

# Activation of Anthraquinone's Electrophilicity by Light for a Dynamic C – O Bond

Published 11 January 2024

*J. Am. Chem. Soc.* **2024**, *146*, 3, 1799–1805.

## Who are the corresponding authors and what are their research areas?



Dr. Andrey Lvov

**2020-present: Independent research group leader** (Laboratory of photoactive compounds)

*National Research Irkutsk State Technical University: Irkutsk, Russia*

**Postdoc in Germany**

*Friedrich-Alexander-Universität Erlangen Nürnberg: Erlangen, DE*

**Ph.D in Russia**

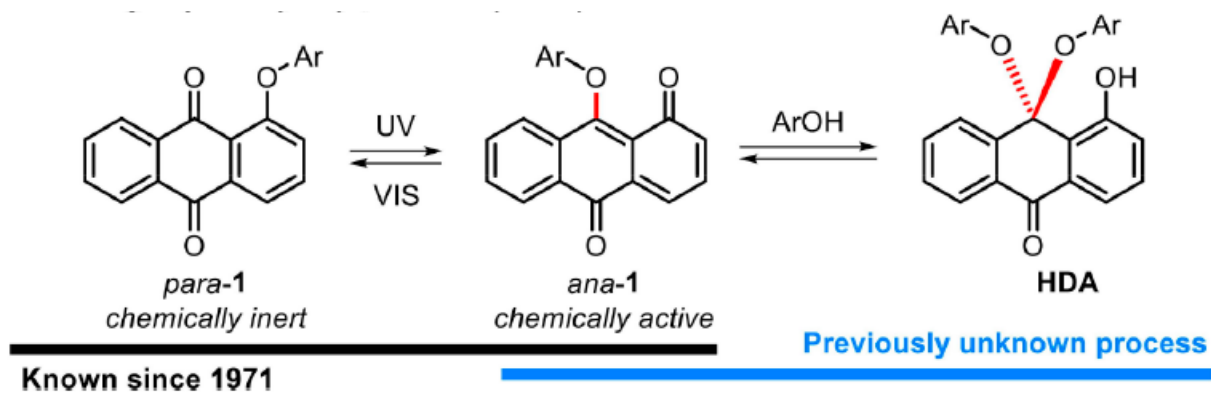
*N.D. Zelinsky Institute of Organic Chemistry Russian Academy of Sciences*

He investigated photochromic and photoswitchable compounds early in his postgraduate studies in Russia and during his Ph.D. on his work on **Synthesis and spectral properties of diarylethenes of azole series**.

He then moved to Germany for his postdoc where he worked on **Valence tautomeric metal complexes for deposition to surfaces**.

## What is the main claim of the article?

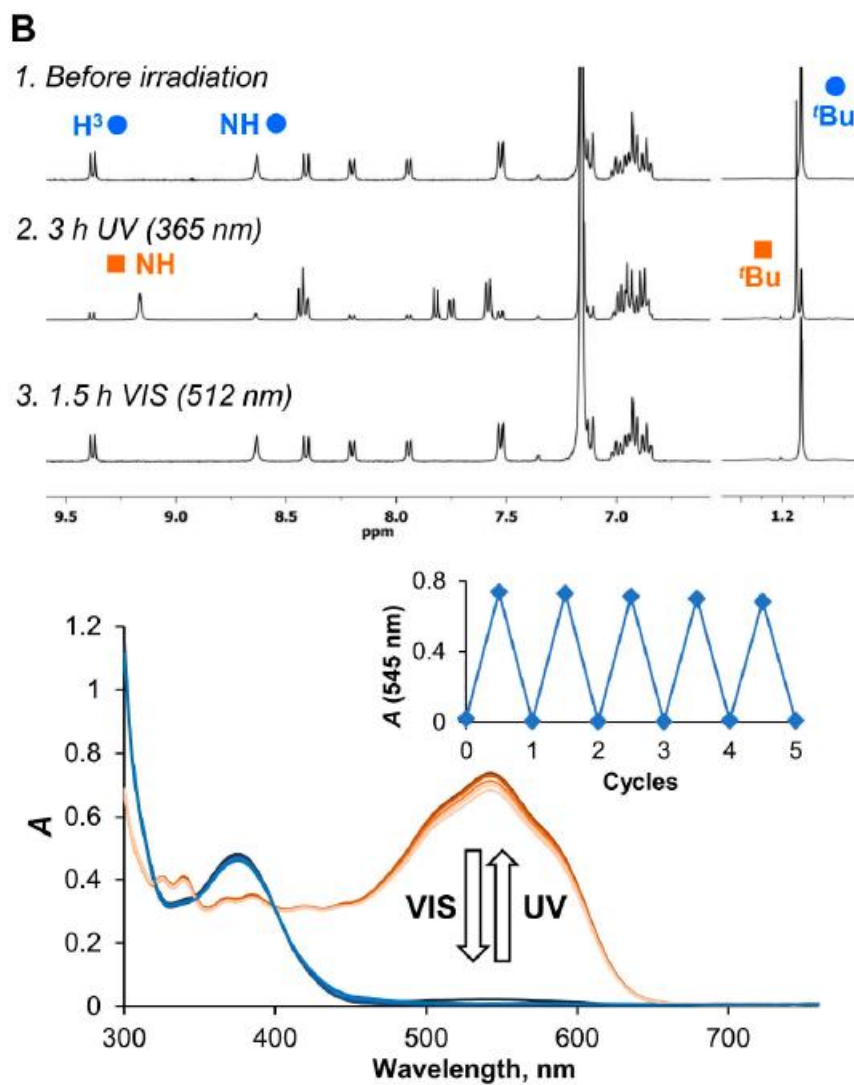
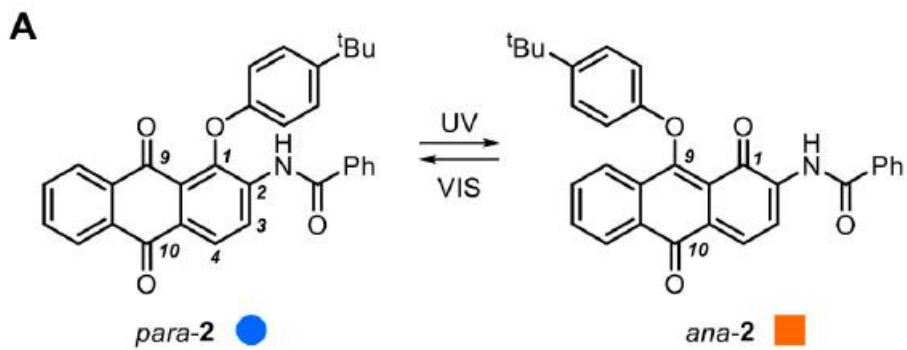
*Photoswitchable peri-aryloxyanthraquinones are known to undergo an oxyaryl migration from position 1 (para-isomer) to position 9 (ana-isomer) upon UV-irradiation. This isomerization yields an activation in the electrophilicity of the molecule which was exploited to produce the **first example** of a dynamic C-O bond in such systems.*



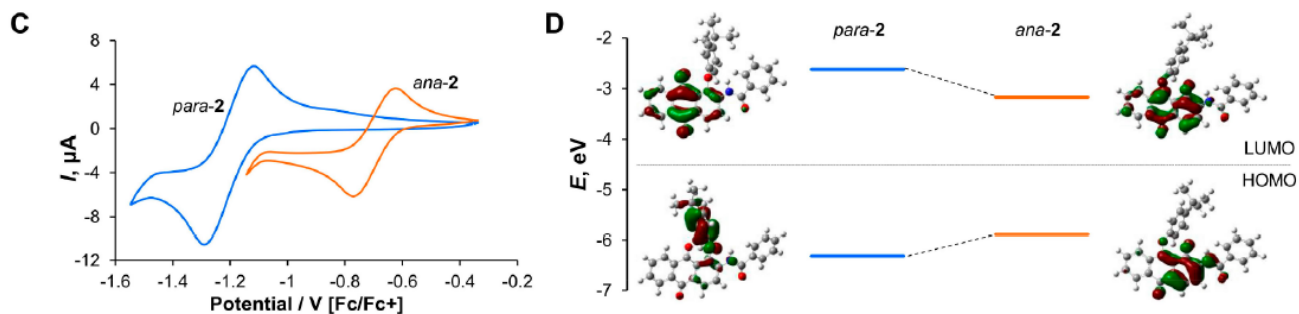
### How is it demonstrated?

The authors demonstrated the *para* ↔ *ana* switching upon UV/vis irradiation through NMR and Absorption measurements.

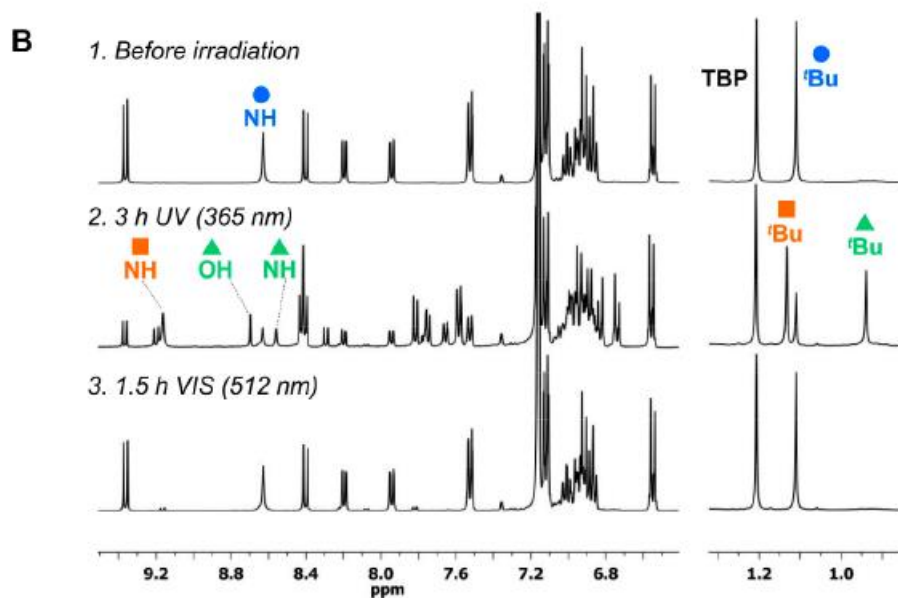
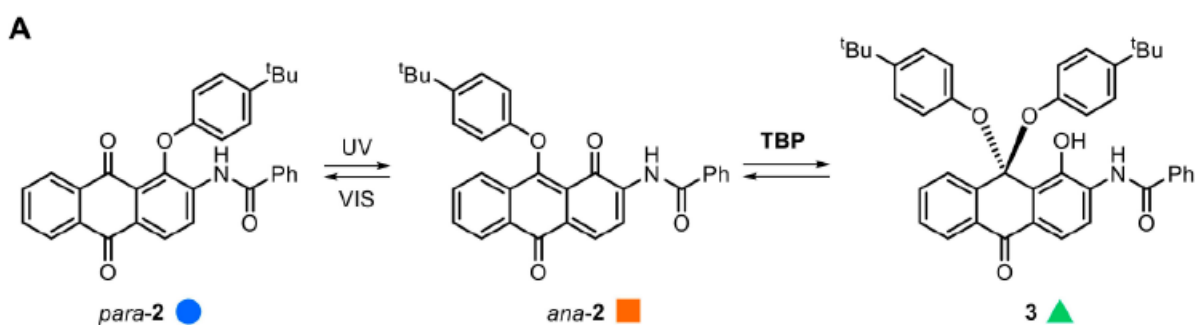
The isomerization proceeded through a radical mechanism and showed less than 10% fatigue after 5 switching cycles, mostly due to hydrolysis of the *ana*-isomer ( $\lambda^{\text{UV}} = 365 \text{ nm}$ ; PSS = 80%;  $\lambda^{\text{vis}} = 512 \text{ nm}$ , quantitative)



The electrophilicity trigger between the *para*- and the *ana*-isomers was proved by cyclic voltammetry measurements where the latter is more easily reduced. This gives a direct insight into the change in the HOMO-LUMO levels which was also supported by DFT calculations.

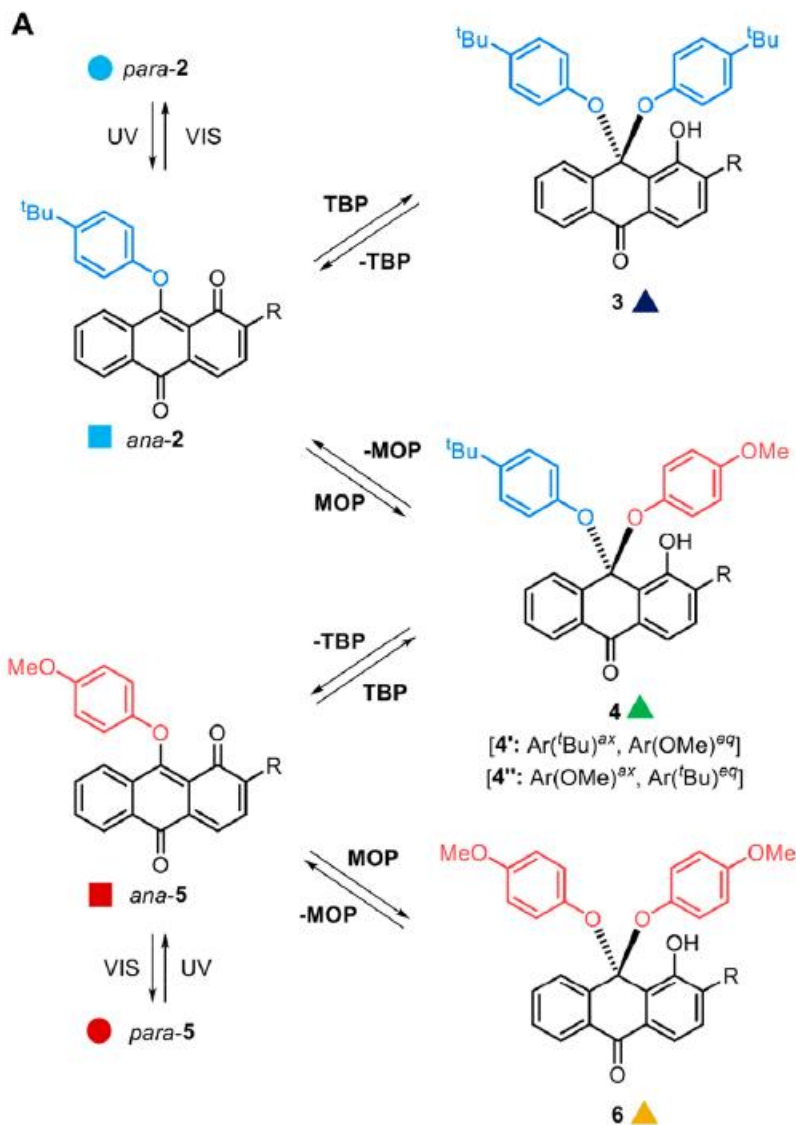


The better electrophile *ana-2* was then subjected to a nucleophilic attack from <sup>t</sup>BuOH yielding adduct **3** which exists in an equilibrium with *ana-2*. This allows for a complete recovery of the *para-2* upon irradiation with vis light, following Le Chatelier's principle. The attack was taking place in the ground state of *ana-2*.



The dynamicity of the C-O bond was further confirmed using a different phenol as the nucleophile. Addition of MOP to a preirradiated solution of *para-2* results in the formation of an unsymmetrical HDA. Following the

distribution of the different species by NMR over time, we can see the formation of species *ana-5* arising exclusively from the breakage of the C-O bond of the TBP.

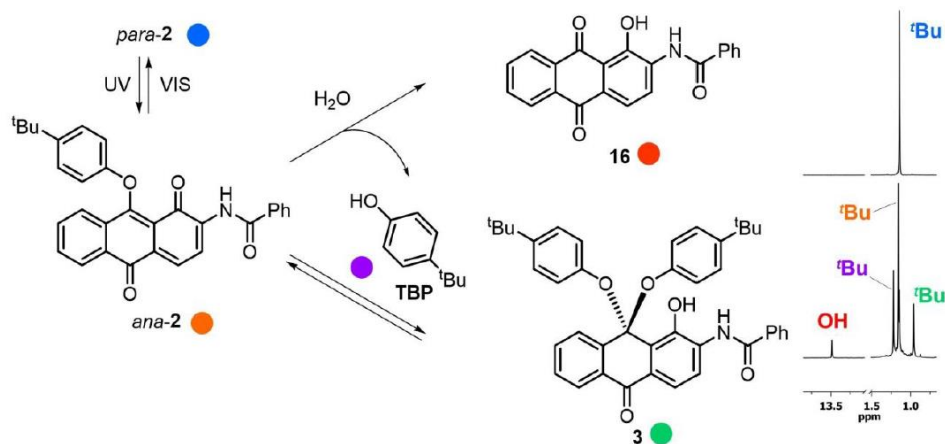


24h in the dark, the distribution of the species shows a major accumulation of adduct **6** resulting from a second nucleophilic attack of **MOP** to *ana-5*, which is more favoured over the attack of **TBP**. This confirms that the distribution is directly dictated by the Nucleophilicity of the phenol. The addition of more than 1 equiv. of **MOP** can further shift the equilibrium in favour of **MOP**-substituted species.

## What are the typical experimental conditions?

**NMR:** dry duterated benzene, 0.02 M, 296 K, in air

**UV:** dry dichloromethane,  $8 \cdot 10^{-5}$  M.



*para* → *ana* isomerization:  $\lambda^{UV} = 365$  nm

*ana* → *para* isomerization:  $\lambda^{vis} = 512$  nm

## Which are the key related papers?

### [Review on the photochromic properties of the anthraquinones and their possible applications in devices](#)

Lvov, A. G.; Klimenko, L. S.; Bykov, V. N.; Hecht, S. Revisiting Peri-Aryloxyquinones: From a Forgotten Photochromic System to a Promising Tool for Emerging Applications. *Chem. Eur. J.* **2024**, No. e202303654.

### [On the mechanism of the concerted Nucleophilic attack of the alkoxy moiety](#)

Lu, H.; Ye, H.; Zhang, M.; Liu, Z.; Zou, H.; You, L. Photoswitchable Dynamic Conjugate Addition-Elimination Reactions as a Tool for Light-Mediated Click and Clip Chemistry. *Nat. Commun.* **2023**, *14* (1), 4015.

### [On the restoration of aromaticity in the anthracene moiety favouring the conjugated Michael addition](#)

Crolais, A. E.; Dolinski, N. D.; Boynton, N. R.; Radhakrishnan, J. M.; Snyder, S. A.; Rowan, S. J. Enhancing the Equilibrium of Dynamic Thia-Michael Reactions through Heterocyclic Design. *J. Am. Chem. Soc.* **2023**, *145* (26), 14427–14434.