

Symmetry drives fused nanographene-metalloporphyrin conjugates photophysics

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Femtosecond optical transient absorption spectroscopy is employed to study, for the first time, photoexcited carrier relaxation in β -,meso-, β -triplyfused porphyrin-nanographene conjugates **AS** and **S**^[1]. These compounds are panchromatic nanographenes (NGs) with an onset of absorption matching the solar spectrum, making these compounds suitable candidate for high efficiency solar cells.

Symmetry has a profound effect of the excited state pathways in these molecules. The symmetric structure, (**S** orange region Fig.1a), depicts a strong picosecond excited state funnelling towards the Ni-Porphyrin centre, which preserves an electronic metal centred character, in contrast with the larger interplay of the nanographene on the absorption spectrum. The asymmetric structure instead (**AS** orange region Fig.1a), displays excited-state among the fused conjugated ribbon, allowing the appearance of stimulated emission and photoluminescence at 955 nm (1.3 eV) as well as an overall faster decay kinetics than in **S**. Hence, the substitution symmetry can be used as a versatile tool for tuning the opto-electronic properties of these NGs.



Figure 1. a) Structures of triply fused porphyrin-nanographene conjugates AS and S [1], the orangre regions indicate the deexcitation regions in each molecule. b) Differential transmission signal obtained for conjugates AS and S after pumping with a 778 nm laser and 605 nm respectively.

[1] Q. Chen, L. Brambilla, L. Daukiya, K. S. Mali, S. De Feyter, M. Tommasini, K. Müllen, A. Narita, Angew. Chem., 2018, 57, 1123.