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Photoinduced Arylation of Acridinium Salts: Tunable Photoredox Catalysts for C=O Bond Cleavage

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PURPOSE OF THE ABSTRACT

The valorization of lignins under sustainable conditions provides greener opportunities for industry and academia to produce aromatic building blocks out of bio-sources. Especially, the visible-light-driven fragmentation of C=O bonds has gained an increasing interest and meets the requirements of sustainability. In this context, the photocleavage of C=O bonds appears to be a suitable strategy for the eco-friendly valorization of lignins, owing to light offers advantages of simple, cheap energy source allowing the production of highly reactive (radical) intermediates under mild conditions.[1,2] Among Photoredox catalysts, acridinium-based molecules are used as strong oxidizing organic photoredox catalysts (OPCs), in which their photophysical and electrochemical properties can be modulated by incorporating functional group(s) at diverse positions. Since the development of Fukuzumi's catalyst (aryl = mesityl) several Fukuzumi's congeners with tuned photoredox properties (E_{Red}^* up to 2.26 V vs SCE) were studied by pioneer research groups.[3] This molecular diversity enables acridinium-dyes to be complementary or be even competitive with polypyridyl transition metal photoredox catalysts.

In this communication we will report the novel access to a wide library of acridinium-based catalysts.[4] The impact of the nature of the C9-aryl group on the photoredox properties will also be discussed in detail. The introduction of only one bulky group, such as bromo, at the 2'-position, is sufficient to improve the quantum yield and the excited live time due to an orthogonal orientation of the Ar and Acr⁺ moieties. This streamline has allowed designing a novel organic photoredox for the C=O/Ar fragmentation of diol monoarylethers to afford 1,2-diols in good yields that constitutes a vital step toward converting lignin to value-added low-molecular-weight aromatics. Current efforts to understand and extend this process to native lignin will be also presented.

FIGURES

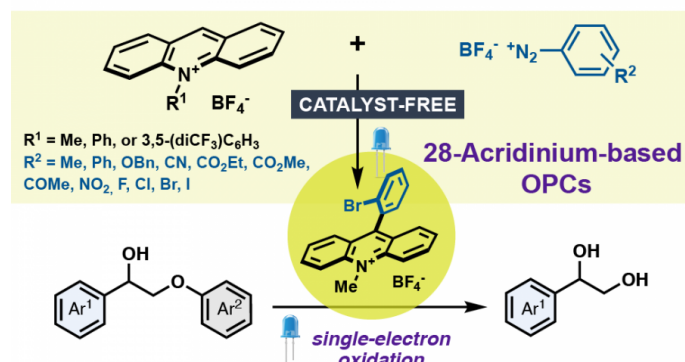


FIGURE 1

Figure 1

Acridinium-based OPC for C-O bond fragmentation

FIGURE 2

KEYWORDS

Photoredox catalysis | lignin | fragmentation | visible light

BIBLIOGRAPHY

- [1] (a) Kärkäs, M. D.; Bosque, I.; Matsuura, B. S.; Stephenson, C. R. J., *Org. Lett.* 2016, 18, 5166-5169; (b) Bosque, I.; Magallanes, G.; Rigoulet, M.; Kärkäs, M. D.; Stephenson, C. R. J., *R ACS Cent. Sci.* 2017, 3, 621-628; (c) Luo, N.; Wang, M.; Li, H.; Zhang, J.; Liu, H.; Wang, F., *ACS Catal.* 2016, 6, 7716-7721; (d) Luo, J.; Zhang, J., *J. Org. Chem.* 2016, 81, 9131-9137; (e) Luo, J.; Zhang, X.; Lu, J.; Zhang, J., *ACS Catal.* 2017, 7, 5062-5070; (f) Yang, C.; Kärkäs, M. D.; Magallanes, G.; Chan, K.; Stephenson, C. R. J., *Org. Lett.* 2020, 22, 8082-8085.
- [2]. Chen, K.; Schwarz, J.; Karl, T. A.; Chatterjee, A.; König, B., *Chem. Commun.* 2019, 55, 13144-13147.
- [3] (a) Lin, Y.-C.; Chen, C.-T., *Org. Lett.* 2009, 11, 4858-4861; (b) Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A., *Science* 2015, 349, 1326-1330; (c) Joshi-Pangu, A.; Lévesque, F.; Roth, H. G.; Oliver, S. F.; Campeau, L.-C.; Nicewicz, D.; DiRocco, D. A., *AJ. Org. Chem.* 2016, 81, 7244-7249; (d) Margrey, K. A.; McManus, J. B.; Bonazzi, S.; Zecri, F.; Nicewicz, D. A., *J. Am. Chem. Soc.* 2017, 139, 11288-11299; (e) Margrey, K. A.; Levens, A.; Nicewicz, D. A., *Angew. Chem. Int. Ed.* 2017, 56, 15644-15648; (f) McManus, J. B.; Nicewicz, D. A., *D2017*, 139, 2880-2883.
- [4] Y.-X. Cao, G. Zhu, J.-F. Soulé*, "Acridinium-based photoredox catalysts, synthesis and use thereof in oxidative cleavage of C–O bonds" 2020, EP 20306217.9.