

# Photophysical characterization of bis(acridinium-porphyrin) and bis(acridane-porphyrin) receptors



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## Introduction

Multi-responsive molecular systems for information transmission can be obtained by exploiting orthogonal stimuli that trigger differentiated behaviours. In this perspective, N-substituted acridinium units are particularly intriguing as building blocks in the design of supramolecular entities since they act as chemo-, electro- or photo-triggered molecular switches by modifying their chemical and electronic structure upon application of different stimuli [1]. Indeed, it is possible to switch between acridinium and acridane units by means of chemical and photochemical triggers. Besides, metallo-porphyrins are interesting components to be included in the design of molecular switches, since they can act as versatile supramolecular receptors thanks to their extended aromatic  $\pi$ -system able to interact with electron poor guest molecules. It has been reported that in some host-guest systems, where acridinium units and porphyrins are involved, a fast photoinduced electron transfer (eT) process between the porphyrin host and the acridinium guest takes place [2,3,4].

## Steady-State Photophysical characterization

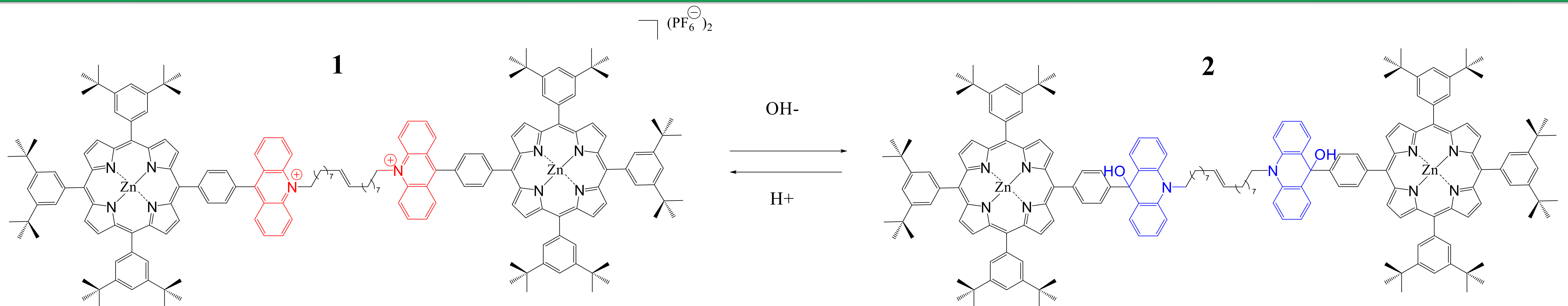


Figure 1: Chemical structure of the bis(porphyrin-acridinium) (1) and bis(porphyrin-acridane) (2) conjugates.

Both acridinium and porphyrin-based emissions of **1** are quenched at RT with respect to isoabsorbing porphyrin and acridinium models, while at 77K porphyrin emission is retrieved (Figure 2). This quenching can be ascribable to the occurrence of a fast photoinduced eT process at RT, which depopulates the lowest singlet excited states of both components in the array and that is disfavoured at 77 K because of the hampered solvent reorganization around the produced charged species.

On the other hand, conjugate **2** retains porphyrin emission properties and a sensitization of the porphyrin emission occurs upon excitation of acridinium moieties (Figure 2, b). This leads to conclude that a quantitative energy transfer process (ET) takes place between acridane and porphyrin units.

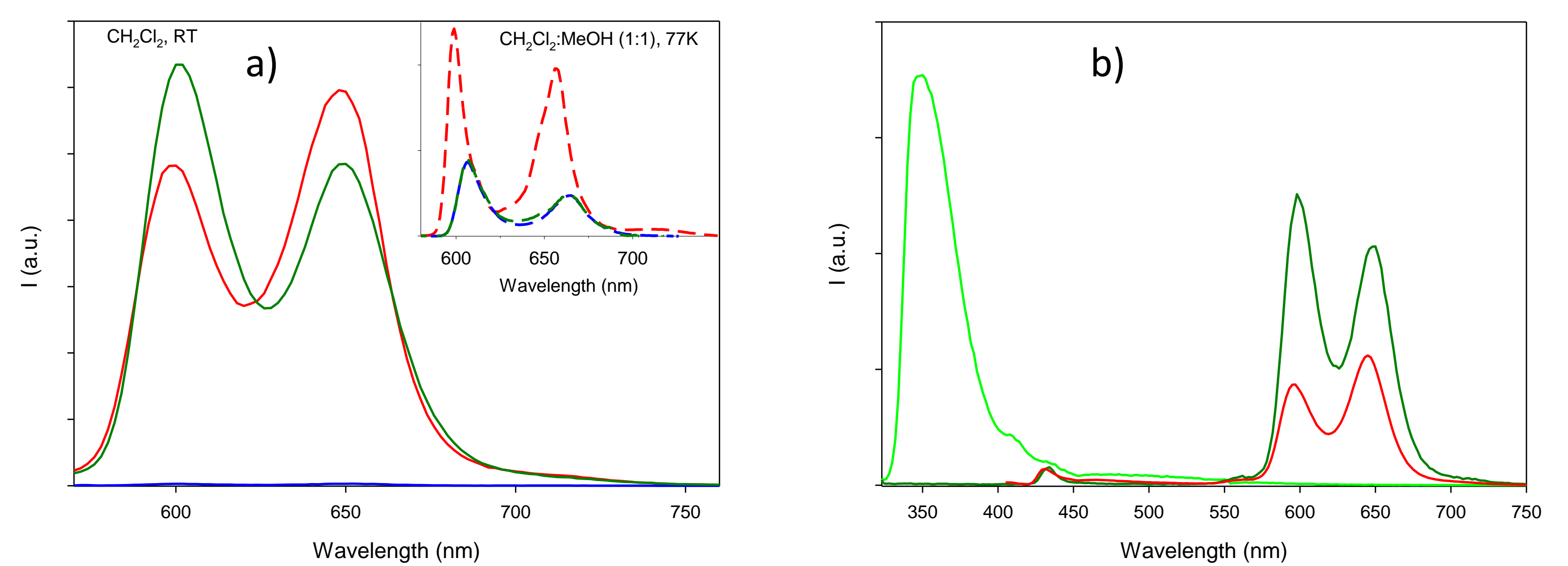


Figure 2: Emission spectra of isoabsorbing solutions of: a) porphyrin (red), **1** (blue) and **2** (dark green) at RT in  $\text{CH}_2\text{Cl}_2$  (inset: at 77 K in  $\text{CH}_2\text{Cl}_2:\text{MeOH}$  (1:1)) upon porphyrin selective excitation ( $\lambda_{\text{exc}} = 550 \text{ nm}$ ); b) acridane (light green), porphyrin (red) and **2** (dark green), upon acridane predominant excitation ( $\lambda_{\text{exc}} = 362 \text{ nm}$ ).

## Transient Absorption Spectroscopy

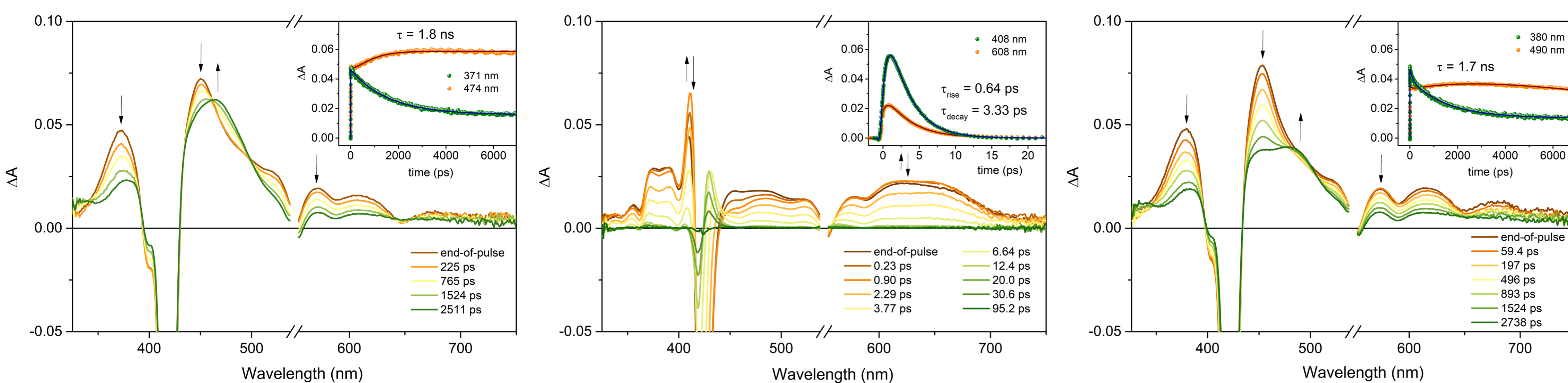


Figure 3: Transient absorption spectra of (a) porphyrin, (b) **1** and (c) **2** in  $\text{CH}_2\text{Cl}_2$  at different delays. Excitation at 550 nm. Insets:  $\Delta A$  time evolutions (dots) and fittings (lines) at the indicated wavelengths.

**2** and the porphyrin model present a spectral evolution typical of  $S_1 \rightarrow T_1$  intersystem crossing: the spectrum of the singlet decays and that of the triplet (470 nm) forms within the same kinetics. In **1** formation of bands in the 600-700 nm region and a peak at 410 nm occurs on a very fast time scale (0.64 ps) and other bands at ca. 480 nm and 520 nm are present at the end-of-pulse. The species that forms on ultrafast time scales can be ascribed to the charge-separated state  $\text{ZnP}^+-\text{Acr}^*$ .

## Conclusions

The presence of acridinium or acridane units strongly affects the photophysical processes involved in the deactivation path occurring in the systems (Figure 4) so, by changing the state of the acridane/acridinium component, we can tune the emission properties. Thanks to this, they can act as efficient multi-responsive switches light-, pH- and voltage-dependent.

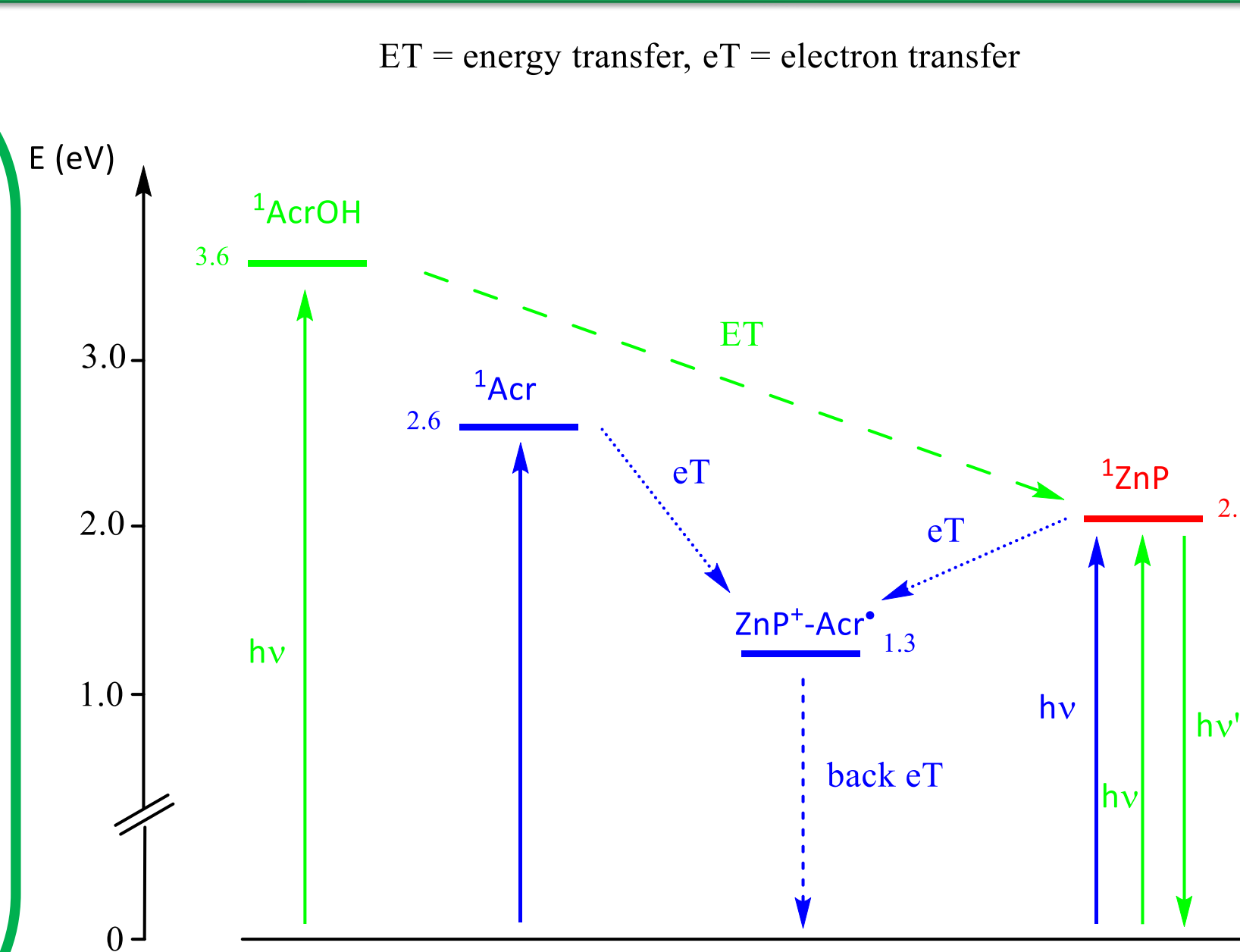


Figure 4: energy levels and photoinduced processes in **1** and **2**.

## References and acknowledgements

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