

Elucidation of the Key Role of $[\text{Ru}(\text{bpy})_3]^{2+}$ in Light-Mediated RAFT Polymerization

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Free Radical PhotoPolymerization (FRPP) is mainly limited by a lack of control of the macromolecular chain size, because of transfer and termination reactions. Photocontrolled processes have been proposed in order to overcome this problem: photoiniferters, photo-ATRP, Reversible Addition-Fragmentation Transfer (RAFT) photopolymerization... Recent works have presented the transition of the latter process from UV sources to visible LEDs thank to the use of organometallic complexes as photosensitizers.^[1-2] This study elucidates the actual photochemical mechanism governing the initiation step photosensitized by the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex (Fig. 1). Cyclic voltammetry and laser flash photolysis experiments are combined to quantum mechanical calculations and show that photoinduced electron transfer has to be excluded in favor of a triplet energy transfer mechanism (PET). Indeed, experimental results are consistent with the Balzani model for energy transfer (Fig. 1). Mechanistic results are finally correlated to polymerization experiments, taking into account the thermodynamics of the reaction and the ease of dissociation of the RAFT agent.^[3]

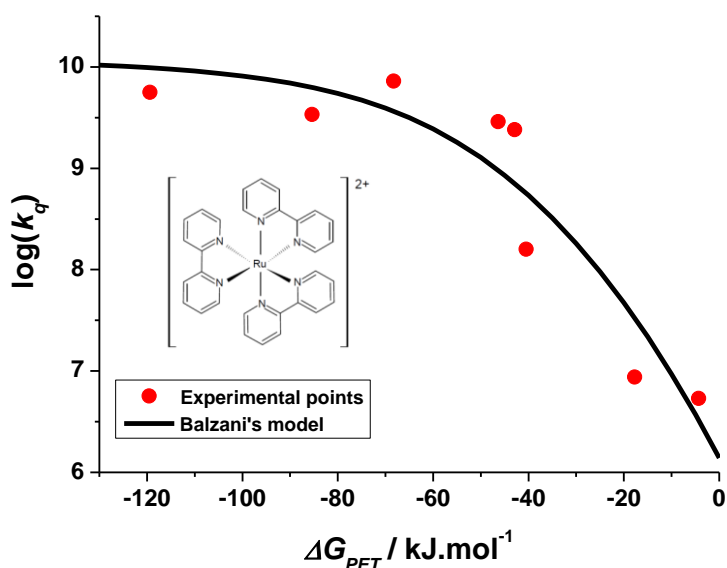


Figure 1. Application of Balzani's non-vertical energy transfer model to experimental data coupled to simulation results (insert: $[\text{Ru}(\text{bpy})_3]^{2+}$ chemical structure).

References:

- [1] J. Xu, K. Jung, C. Boyer, *Macromolecules*, **2014**, 47, 4217.
- [2] J. Yeow, J. Xu, C. Boyer, *ACS Macro Lett.*, **2015**, 4, 984.
- [3] J. Christmann, A. Ibrahim, V. Charlot, C. Croutxé-Barghorn, C. Ley, X. Allonas, *ChemPhysChem*, **2016**, 17, 2309.