ENZYMATIC SYNTHESIS OF NOVEL INDIGOID PIGMENTS

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Indigo is one of the oldest pigments used in the dyeing industry. With the rise of modern sciences, we gained the ability to modify the indigo molecule and create new pigments with novel applications, based on special semiconductor properties [1-3]. Compared to silicon semiconductors, indigoid pigments have the advantage of being biodegradable and also very stable when exposed to air and water [4]. In order to overcome the hazardous effects of chemical indigo modifications, enzymatic synthesis was used to obtain novel variants of indigo [5,6]. Nevertheless, the selection of indigoids with desirable chemical modifications is still insufficient.

Here, a set of new indigoid pigments synthesized by employing bacterial enzymes is presented. Screening of metagenomic libraries for indole-oxidizing activities revealed several oxygenase enzymes, capable of oxidizing indole derivatives to corresponding indigo derivatives. In total, seven different oxygenases capable of performing oxidation of 24 different indole derivatives to corresponding indigoid pigments were characterized. Indigoids synthesized by these enzymes were the following: different regioisomers of indigo dimethanol and indigo dicarboxaldehyde, 5,5'-diaminoindigo, 5,5'-di(aminoethyl)indigo, 5,5'-difluoroindigo, 5,5'-dihydroxyindigo, indigo-5,5'-dicarbonitrile, indigo-5,5'-dicarboxamide, 5,5'-dibrom-7,7'-diiodoindigo, 5,5'-dichloro-7,7'-diiodoindigo, 7,7'-diiodoindigo, 7,7'-diiodoindigo,

To our knowledge, production of some of these pigments has not been reported neither by chemical nor enzymatic methods to date. Due to different spectral properties and additional chemical modifications, these indigoid pigments are potential nanomaterials for novel applications.

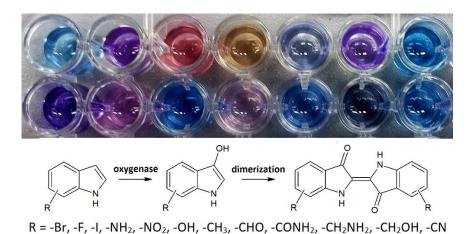


Fig. 1. Diversity of indigoid pigments obtained using oxygenases.

^[1] K. Ramig, O. Lavinda, D. J. Szalda et al., The nature of thermochromic effects in dyeings with indigo, 6-bromoindigo, and 6,6'-dibromoindigo, components of Tyrian purple, Dyes and Pigments, 117, 37–48 (2015).

^[2] P. Deng, Y. Lei, X. Zheng et al., Polymer based on benzothiadiazole-bridged bis-isoindigo for organic field-effect transistor applications, Dyes and Pigments, 125, 407–413 (2016).

^[3] B.-Y. Ren, Q. Xu, M. Kolaczkowski et al., Bay-annulated indigo derivatives based on a core of spiro[fluorene-9,9'-xanthene]: Synthesis, photophysical, and electrochemical properties, Dyes and Pigments, 160, 25–27 (2019).

^[4] E. D. Glowacki, G. Voss, N. S. Sariciftci. 25th anniversary article: progress in chemistry and applications of functional indigos for organic electronics, Advanced Materials, 47, 6783–6800 (2013).

^[5] Frabel S, Wagner B, Krischke M, Schmidts V, Thiele CM, Staniek A, Warzecha H. Engineering of new-to-nature halogenated indigo precursors in plants. Metabolic Engineering, 46, 20–27 (2018).

^[6] Namgung S, Park HA, Kim J, Lee PG, Kim BG, Yang YH, Choi KY. Ecofriendly one-pot biosynthesis of indigo derivative dyes using CYP102G4 and PrnA halogenase. Dyes and Pigments, 162, 80–88 (2019).