Accelerating the characterisation of molecular photoswitches for solar thermal energy storage

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1. Introduction

To combat climate change and contamination, the drive from fossil fuels to renewable energy sources is a necessity. A recent development to limit carbon dioxide emissions from heating uses molecular photoswitches capable of storing solar energy in a meta-stable isomer and releasing the energy as heat [1]. Molecular solar thermal energy storage is garnering interest as a zero-emission alternative to conventional heating methods. The molecular properties of the molecular photoswitch are crucial in determining the efficiency. The most important properties include the energy density, the storage time, photoconversion quantum yield and solar spectrum overlap. Fortunately quantum chemistry can assist in predicting most of the properties in a reasonable time frame [2, 3, 4]. However, the photoconversion quantum yield can be very time-consuming to predict computationally, such that in some cases the faster method is simply to synthesise and measure [5]. Previously, we have examined the prospects of experiment acceleration using flow chemistry and advanced spectroscopic methods [6, 7]. In this work, we present an accelerated method for determining the photoconversion quantum yield experimentally. Additionally, we showcase the potential for utilising artificial intelligence in predicting the photoconversion quantum yield for novel and existing compounds.

2. Results and discussion

Here, we present a fully automated photoisomerisation and kinetics characterization setup designed to quantitatively study key physical properties of molecular photoswitches. As shown in Fig 1, the system integrates high-precision spectroscopic measurements with programmable light sources, valves and pumps, leading to a system that enables simultaneous monitoring of both photoconversion and thermal back-conversion rates. The setup is optimised for high-throughput investigations and provides real-time data that allows for monitoring the behaviour of the photoswitches. The design allows for precise control of the experimental parameters, including light intensity, wavelength, and temperature, ensuring accurate and reproducible results across diverse molecular systems. We demonstrate the utility of the automated system by characterizing the photoisomerisation kinetics and thermal back-conversion of three representative photoswitch classes: norbornadiene-quadricyclane (NBD-QC), bicyclooctadiene-tetracyclooctane (BOD-TCO), and the *trans-cis* isomerisation of azobenzene (AB). These molecules have been selected for their relevance in energy storage (NBD and BOD) and molecular machine applications (azobenzene). Employing this automated platform, we provide detailed insights into the kinetic behaviour of these systems, highlighting the role of structural features and local environmental factors in influencing their isomerisation dynamics. The data is analysed using an in-house developed Python program with broad and generalised applicability. The results underscore the potential of this setup to accelerate the development and optimization of molecular photoswitches for advanced technological applications.

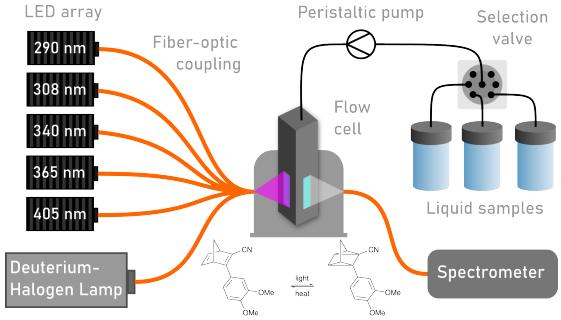

Fig. 1: Schematic of the automated photoswitch characterisation setup.

	This work		Reference work	
Molecule	QY	HL (25 °C)	QY	HL (25 °C)
NBD	0.689	27 d	0.681	28.7 d [8]
BOD	0.146	63 s	0.14432	79.8 s [9]
AB	0.148	6.78 d	0.1553	7.34 d [10]

Table 1: A comparison of obtained values in this work and reference values from the literature to establish credibility.

Furthermore, the acceleration of molecular property characterisation can lead to more data which can be used to develop or improve machine learning algorithms. Here, we present a small-scale example of a graph convolutional neural network predicting photoconversion quantum yields for norbornadiene type photoswitches with a dataset consisting of 50 molecules.

Parameter	Value
Dataset size	50
Max epochs	100
Learning rate	0.005
Test ratio	80/20
Sample ratio	80/20

Table 2: List of hyperparameters used in the graph-convolutional neural network.

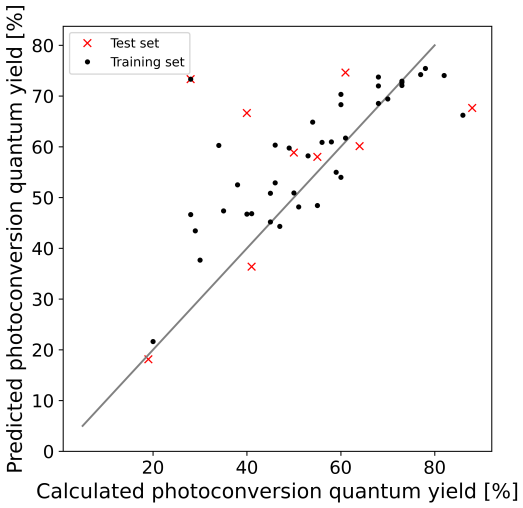

Fig. 2: Comparison of the results from the machine learning algorithm and the actual measurements of photoconversion quantum yield.

2.1 Photoconversion quantum yield prediction

Several works in recent years has combined machine learning with prediction of molecular physiochemical properties [11, 12]. These works include the prediction of molecular properties such as fluorescence emission wavelength and quantum yield, however, no published works has shown the prospects of predicting photoisomerisation quantum yield. In this work, a graph-convolutional neural network was developed to predict the photoisomerisation quantum yield of the 2,2-cyclo-addition of the norbornadiene-quadricyclane photoswitch pair (NBD-QC).

The neural network was constructed using Python and the Python program package Pytorch. Using a set of hyperparameters described in Table 2, we obtain a the correlation between the actual and the predicted values for the photoconversion quantum yield as shown in Fig. 2.

As generally known, the size of the dataset when using machine learning is a huge factor. Unfortunately, this type of data has been too laborious to obtain, but with with our accelerated platform for characterising the molecular properties, we hope to increase the production of solid data for future machine learning algorithms.

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