Probing the formation of reactive oxygen species by a porous self-assembled benzophenone *bis*-urea host

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Abstract: Sensitized photooxidations are of interest due to their diverse range of applications spanning from wastewater treatment to medicinal chemistries, including photodynamic therapy for cancer treatment. Sensitized photooxidations occur through two distinct reactive oxygen species, singlet oxygen and superoxide. Superoxide is generated through a one-electron reduction of molecular oxygen, which can go on to form a variety of peroxide species such as hydrogen peroxide and hydroxyl radicals. Conversely, singlet oxygen is a simple yet reactive oxidant generated through a triplet-triplet annihilation pathway when molecular oxygen is irradiated in the presence of a photosensitizer at an appropriate wavelength. Here, we investigate the role of oxygen in the selective photooxidation of small molecules within a self-assembled benzophenone *bis*-urea macrocycle (host **1**) using electron paramagnetic resonance (EPR) and UV visible spectroscopy. EPR studies indicate that host **1** can activate O_2 to singlet oxygen as well as superoxide. Although superoxide formation was only observed in polar protic solvents, which introduces the possibility of tuning the photooxidation mechanism based on solvent choice. We further explored the quantum yield for singlet oxygen production by host **1** using UV-vis and EPR spectroscopy in order to compare the two methods. Current work is focused on applying this host to mediate singlet oxygen photoreactions of small alkene guests catalytically.