

## Electron/energy transfer interplay in Quantum Dot-Ir(III) dyads: the role of the connecting unit.

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The electronic processes taking place in Semiconductor Quantum Dots (QDs) functionalised with transition metal complexes (dyads) are object of a growing interest because of their possible applications to water splitting.<sup>[1]</sup> In fact, QDs have recently proved to be among the best sensitizers for light-driven hydrogen evolution in the presence of transition metal complexes.<sup>[2,3]</sup> However, most of the systems reported so far are based on a multicomponent strategy, which does not enable to tune the electron transfer kinetics and may reduce the efficiency of the process. Sensitizer-catalyst conjugated systems are expected show superior catalytic efficiencies with respect to multicomponent architectures.<sup>[4]</sup> A limited number of dyads based on QDs and transition metal complexes has been reported and the role played by the connecting unit in the modulation of electron transfer dynamics in such systems is basically unexplored.

We report the photo and electrochemical study of a family of systems based on CdSe/ZnS core/shell QDs functionalised with several Ir(III) derivatives which differ only in the connecting unit. The most common connecting units (i.e. amine, dithiocarbamate, carboxylic and phosphonic acids) used for QDs functionalization have been investigated (Fig. 1).<sup>[5]</sup>

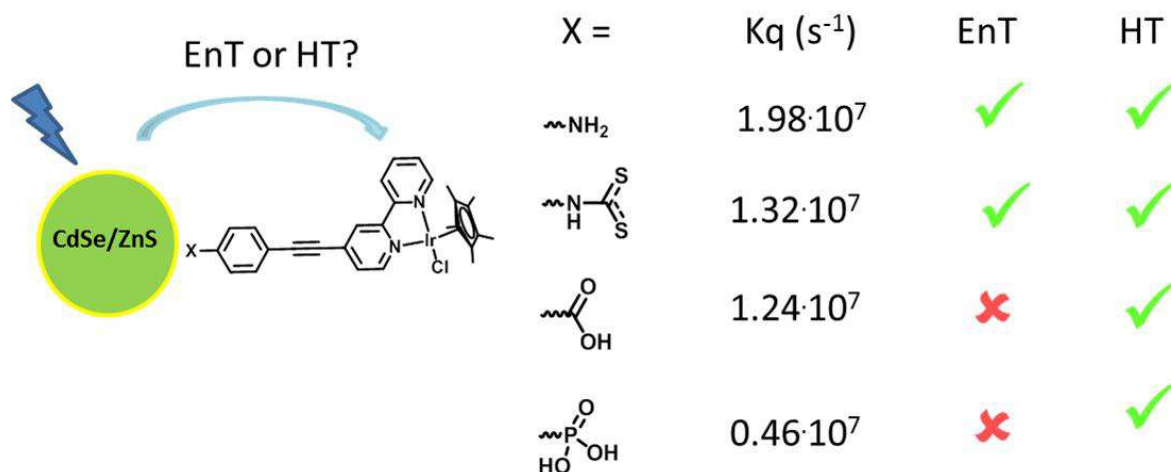


Figure 1. Quenching constants (k<sub>q</sub>) of QD-based dyads conjugated with a family of Ir(III) complexes with different conjugation unit.

The results of this study show that the chemical nature of the connecting unit induces major changes in the energy/electron transfer efficiency and suggest that the most common connecting units used for the functionalization of QDs (namely amine and dithiocarbamate) are probably not suitable for an efficient electron transfer in dyads.

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**References:**

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