Library of Cationic Organic Dyes for Visible-Light-Driven Photoredox Transformations

The field of photoredox catalysis has grown exponentially in the last decade because it provides synthetic chemists with a means to perform free-radical reactions under mild conditions and irradiation from simple, household light sources. In a vast majority of the contributions, these transformations have been mediated by transition-metal catalysts, in particular polypyridyl ruthenium and iridium complexes, decreasing the economic benefit of these reactions. However, the possibility of using metal-free catalysts, such as organic dyes, for achieving efficient light-mediated photoredox reactions is an attractive option, as they offer a variety of environmental and economic benefits. Recently, the group of Professor Juan C. (Tito) Scaiano from the University of Ottawa (Canada) has reported a systematic study of the efficiency of cationic organic dyes as catalysts for photoredox transformations. In this work, the ability of four different classes of organic dyes to mediate photoredox transformations was examined using two model reactions, the debromination of *meso*-1,2-dibromo-1,2-di-phenylethane, and the nitromethylation of a tertiary amine at the α-amino position, also known as the light-mediated aza-Henry reaction (Scheme 1). The authors were able to correlate the observed activity of the organic dye with the rate constants of mechanistically key steps, demonstrating the importance of proper kinetic analysis for understanding the underlying mechanism of photoredox systems. However, the

goal of this contribution by Scaiano and co-workers was not only to demonstrate that these dyes can mediate photoredox reactions, but also to increase their popularity among practitioners of photoredox by carefully analyzing all of the relevant photophysical and electrochemical properties of these dyes, and to compile this information in a single, open-access contribution that would allow practitioners of photoredox easy access to the data.
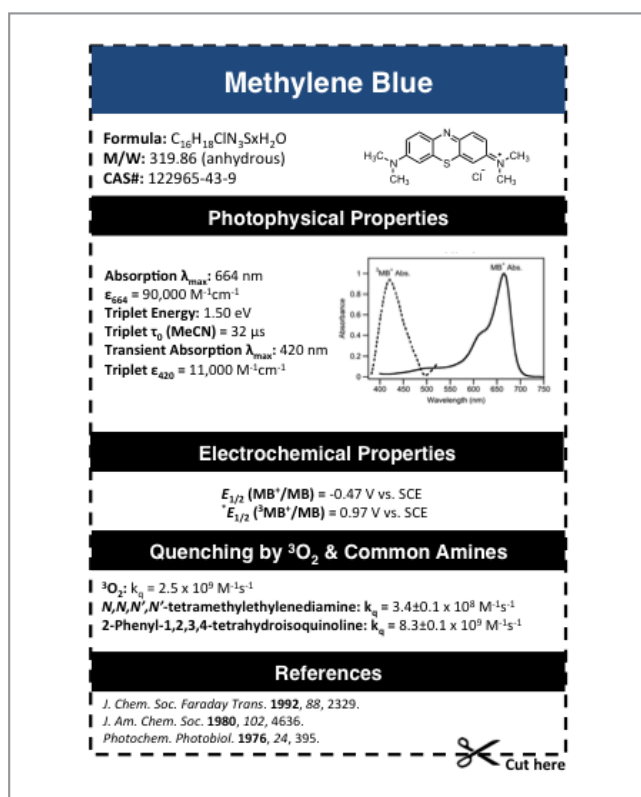
"The popularity of transition-metal catalysts, in particular $Ru(bpy)_3Cl_2$, in photoredox transformations stems from the fact that these complexes are well characterized in the literature. In fact, much of this data has been available since the 1970s for many of these complexes, including countless reviews on the photophysics of $Ru(bpy)_3Cl_2$," said Professor Scaiano. "On the other hand, organic dyes, which we have shown can be excellent metal-free alternatives for photoredox transformations, do not have the same collection of data available. Therefore, chemists who practice photoredox catalysis tend to stick with catalysts where the electrochemistry and photophysics are already known, instead of using organic dyes where the same data is either unknown or difficult to find," he added.

Professor Scaiano explained: "We hand-picked 13 different organic dyes, as well as three popular photoredox catalysts in $Ru(bpy)_3Cl_2$, $Ir(ppy)_3$, and 9-mesityl-10-methylacridinium
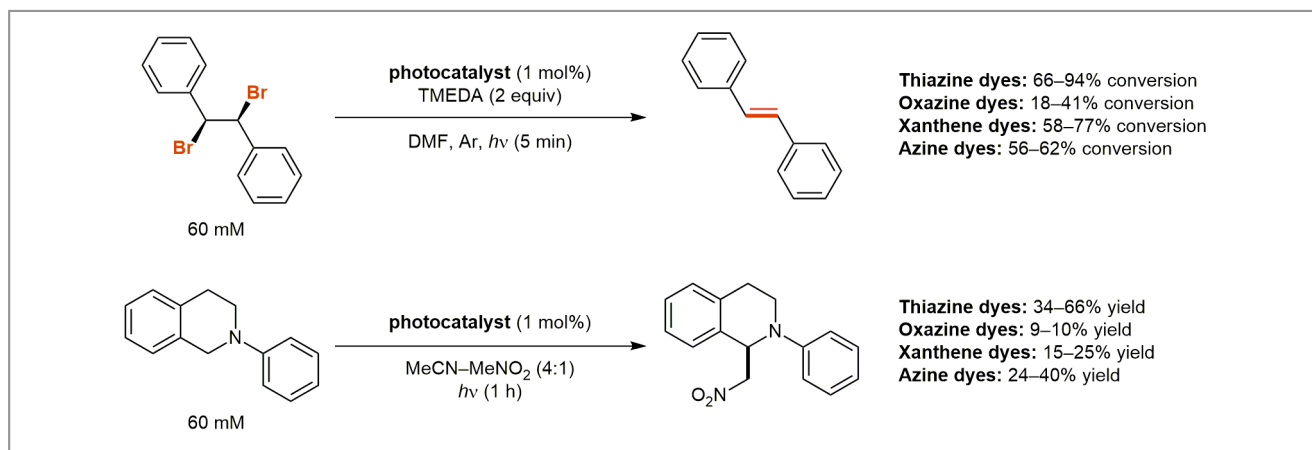
Scheme 1 The model photoredox reactions used to evaluate the photocatalytic efficiency of the organic dyes examined in this work

perchlorate, and fully characterized both their photophysical and electrochemical properties. We compiled these data, and included them as an Appendix section in our recent contribution in *ACS Omega*." The Appendix, located in the later pages of the manuscript, provides 'cards' with detailed descriptions of all the relevant photophysical and electrochemical data chemists who practice photoredox would require to design a photocatalytic system. An example of information the Appendix provides is demonstrated in Figure 1, which shows the Appendix 'card' for the thiazine dye Methylene Blue.

Methylene Blue

Formula: $C_{16}H_{18}ClN_3SxH_2O$
M/W: 319.86 (anhydrous)
CAS#: 122965-43-9

Photophysical Properties

Absorption λ_{max}: 664 nm
ε_{664} = 90,000 $M^{-1}cm^{-1}$
Triplet Energy: 1.50 eV
Triplet τ_0 (MeCN) = 32 μs
Transient Absorption λ_{max}: 420 nm
Triplet ε_{420} = 11,000 $M^{-1}cm^{-1}$

Electrochemical Properties

$E_{1/2}$ (MB^+/MB) = -0.47 V vs. SCE
$^*E_{1/2}$ ($^3MB^+/MB$) = 0.97 V vs. SCE

Quenching by $^3O_2$ & Common Amines

$^3O_2$: k_q = 2.5 x 10^9 $M^{-1}s^{-1}$
N,N,N',N'-tetramethylethylenediamine: k_q = 3.4±0.1 x 10^8 $M^{-1}s^{-1}$
2-Phenyl-1,2,3,4-tetrahydroisoquinoline: k_q = 8.3±0.1 x 10^9 $M^{-1}s^{-1}$

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Figure 1 Appendix card for Methylene Blue as published in *ACS Omega* (image reused with permission from: Pitre, S. P.; McTiernan, C. D.; Scaiano, J. C., "Library of Cationic Organic Dyes for Visible-Light-Driven Photoredox Transformations", *ACS Omega* **2016**, *1*, 66–76)

To conclude, Professor Scaiano stated: "We envision that this collection of data will help popularize organic dyes as photoredox catalysts, as for the first time all the pertinent information for these dyes will be easily accessible in a single document."

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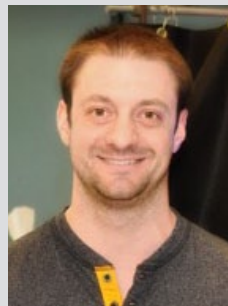
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Spencer P. Pitre received his B.Sc. in chemistry in 2012 from the University of Prince Edward Island (Canada) before joining the Scaiano group at the University of Ottawa (Canada) in autumn 2012 as a Ph.D. candidate. His current research interests involve the development of both precious-metal-free and heterogeneous alternatives for photoredox catalysis.

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Christopher D. McTiernan received his B.Sc. in biochemistry (2008) and M.Sc. in chemical sciences (2010) from Laurentian University (Canada) before joining the Scaiano group at the University of Ottawa (Canada) in autumn 2011 as a Ph.D. candidate. His current research interests involve the study of photoredox reaction mechanisms and the development of heterogeneous systems for photocatalysis.

Prof. J. C. (T.) Scaiano

Juan C. (Tito) Scaiano came to the National Research Council (NRC) in Ottawa (Canada) from Argentina in 1975 to join the Ingold group. After holding a position at the University of Notre Dame (USA, 1976–1979), he returned to the NRC in 1979, where he studied organic reaction intermediates using laser techniques. In 1991, he joined the University of Ottawa, where he is currently a Distinguished University Professor and holds the Canada Research Chair in Applied Photochemistry. His current interests include the study of organic photochemistry and reaction mechanisms, the application of nanomaterials to organic chemistry, single-molecule catalysis, and biomaterials.