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(G*) Bio-Inspired Azobenzene Photoswitches as a Novel Platform for Optical Oxygen Sensing

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Hypoxia is a characteristic pathophysiological property of advanced solid tumours which influences aggressiveness and resistance to treatment. Real-time measurement of tumour oxygenation is thus vital for stratifying treatment plans by hypoxic severity and monitoring variations in partial pressure of oxygen (pO_2) caused by high energy X-ray and other photonic therapies. Azobenzene photoswitches present a novel form of oxygen sensing predicated on their photophysical properties. Upon irradiation with light, azobenzenes undergo reversible geometric isomerization between stable *trans* and metastable *cis* isomers. The rate of *cis-trans* thermal relaxation is a first-order process sensitive to the molecular environment, which translates into sensor functionalities. In this work, we investigate a novel bio-inspired azobenzene photoswitch for oxygen sensitivity in solution.

A biomimetic material, $FePc(PAP)_2$ was synthesized by coordination of 4-phenylazopyridine (PAP) to iron (II) phthalocyanine (FePc). As a model system for oxygen sensing, FePc is capable of binding oxygen similarly to heme-porphyrin in blood. Solutions were purged with argon gas or flowed with oxygen gas to modulate pO_2. Isomerization kinetics were measured by pump-probe isomerization spectroscopy, wherein photoisomerization was initiated by irradiation with a 600 mW 365 nm LED, and then recovery of the π-π^* absorption band was monitored as a function of time with a spectrophotometer. In addition, density functional theory (DFT) was used to theoretically calculate the activation barrier between *cis* and *trans* isomers, which can be related to isomerization rates in the presence or absence of oxygen.

To validate our experimental setup, *cis-trans* isomerization rates of methyl orange and methyl red photoswitches were measured to be insensitive to oxygen, as expected from literature. As a control, the isomerization lifetime of PAP was found to be several hours in ambient oxygenation. DFT calculations predict that the isomerization rate of a PAP-porphyrin system is an order of magnitude faster than PAP. As a proof-of-principle demonstration of a new molecular sensor for evaluating tumour oxygenation, the isomerization rates of PAP and $FePc(PAP)_2$ were experimentally and computationally determined as a function of oxygen concentration and will be reported in this work.

Keyword-1

Photoswitches

Keyword-2

Optical sensing

Keyword-3

Oxygen

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