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

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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 the 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 high 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 structures 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 properties owing to their dipyran-containing extended π-conjugation.

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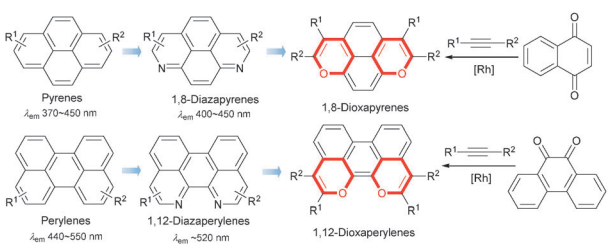
Relative to pyrene, perylene and their diaza-analogs, the reports about dioxapyrenes and dioxaperylenes are scarce.[7] Derivatives of 1,8-dioxapyrene have been known since the 1990s, an eight-step synthesis and the NMR characterization were reported in 1993,[7a] and a simplified four-step synthesis through intramolecular addition of anthraquinone with alkyne was described in 2011.[7b,c] 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.

Transition-metal-catalysed C–H bond activation has made significant advancement in 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 the 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, ESI†). Pleasingly, the expected reaction occurred, when 5 mol% of $[RhCp^*Cl_2]_2$ was employed as a catalyst and



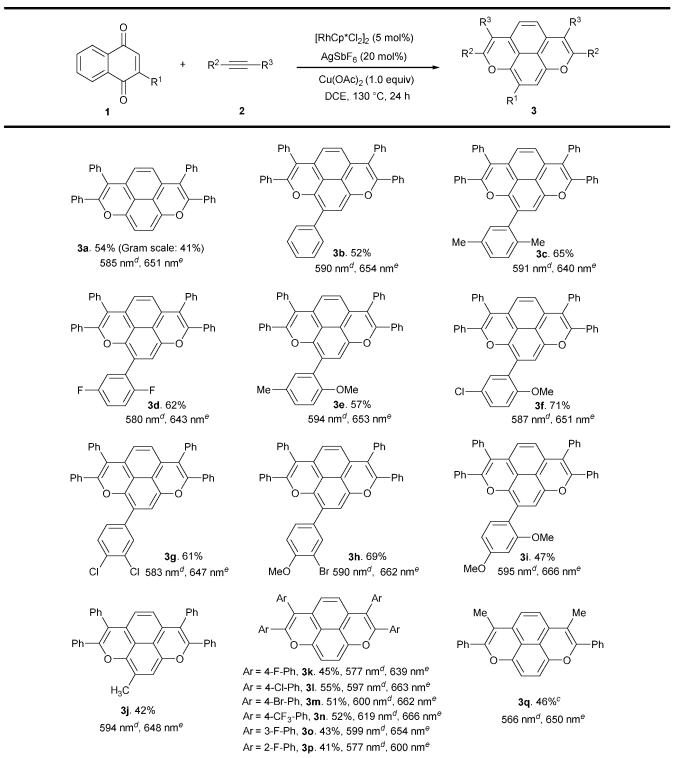

Scheme 1 Synthesis of 1,8-dioxapyrenes and 1,12-dioxaperylenes *via* Rh-catalysed direct cyclisation.

2.0 equiv. of $Cu(OAc)_2$ as an oxidant (Table S1, entry 2, ESI†). $[Ru(p\text{-cymene})Cl_2]_2$ was also found to be an effective catalyst (Table S1, entry 4, ESI†). 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, ESI†). 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, ESI†). Further reducing the loading of $Cu(OAc)_2$ and the amount of solvent led to apparently decreasing yields (Table S1, entries 8 and 9, ESI†). Other oxidants were screened and $Cu(OAc)_2$ still turned out to be the best choice (Table S1, entries 11–13, ESI†). 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, ESI†).

With optimized reaction conditions, we next examined the scope of 1,4-naphthoquinone and alkyne substrates. As depicted in Table 1, 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, and trifluoromethyl were also subjected to these reaction conditions, and 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, ESI†). 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 the solid state compared with in $CH_2Cl_2$ 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 was also explored (Table 2). Under optimal conditions, various 9,10-phenanthraquinones and 1,2-diarylacetylenes underwent smooth conversion to their corresponding 1,12-dioxaperylene derivatives in moderate to good yields.

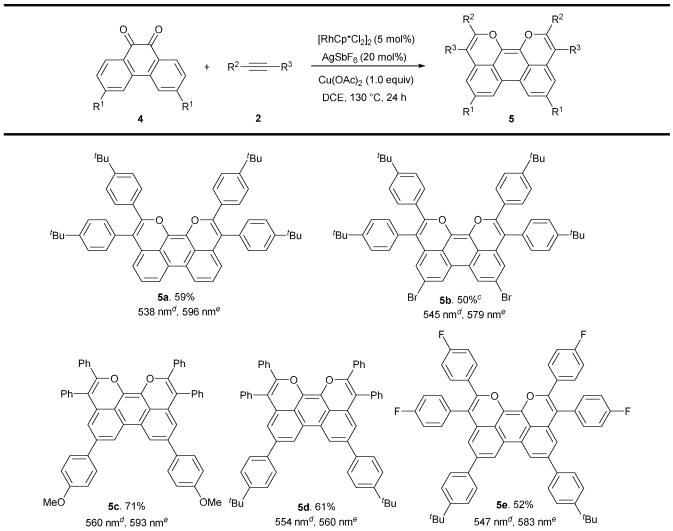
Given that this catalytic system needs only 1.0 equiv. of $Cu(OAc)_2$ as the external oxidant and, moreover, this reaction could occur in the absence of $Cu(OAc)_2$ (Table S1, entries 6, 18 and 19, ESI†), we speculated that 1,4-naphthoquinone could play the role of an internal oxidant. Therefore, a possible mechanism for the direct cyclisation is depicted in Scheme S1 (ESI†). 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 produce a Rh(V) species **C**, which then undergoes reductive elimination to form 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]

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.), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (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 $CH_2Cl_2$ ($5.0 \times 10^{-5}$ M). [e] Emission maximum in the solid state.

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.), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (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 $CH_2Cl_2$ ($5.0 \times 10^{-5}$ M). [e] Emission maximum in the solid state.

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

| Comp. | $\lambda_{onset}$ [a] (nm) | $E_g^{opt}$ [b] (eV) | $E_{on}^{ox}$ (V) | HOMO [c] (eV) | $E_{on}^{red}$ (V) | LUMO [d] (eV) | $E_g^{CV}$ (eV) | $T_d$ [e] (°C) |
|---|---|---|---|---|---|---|---|---|
| **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 $CH_2Cl_2$ ($\sim 5 \times 10^{-5}$ M). [b] $E_g^{opt} = 1240/\lambda_{onset}$ eV. [c] HOMO = $-(4.8 + E_{on}^{ox})$ eV. [d] LUMO = $-(4.8 + E_{on}^{red})$ eV. [e] Detected by TGA analysis and heating rate = 10 °C $min^{-1}$.

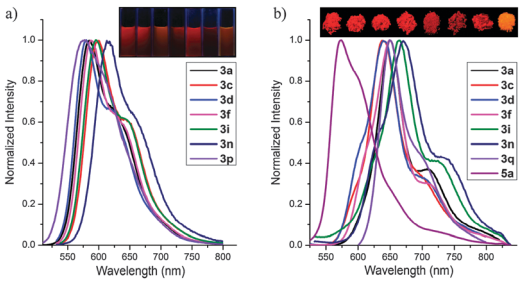



Fig. 1 (a) Fluorescence spectra of selected orange and red-emitting 1,8-dioxapyrenes and 1,12-dioxaperylenes in $CH_2Cl_2$ ($\sim 5 \times 10^{-5}$ M) and (b) in the solid state. Inset: their fluorescence images under UV light (365 nm). From left to right: (a) **3a**, **3c**, **3d**, **3f**, **3i**, **3n**, and **3p**; (b) **3a**, **3c**, **3d**, **3f**, **3i**, **3n**, **3q** and **5a**.

Subsequently, the photophysical, electrochemical and thermal properties of the resulting 1,8-dioxapyrenes and 1,12-dioxaperylenes were investigated (Tables 1–3 and Table S2, ESI†). Fluorescence 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 the compounds show large Stokes shifts up to 8810 $cm^{-1}$. The emission bands of most of the 1,8-dioxapyrenes in $CH_2Cl_2$ mainly focus on the orange-red region. Except for **3p**, emission maxima of all the resulting 1,8-dioxapyrenes in the solid state locate at the red light region. However, 1,12-dioxaperylenes show shorter-wavelength orange-yellow emissions in the solid state than those of 1,8-dioxapyrenes.

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, ESI†). The electrochemical band gaps are 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, ESI†). 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 high thermal stability.

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 high 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-dioxapyrene and 1,12-dioxaperylene-based organic materials.

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