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From DPZ to DTQ: Organic Catalysts for Homo- and Heterogeneous Photoredox Processes

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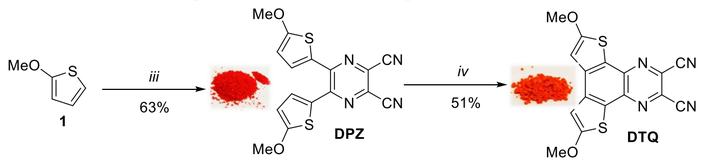
Introduction

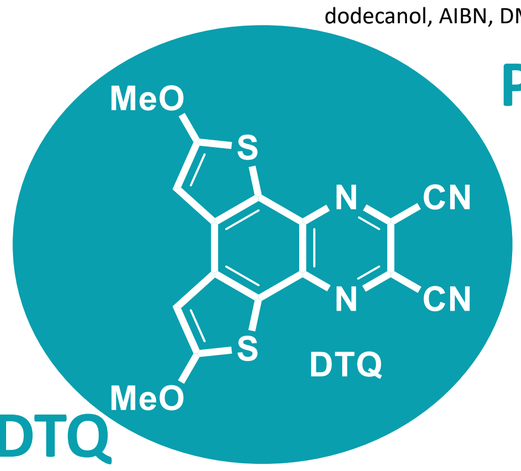
Photoredox catalysis enables radical generation under mild conditions using visible light and has become a powerful tool for modern organic synthesis. Alongside inorganic semiconductors and metal complexes, purely organic dyes represent an important class of photocatalysts.[1]

Dicyanopyrazine **DPZ**, introduced in 2014, has emerged as an efficient metal-free photocatalyst applied across numerous photoredox transformations. Its photophysical properties and catalytic behavior have been thoroughly investigated, and recent studies revealed that **DPZ** undergoes a blue-light-induced Mallory-type photocyclization to form dithienoquinoxaline **DTQ**.[2]

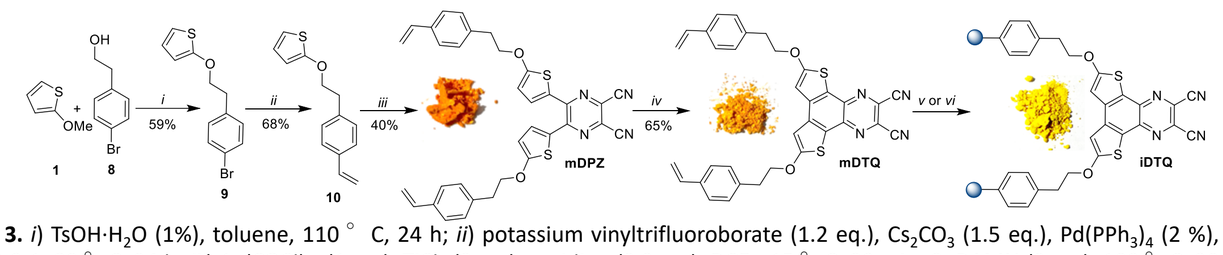
Synthetic pathway towards DTQ



Scheme 1. *iii*) 1. $(COCl)_2$, (1 eq.), $TiCl_4$ (2 eq.); pyridine (2.2 eq.), DCE, -15 °C, 20 min; 2. DAMN (2 eq.), 100 °C, 30 min; *iv*) 1,4-dioxane, Royal-Blue LED, 25 °C, 5 h.



Synthetic pathway towards iDTQ



Scheme 3. *i*) TsOH·H_2O (1%), toluene, 110 °C, 24 h; *ii*) potassium vinyltrifluoroborate (1.2 eq.), Cs_2CO_3 (1.5 eq.), $Pd(PPh_3)_4$ (2 %), THF/H_2O 9:1, 80 °C, 24 h; *iii*) 1. $(COCl)_2$, (1 eq.), $TiCl_4$ (2 eq.); pyridine (2.2 eq.), DCE, -15 °C, 20 min; 2. DAMN (2 eq.), 100 °C, 30 min; *iv*) 1,4-dioxane, Royal-Blue LED, 25 °C, 5 h; *v*) divinylbenzene, AIBN, DMF, 100 °C, 24 h; *vi*) divinylbenzene, styrene, dodecanol, AIBN, DMF, 20 to 110 °C, 16 h.

Redox and optical properties of DTQ

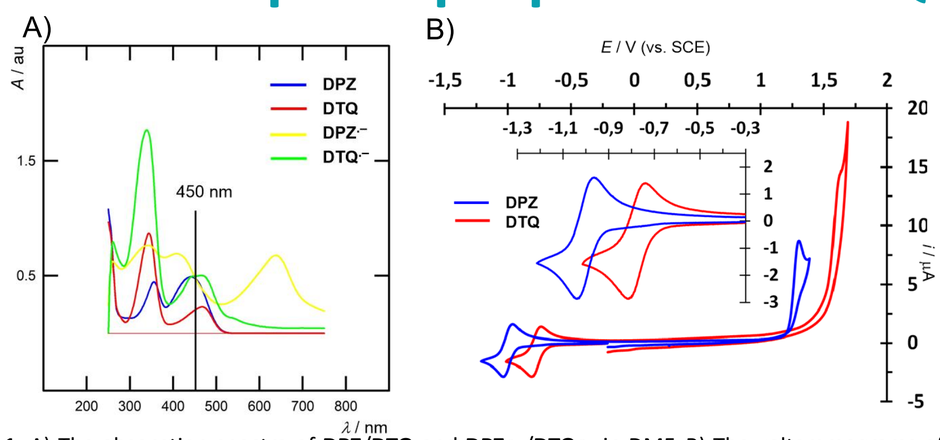
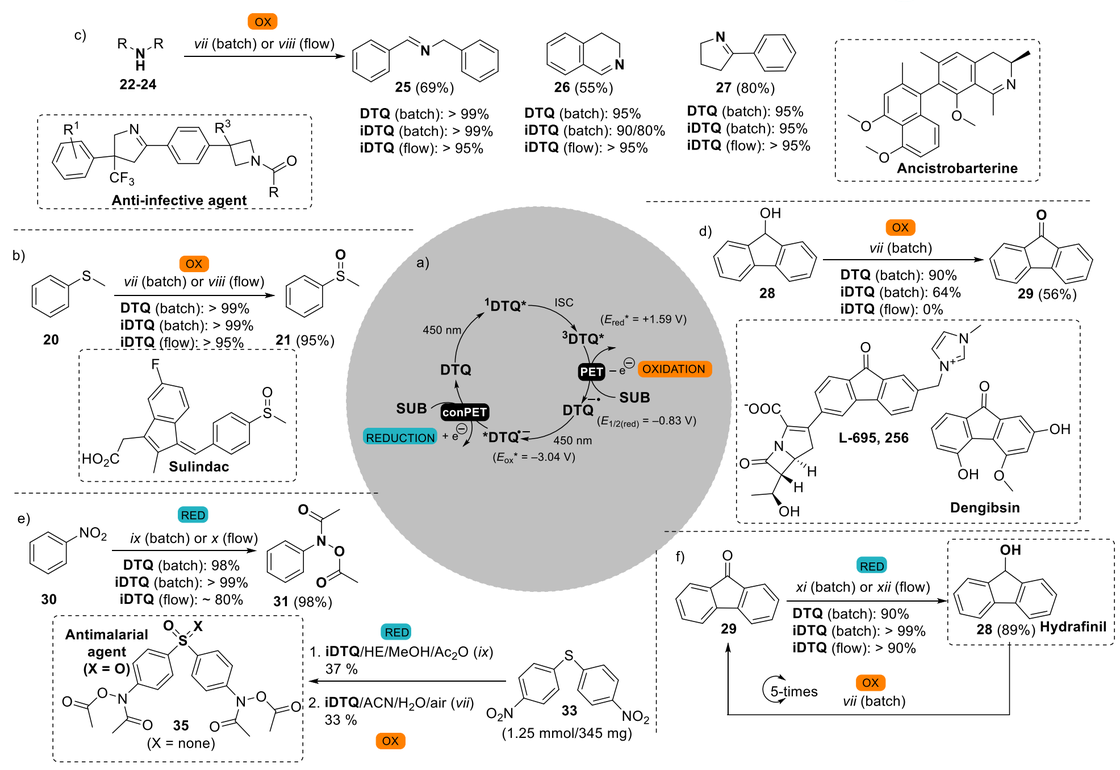
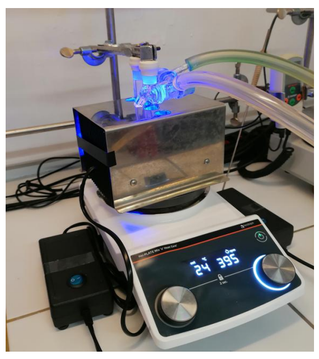


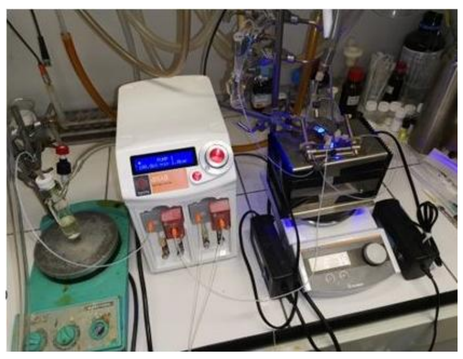
Figure 1. A) The absorption spectra of **DPZ/DTQ** and **DPZ•-/DTQ•-** in DMF, B) The voltammograms of both catalysts in DMF at a scan rate of100 mV s^{-1}.

Photoredox transformations using iDTQ



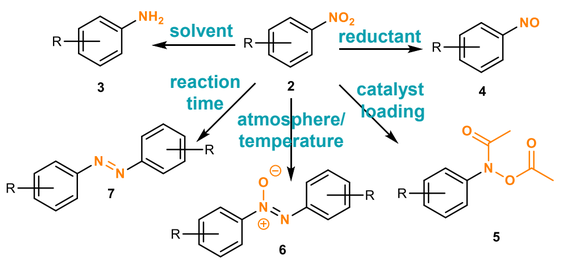
Scheme 4. General catalytic cycle of (**i**)**DTQ** (a) and the performed photoredox transformations (b–f). *vii*) **DTQ/iDTQ** (1/2.5 or 4 mol%), ACN:H_2O (95:5) for **20** and **22**–**24** or DMSO for **28**, Royal Blue LED, air/oxygen (1.5 bar), 25–60 °C, 20–180 min. *viii*) **iDTQ**-based monolithic column, *c*(**20**/**22**–**24**) = 0.1563/0.0625 mol·l^{-1}; ACN:H_2O; a flow of 200/50 mL·min^{-1} for **20**/**22**–**24**, O_2 (2 bar), RoyalBlue LED. *ix*) **DTQ/iDTQ** (0.5/4 mol%), MeOH, HE, Ac_2O, Royal Blue LED, Ar, 25 °C, 60 min. *x*) **iDTQ**-based monolithic column, *c*(**30**) = 0.1218 mol·l^{-1}; HE, DMF, 17 mL·min^{-1}, RoyalBlue LED. *xi*) **DTQ/iDTQ** (1/4 mol%), DIPEA, ACN, Royal Blue LED, 25 °C, 90 min. *xii*) **iDTQ**-based monolithic column, *c*(**29**) = 0.0625 mol·l^{-1}; DIPEA, ACN, 150 mL·min^{-1}, RoyalBlue LED, 35 °C. The redox properties are referred to SCE. The percentage refer to a conversion (after the first cycle) as determined by GC/MS or NMR; the isolated yields are shown in brackets following the number of the particular product.

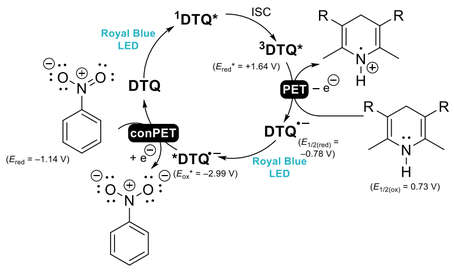




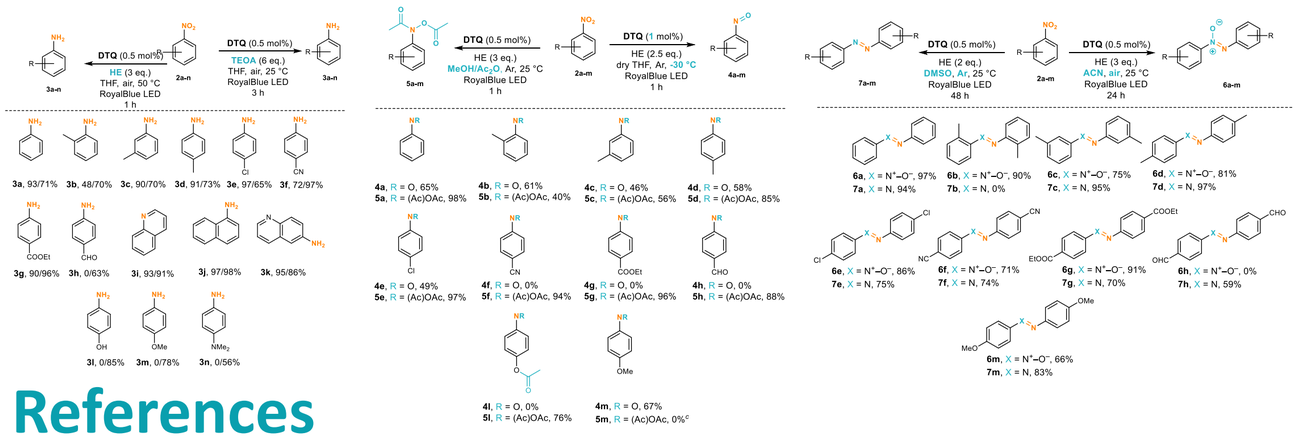
Reduction of nitroaromatic compounds

Nitroarenes are valuable synthetic intermediates, yet their selective, stepwise reduction remains difficult to control. With DTQ, we discovered that the entire reduction pathway can be directed simply by tuning basic reaction parameters. As summarized in the Scheme 2, starting from a nitroarene **2** we can access five distinct product classes: nitroso compounds **4**, hydroxylamines (isolated as bis-(N,O-diacyl) derivatives) **5**, azoxy and azo species **7** and finally, anilines **3**.[3]





Scheme 2. Chemodivergent photoreduction of nitroaromatics toward various reduction stages via modulation of the reduction power of ***DTQ•-**.



Conclusion

- Mallory type photocyclization of **DPZ** was performed affording **DTQ**
- Photocatalytic activity was probed in chemoselective photoreductions of nitroaromatics
- **DTQ** proved to be superior in all transformations
- Heterogenization of **DTQ** provide **iDTQ** suitable for batch as well as flow heterogeneous photoredox reactions

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5 B 92 U 75 Re 16 S Department of Organic Materials group

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