

## A new photophysical insight into high turn-over numbers for H<sub>2</sub> generation by bimetallic photocatalytic complexes

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Hydrogen generating photocatalysts that mimic photosynthesis have been studied intensively in recent years.<sup>[1]</sup> Since the first reports on H<sub>2</sub> evolving bimetallic photocatalysts by Sakai and Rau in 2006<sup>[2]</sup>, many efforts have been made to increase the efficiency. The general structure of a bimetallic photocatalyst involves a number of peripheral ligands connected to a metal centre, and a bridging ligand connecting this photosensitiser and the catalytic centre. Understanding of the fundamental photodynamics is an important step towards the design of improved photocatalysts.

The early-time photodynamics and photocatalytic efficiency have been shown to depend on the nature of the ligands and the catalytic centre.<sup>[3]</sup> A common view is that a favouring population of excited states localised on the bridging ligand is essential for efficient photocatalysis. Hence, the bridging ligand is generally designed to facilitate electron transfer from the photosensitiser to the catalytic centre, and store the photogenerated electron prior to subsequent photochemical reactions. This work however shows that violating this design approach largely improves the hydrogen generation efficiency.

We observed that functionalisation of the peripheral ligands with electron-withdrawing ester moieties largely improves the hydrogen turn-over number (TON). The non-functionalised photocatalyst RuPt (see Fig. 1) shows a TON value of 80, whereas the functionalised analogue EtOOCRuPt outperforms RuPt with a TON of 650.<sup>[4]</sup>

An important effect of ester functionalisation of the peripheral ligands involves a lowering in triplet metal-to-ligand charge transfer (<sup>3</sup>MLCT) energy levels.<sup>[5]</sup> A major consequence is an inversion in inter-ligand internal conversion direction, as evident from femtosecond transient absorption studies (Fig. 1). Ultrafast equilibration (535±17 fs) creates an electron reservoir on

the peripheral ligands of EtOOCRuPt, allowing for a major increase in photocatalytic performance. This insight opens the way towards a novel design strategy for H<sub>2</sub> generating photocatalysts.

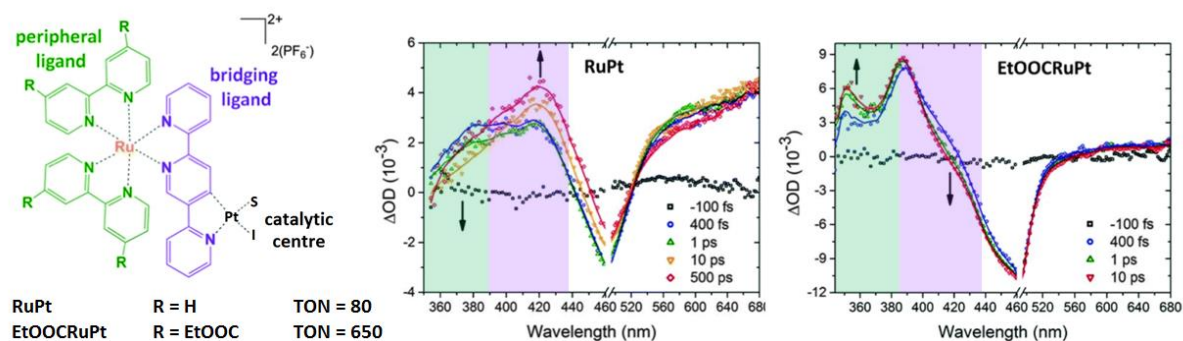


Figure 1. Structure and transient absorption spectra of RuPt and EtOOCRuPt (S = solvent), with fits included as solid curves.<sup>[5]</sup>

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