simplified four-step synthesis through intramolecular addition of anthraquinone with alkyne was described in 2011.^{7b,7c} In addition, the synthesis of 1,12-dioxaperylene has not been known. Thus, it is necessary to develop a facile and efficient approach to forge 1,8-dioxapyrenes and 1,12-dioxaperylenes for the rapid screening of red light-emitting molecules.



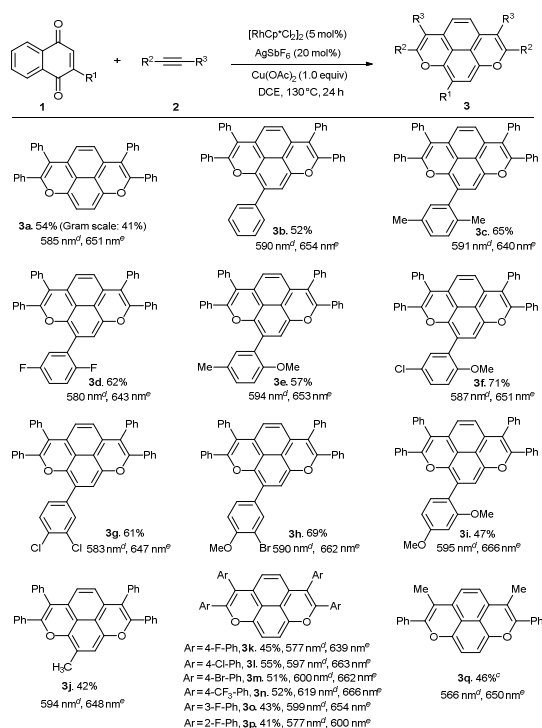
Scheme 1 Synthesis of 1,8-dioxapyrenes and 1,12-dioxaperylenes via Rh-catalysed direct cyclisation.

Transition-metal-catalysed C–H bond activation has made significant advances at the beginning of the 21st century and emerged as one of the most attractive approaches for the straightforward and highly efficient construction of various carbon–carbon and carbon–heteroatom bonds.⁸ Recently, a variety of elaborate design strategies to generate extended π -conjugated PAHs have also been achieved through direct C–H bond functionalisation.⁹ From the viewpoint of synthetic simplicity and atom economy, the direct cyclisation of 1,4-naphthoquinones and 9,10-phenanthraquinones with alkynes through C–H activation strategy is undoubtedly one of the most ideal approaches to forge 1,8-dioxapyrenes and 1,12-dioxaperylenes (Scheme 1).

We began our investigation using the easily accessible 1,4-naphthoquinone (**1a**) and 1,2-diphenylacetylene (**2a**) as model substrates for evaluating the feasibility of the direct cyclisation (Table S1). Pleasingly, the expected reaction occurred, when 5 mol% of [RhCp*Cl₂]₂ was employed as a catalyst and 2.0 equiv of Cu(OAc)₂ as an oxidant (Table S1, entry 2). [Ru(*p*-

cymene)Cl₂]₂ was also found to be an effective catalyst (Table S1, entry 4). Consideration of the reaction mechanism led us to infer that the 1,4-naphthoquinone itself could be used as the internal oxidant, and thus it might be needless to use 2.0 equiv of Cu(OAc)₂ as the external oxidant.¹⁰ Indeed, reducing the amount of Cu(OAc)₂ to 1.0 equiv was found to increase the isolated yield (Table S1, entry 6). A more significant improvement of yield was observed when the amount of solvent was reduced from 1 mL to 0.5 mL (Table S1, entry 7). Further reducing the loading of Cu(OAc)₂ and the amount of solvent led to apparently decreasing yields (Table S1, entries 8 and 9). Other oxidants were screened and Cu(OAc)₂ still turned out to be the best choice (Table S1, entries 11-13). Moreover, it was found that in the absence of PivOH, the use of 1,2-dichloroethane (DCE) as the solvent could further improve the yield (Table S1, entry 17).

Table 1 Rh-catalysed direct cyclisation of 1,4-naphthoquinones with alkynes^{a,b}

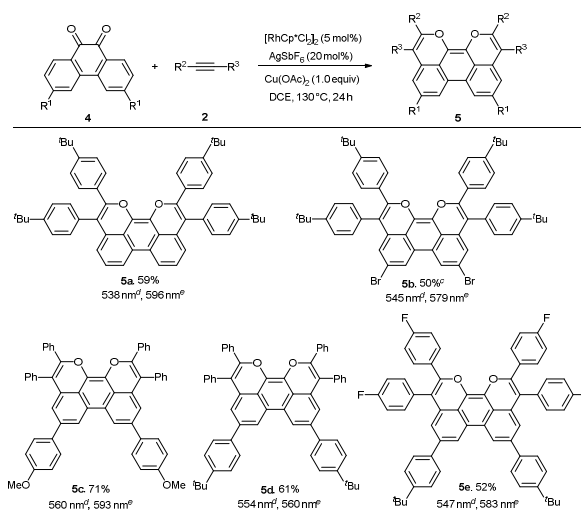


^a Reaction conditions: **1** (0.1 mmol), **2** (3.0 equiv), [RhCp*Cl₂]₂ (5 mol%), AgSbF₆ (20 mol%), Cu(OAc)₂ (1.0 equiv) in DCE (0.5 mL) at 130 °C for 24 h. ^b Isolated yield. ^c PivOH (2.0 equiv) and 1,4-dioxane (0.5 mL) was used instead of DCE. ^d Emission maximum in CH₂Cl₂ (5.0 × 10⁻⁵ M). ^e Emission maximum in solid state.

With optimized reaction conditions, we next examined the scope of 1,4-naphthoquinone and alkyne substrates. As depicted in Scheme 2, a wide range of 2-substituted 1,4-naphthoquinones reacted smoothly with 1,2-diphenylacetylene to afford the 1,8-dioxapyrenes in moderate to good yields. In particular, the bromine-substituted substrate **1h** could be tolerated, giving 69% of **3h**. Various 1,2-diarylacetylenes with fluorine, chlorine, bromine, trifluoromethyl were also subjected to this reaction condition, the desired compounds (**3k-3p**) were obtained in synthetically useful yields. The asymmetrical 1-phenyl-1-propyne could undergo the reaction with 1,4-naphthoquinone, when 1,4-dioxane was employed as solvent and PivOH as an additive,

affording a highly regioselective product **3q**. Unfortunately, this cyclisation reaction did not work for terminal alkynes and dialkyl alkynes. The structure of **3q** was verified by single-crystal X-ray analysis (Fig. S1). The X-ray diffraction (XRD) crystallography data of **3q** showed good planarity of the dioxapyrene core and a strong intermolecular π - π stacking, which explains why the emission of **3q** is significantly red-shifted in solid state compared with in CH₂Cl₂ solution. The large plane structure of **3q** may also be beneficial to a closer molecular packing for efficient charge/hole transport in the material. The direct cyclisation of 9,10-phenanthraquinones with alkynes were also explored (Table 2). Under the optimal condition, various 9,10-phenanthraquinones and 1,2-diarylacetylenes underwent smooth conversion to their corresponding 1,12-dioxaperylene derivatives in moderate to good yields.

Table 2 Rh-catalysed direct cyclisation of 9,10-phenanthraquinones with alkynes^{a,b}



^a Reaction conditions: **4** (0.1 mmol), **2** (3.0 equiv), [RhCp*Cl₂]₂ (5 mol%), AgSbF₆ (20 mol%), Cu(OAc)₂ (1.0 equiv) in DCE (0.5 mL) at 130 °C for 24 h. ^b Isolated yield. ^c PivOH (2.0 equiv) and 1,4-dioxane (0.5 mL) was used instead of DCE. ^d Emission maximum in CH₂Cl₂ (5.0 × 10⁻⁵ M). ^e Emission maximum in solid state.

Given that this catalytic system need only 1.0 equiv of Cu(OAc)₂ as the external oxidant and, moreover, this reaction could occur in the absence of Cu(OAc)₂ (Table S1, entries 6 and 18-19), we speculated that 1,4-naphthoquinone could play a role of the internal oxidant. Therefore, a possible mechanism for the direct cyclisation is depicted in Scheme S1. The coordination of the carbonyl oxygen atom to Cp*Rh(III) and C-H bond activation initially forms a rhodacycle **A**.¹¹ Insertion of alkyne **2a** to the Rh-C bond generates a Rh(III) species **B**. The internal oxidation of quinone to the Rh(III) center might produces a Rh(V) species **C**, which then undergoes reductive elimination to form the naphthol intermediate **D** as the first-step annulation product and regenerates the Rh(III) catalyst.¹² Subsequently, the second-step annulation of 1-naphthol with alkyne through a catalytic cycle between Rh(I) and Rh(III) gives the desired product **3a**.¹³

Subsequently, the photophysical, electrochemical and thermal properties of the resulting 1,8-dioxapyrenes and 1,12-dioxaperylenes were investigated (Table 2, 3 and S2). Fluorescent

spectra and images of partly selected orange and red-emitting 1,8-dioxapyrenes and 1,12-dioxaperylenes are shown in Fig. 1. Notably, most of compounds showed large Stokes shifts up to 8810 cm⁻¹. The emission bands of most of 1,8-dioxapyrenes mainly focus on the orange-red region in CH₂Cl₂. Except for **3p**, emission maxima of all of the resulting 1,8-dioxapyrenes locate at the red light region in solid state. However, 1,12-dioxaperylenes show shorter-wavelength orange-yellow emissions in solid state than those of 1,8-dioxapyrenes.

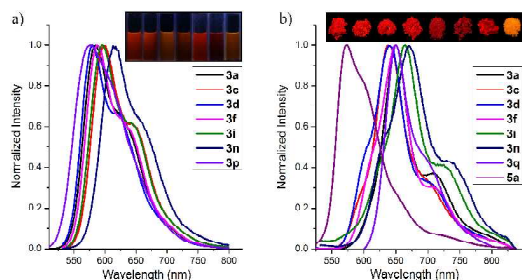


Fig. 1 (a) Fluorescence spectra of selected orange and red-emitting 1,8-dioxapyrenes and 1,12-dioxaperylenes in CH₂Cl₂ (~5×10⁻⁵ M) and (b) in solid state. Insert: Their fluorescence images under UV light (365 nm). From left to right: (a) **3a**, **3c**, **3d**, **3f**, **3i**, **3n**, and **3p**; (b) **3a**, **3c**, **3d**, **3f**, **3i**, **3n**, **3q** and **5a**.

The HOMO and LUMO energy levels determined *via* cyclic voltammetry for **3d**, **3i** and **3q** vary from -4.73 to -4.84 eV and -2.33 to -2.82 eV, respectively (Table 3 and Fig. S3). The electrochemical band gaps were roughly consistent with the optical energy gaps estimated from the absorption edges. The thermal stabilities were evaluated by thermogravimetric analysis (TGA, Table 3, and Fig. S4). Thermal decomposition temperatures (*T_d*, the temperature at which the compounds lose 5% of their weight) of **3d**, **3i** and **3q** range from 342 °C to 419 °C, indicating highly thermal stability.

Table 3 Photophysical, electrochemical and thermal properties of **3d**, **3i** and **3q**

Comp	λ_{onset}^a nm	$E_g^{\text{opt}b}$ eV	$E_{\text{on}}^{\text{ox}}$ V	HOMO eV ^c	$E_{\text{on}}^{\text{red}}$ V	LUMO eV ^d	E_g^{CF} eV	T_d °C ^e
3d	571	2.17	0.04	-4.84	-1.98	-2.82	2.02	373
3i	582	2.13	-0.06	-4.74	-2.07	-2.73	2.01	419
3q	545	2.28	-0.07	-4.73	-2.47	-2.33	2.40	342

^a Estimated from the absorption band edge in CH₂Cl₂ (~5×10⁻⁵ M). ^b $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$ eV. ^c HOMO = -(4.8 + $E_{\text{on}}^{\text{ox}}$) eV. ^d LUMO = -(4.8 + $E_{\text{on}}^{\text{red}}$) eV. ^e Detected by TGA analysis and heating rate = 10 °C/min.

In conclusion, we have developed a facile and efficient method for the synthesis of 1,8-dioxapyrenes and 1,12-dioxaperylenes through Rh-catalysed direct cyclisation of 1,4-naphthoquinones and 9,10-phenanthraquinones with alkynes. Most of the synthesized compounds exhibit orange/red-emitting performance, large Stokes shifts, and highly thermal stability. We expect that these compounds would be applied in optoelectronic devices, such as orange/red-emitting materials in OLEDs, or as models for further developing other 1,8-dioxapyrenes and 1,12-dioxaperylene-based organic materials.

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Notes and references

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