Unlocking the ConPeT Mechanism: Correspondence on “Catalytic Asymmetric Redox-Neutral [3 + 2] Photocycloadditions of Cyclopropyl Ketones with Vinylazaarenes Enabled by Consecutive Photoinduced Electron Transfer”

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Unlocking the ConPeT mechanism: Correspondence on "Catalytic Asymmetric Redox-Neutral [3+2] Photocycloadditions of Cyclopropyl Ketones with Vinylazaarenes Enabled by Consecutive Photoinduced Electron Transfer"

Marco Villa,[a,b] Andrea Fermi,[a,b] Francesco Calogero,[a,b] Andrea Gualandi,[a,b] Paola Franchi,[a] Marco Lucarini,[a,b] Barbara Ventura,[c,*] Pier Giorgio Cozzi,[a,b,*] Paola Ceroni[a,b,*]

[a] Dr. M. Villa, Dr. A. Fermi, Dr. F. Calogero, Prof. A. Gualandi, Prof. P. Franchi, Prof. M. Lucarini, Prof. P. Ceroni, Prof. P. G. Cozzi
Dipartimento di Chimica "Giacomo Ciamician"
Alma Mater Studiorum – Università di Bologna
Via Gobetti 85, 40129 Bologna, Italy
E-mail: paola.ceroni@unibo.it; piergiorgio.cozzi@unibo.it

[b] Dr. M. Villa, Dr. A. Fermi, Dr. F. Calogero, Prof. A. Gualandi, Prof. M. Lucarini, Prof. P. Ceroni, Prof. P. G. Cozzi
Center for Chemical Catalysis – C3
Alma Mater Studiorum – Università di Bologna
Via Gobetti 85, 40129 Bologna, Italy

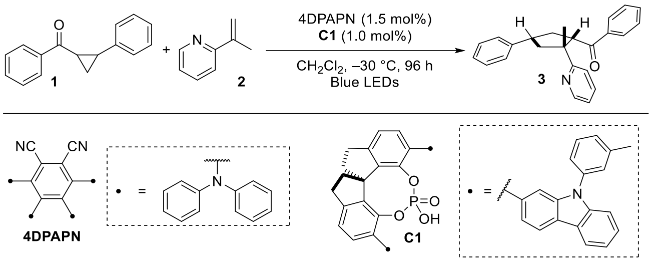
[c] Dr. B. Ventura
Institute for Organic Synthesis and Photoreactivity (ISOF)
National Research Council (CNR),
Via P. Gobetti 101, 40129 Bologna, Italy Italy
E-mail: barbara.ventura@isof.cnr.it

Abstract: Recently, in a communication to this journal, Qiao, Jang and co-workers described an asymmetric photoredox reaction promoted by TADF cyanoarene photocatalysts (specifically **4DPAPN** (3,4,5,6-tetrakis(diphenylamino)phthalonitrile). The authors claimed that the high reduction potential required for the reaction in acetonitrile was achieved by the radical anion of the photocatalyst in its excited state, which initiated the reaction. This mechanism is usually named as consecutive photoinduced electron transfer(ConPeT), in which two photons are involved, the first one to excite the photocatalyst and generate the radical anion **4DPAPN**$^{\bullet-}$ and the second photon to promote **4DPAPN**$^{\bullet-}$ to its excited state ***4DPAPN**$^{\bullet-}$. Employing ultrafast transient absorption spectroscopy, here we report that, although two photons are indeed involved in this transformation, the excited state ***4DPAPN**$^{\bullet-}$ is short lived, not emissive, and not quenched by the organic substrate employed in the reaction, opposite to what claimed by the authors. The photocatalyst in the excited state ***4DPAPN**$^{\bullet-}$ can generate a solvated electron that is able to reduce the substrate involved in this chemistry. It is worth noting that a different photochemical mechanism is likely to be operative in CH_2Cl_2, where solvated electrons are much less stabilized and reduction of the solvent might occur.

Photocatalysis combines photochemistry and catalysis to drive challenging reactions under mild conditions.[1, 2] Most of the reaction mechanisms involve photoinduced electron transfer processes, also known as photoredox catalysis, by taking advantage of the better reductive and oxidative properties of the photocatalyst excited states.[3] To widen the available redox window, the consecutive photoinduced electron transfer (ConPeT) mechanism[4, 5] has been proposed: upon absorption of a photon, the photocatalyst (PC) is promoted to its excited state *PC, which is reductively quenched by a suitable electron donor sacrificial agent to afford the radical anion PC$^{\bullet-}$. The stable radical anion absorbs a second photon to generate the excited radical anion *PC$^{\bullet-}$ with a much more negative reduction potential, capable of reducing the substrate, leading to product formation.

The ConPeT process was proposed as the active reaction mechanism employing several classes of organic chromophores,[6] comprising cyanoarenes,[7, 8] in a variety of reactions, including reduction of aryl halides (the first and the most investigated one),[9] ketyl radical coupling of carbonyls with *N*-aryl acrylamides[10] or styrenes and dienes[11] and dehalogenation or desulfonylation reactions.[12]

The article by Qiao and Jang[13] represents the first example in which ConPeT is combined with asymmetric catalysis. The reaction is a [3+2] photocycloaddition of cyclopropyl ketones with vinylazaarenes in the presence of the cyanoarene **4DPAPN** photocatalyst (3,4,5,6-tetrakis(diphenylamino)phthalonitrile) and SPINOL derived **C1** phosphoric acid (1,1'-spirobiindane-7-7'-diyl phosphoric acid) as a chiral Brønsted acid catalyst (Scheme 1).



Scheme 1. Investigated reaction

The combination of the photocatalyst and the chiral phosphoric acid gives a very high enantiomeric excess (> 90%) for the final cyclopentane products, with a good diastereomeric ratio (>19:1). A wide range of cyclopropyl ketones have been successfully converted to the desired products by reaction with 3-vinylpyridine and other vinyl heterocycles. The catalytic system is based on a synergistic combination of the chiral phosphoric acid **C1**, capable of preferentially activating vinylazaarenes by hydrogen-bonding, under reducing photocatalytic conditions, which are able to open up the cyclopropyl ketones. Although activation of vinylaazarene with chiral phosphoric acid under photoredox conditions has been described and is well known in literature,[14-16] the idea of opening a cyclopropyl ketone and capturing the radical anion in an enantioselective environment is unprecedented. High reduction potentials are required to open these cyclopropyl derivatives and the authors hypothesized a ConPeT photochemical mechanism. The proposed mechanism in acetonitrile is depicted in Figure 1.

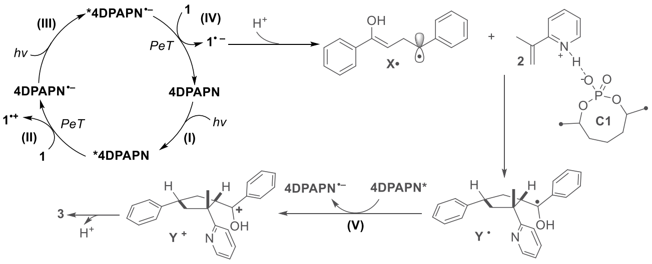


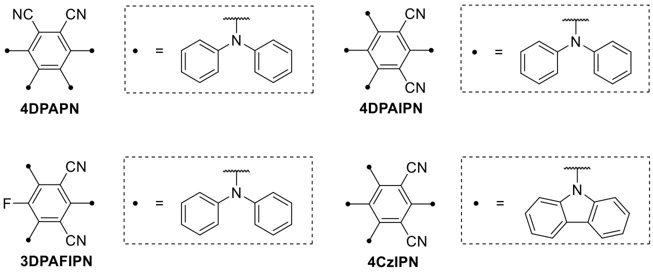
Figure 1. Mechanism proposed by the authors of ref. [13]

It is worth noting that, unexpectedly, substrate **1** acts both as a reductant (process **II**) and as an oxidant (process **IV**). For the sake of simplicity, process **II** reports a reductive quenching of the ***4DPAPN** excited state by **1**, the authors demonstrated that the ***4DPAPN** excited state in acetonitrile solution is not quenched by either **1** or **2**, but only by a mixture of **1** and **2**. However, there is no clear explanation for this phenomenon. After the formation of $\mathbf{1}^{\bullet-}$ (process **IV**), the reaction proceeds by protonation and ring opening, to give the intermediate $\mathbf{X}^{\bullet}$, followed by the reaction with substrate **2** coordinated to the asymmetric catalyst (**C1**) to generate the radical species **Y**$^{\bullet}$ (Figure 1). **Y**$^{\bullet}$ then acts as the reductant of ***4DPAPN** and event **II** is replaced by the event **V**. The final product **3** is then formed by deprotonation of **Y**$^{+}$.

Similar results were obtained with the photocatalysts **4CzIPN** (2,4,5,6-tetrakis(9H-carbazol-9-yl) isophthalonitrile) and **3DPAFIPN** (2,4,6-tris(diphenylamino)-5-fluoroisophthalonitrile), while **4DPAIPN** (2,4,5,6-tetrakis(diphenylamino)isophthalonitrile), an isomer of **4DPAPN**, is unable to promote the reaction (reported yield for **3** = 8%). This is a surprising result given the similar photophysical and electrochemical properties of the two photocatalysts. For a comparison of the four photocatalysts, see the data reported in Table 1.

Puzzled by this mechanism and inspired by our recent findings that some cyanoarene photocatalysts are strong photoreductants as a result of the photogeneration of solvated electrons

Table 1. Most relevant photophysical and electrochemical properties (redox potentials in V *vs* SCE) of photocatalysts in degassed acetonitrile solution at room temperature.



	Photophysical properties				Electrochemical properties	
	λ_{abs} /nm	λ_{em} /nm	τ_{PF}/ ns	τ_{TADF} /µs	E(PC/PC$^{\bullet-}$)/ V	E(PC$^{\bullet+}$/PC)/ V
4DPAPN[a,b]	465	589	4.6	70	-1.46	+1.27
4DPAIPN[a,c]	470	536	3.4	67	-1.66	+1.34
4CzIPN[a,c]	430	545	13.4	1.82	-1.21	+1.52
3DPAFIPN[d]	364	510	3.2	130	-1.53	+1.28

[a] ref [17]; [b] ref. [13]; [c] ref. [18]; [d] ref [19].

in a consecutive two-photon induced mechanism (ConPies),[20] we decided to investigate the photophysical properties of **4DPAPN** and of its radical anion **4DPAPN**$^{\bullet-}$.

We performed the study in acetonitrile solution to be consistent with the electrochemical, photochemical and NMR studies reported by Qiao and Jang in acetonitrile to support the mechanism of Figure 1. It is worth noting that the reaction was also reported by the same authors in acetonitrile and other solvents in the supporting material. To photogenerate the radical anion **4DPAPN**$^{\bullet-}$, we used either DIPEA (see SI), as reported by the authors in their photophysical study, or tetrabutylammonium oxalate (TBAOx),[21] as sacrificial donor in process **II** (Figure 1). **4DPAPN** displays an absorption band tailing up to 540 nm and an emission band peaked at 589 nm (green lines in Figure 2).

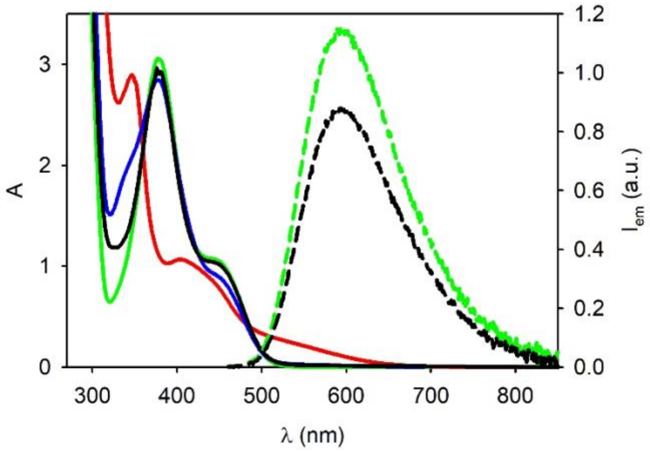


Figure 2. Absorption (solid lines) and emission (dashed lines) in degassed acetonitrile solution of **4DPAPN** 0.15 mM before (green line) and after addition of TBAOx (5.2 mM, black line) and subsequent irradiation at 390 nm (red line). The absorption spectrum reported in blue is recorded after air bubbling inside the acetonitrile solution. Optical path of 0.2 cm for absorption spectra, and 1 cm for emission spectra .

The emission intensity decay is biexponential in degassed solution with a short component related to the prompt fluorescence (τ_{PF} = 4.6 ns) and a long component related to the thermally activated delayed fluorescence (τ_{TADF} = 70 µs). Upon addition of TBAOx (5.2 mM), emission quenching is observed (dashed black lines in Figure 2) and upon irradiation at 390 nm, a new absorption band at lower energy appears (500-650 nm, red line in Figure 2), which is consistent with the formation of the radical anion **4DPAPN**$^{\bullet-}$ by comparison with isophtalonitrile-based TADF chromophores reported in the literature.[18] By air bubbling, an almost complete (>95%) recovery of the initial spectrum of **4DPAPN** is observed (blue line in Figure 2).

The formation of the radical anion of **4DPAPN** was also confirmed by EPR under the same experimental conditions described above. While no EPR signal is observed for a **4DPAPN** solution (0.45 mM) in acetonitrile in the presence of TBAOx (5.2 mM) in the dark, as soon as irradiation at 390 nm is applied in the EPR cavity, a signal appears (see Figure 3). On the basis of the the spectroscopic parameters determined through theoretical simulation of the experimental spectrum (a_{2N}=0.30 G, a_{2N}=0.72 G and a_{2N}=1.62 G), it has been attributed to **4DPAPN**$^{\bullet-}$. The same radical was also obtained electrochemically in dichloromethane and is reported in the Supporting Information.

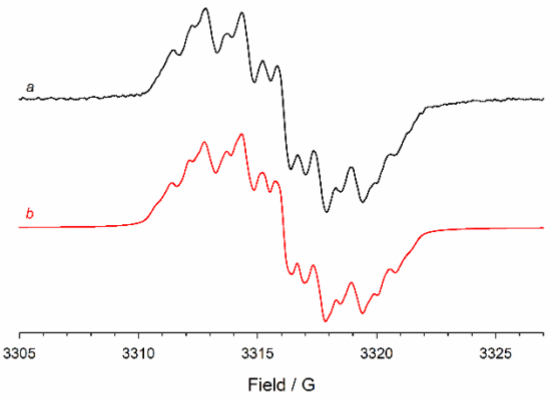


Figure 3. EPR spectrum of **4DPAPN**$^{\bullet-}$ recorded at 298K in a degassed acetonitrile solution (a) and the corresponding theoretical simulation obtained with a_{2N}=0.30 G, a_{2N}=0.72 G and a_{2N}=1.62 G (b).

No emission is observed by selective excitation of the radical anion **4DPAPN**$^{\bullet-}$ at 560 nm, contrary to what reported by Qiao, Jang and co-workers.[13] Therefore, to investigate the reactivity of this anion in the excited state, we performed ultrafast transient absorption analysis (Figures 4 and 5).

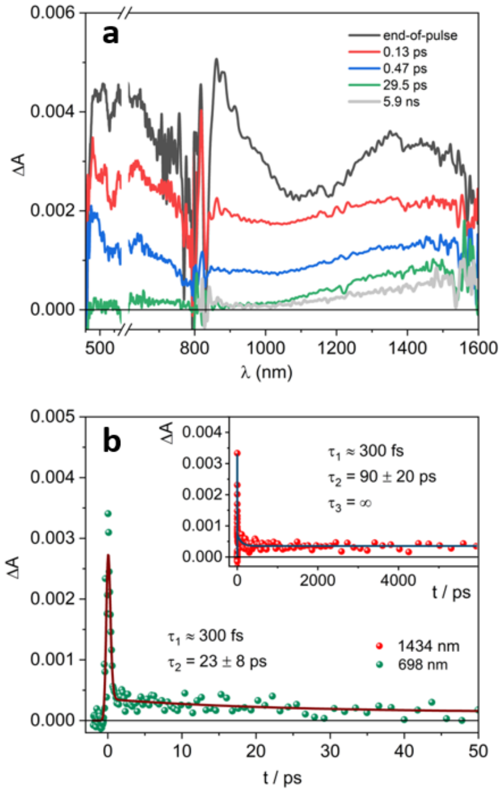


Figure 4. Transient absorption spectra at different delays of a degassed acetonitrile solution of **4DPAPN**$^{\bullet-}$ (a) and the corresponding ΔA temporal evolution at significant wavelengths (b). λ_{ex} = 600 nm, A_{600nm} = 0.1, 0.2 cm optical path, 8 μJ/pulse.

Upon excitation of the radical anion **4DPAPN**$^{\bullet-}$ at 600 nm, the transient spectrum displays absorption bands in the visible and near infrared (NIR) spectral region at the end of the pulse (Figure 4a). The signal observed in the 450-900 nm range decays to zero on a very short timescale, according to a biexponential evolution: $\tau_1 \approx$ 300 fs (close to the instrumental time resolution) and τ_2 = 23 ps (Figure 4b). The ultrafast component, which account for 95% of the decay, is likely related to the internal conversion from the upper lying doublet excited states to the lowest doublet excited state D_1, while the longer component is attributable to the decay of D_1 to the ground state. It is worth mentioning that in the NIR spectral region, the signal initially decays with two fast processes, similar to what was observed in the visible region, but, in addition to that, a broad band peaking at ca. 1440 nm remains stable on much longer time scales (Figure 4b, inset, τ_3= ∞, meaning that it does not decay significantly in the available time window). This band resembles the absorption of the solvated electron observed in acetonitrile upon pulse radiolysis (see Figure S5).[22, 23] A very similar behavior was recently reported by us in acetonitrile solutions of the photocatalysts **4CzIPN$^{\bullet-}$** and **4DAPIPN$^{\bullet-}$**.[20]

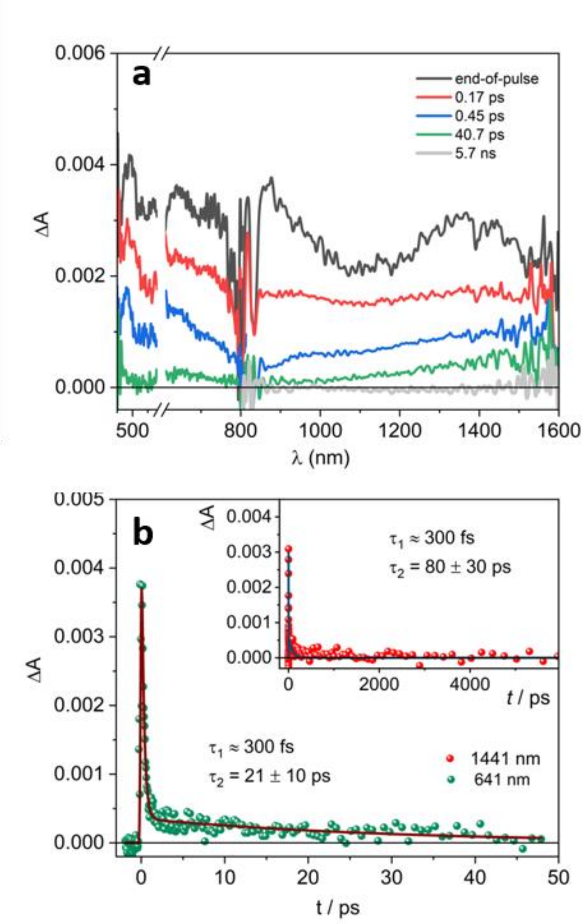


Figure 5. Transient absorption spectra at different delays of a degassed acetonitrile solution of **4DPAPN$^{\bullet-}$** in presence of **1** 0.1 M (a) and the corresponding ΔA temporal evolution at significant wavelengths (b). λ_{ex} = 600 nm, A_{600nm} = 0.06, 0.2 cm optical path, 8 μJ/pulse.

The transient absorption study clearly shows that the D_1 excited state of **4DPAPN$^{\bullet-}$** is extremely short-lived (τ = 23 ps), as previously observed for other organic radical anions.[24, 25] Therefore, a diffusional bimolecular quenching process with substrate **1** (process **IV**, Figure 1) is extremely unlikely. This was experimentally verified by repeating the transient absorption measurements in the presence of **1** (0.1 M, see Figure 5): the transient features in the visible spectral range are similar (comparison of Figure 4a and Figure 5a) and no change in the lifetime of the D_1 excited state is observed (Figure 5b). On the other hand, in the NIR spectral region the long-lived species absorbing at 1440 nm is not detected, as confirmed by the absence of the "infinite" component in the decay of the signal at this wavelength (Figure 5b, inset). Moreover, as a confirmation of the reaction mechanism, the lifetime of the long-lived component of the band at 1440 nm shows an inversely proportional dependence on the concentration of substrate **1** (Figure S6). It is worth noting that, in contrast with previous literature reports on 4,4'-dicyanobiphenyl and 4,4''-dicyano-*p*-terphenyl radical anions,[26] no evidence of preassociation between **4DPAPN**$^{\bullet-}$ and **1** was observed, ruling out the possibility of a static quenching process: upon addition of substrate **1**, the amplitude of the transient absorption signal does not decrease significantly (as observed by comparing the end-of-pulse spectra of Figures 4a and 5a).

Therefore, the mechanism proposed in ref. [13] in acetonitrile solution is not plausible as the process **IV** (Figure 1) is not observed experimentally. A possible reaction mechanism involves the reduction of substrate **1** by the photogenerated solvated electron:

*$\mathbf{4DPAPN}^{\bullet-} \rightarrow \mathbf{4DPAPN} + e^{-}_{solv}$ (**VI**)

$e^{-}_{solv} + \mathbf{1} \rightarrow \mathbf{1}^{\bullet-}$ (**VII**)

The solvated electron generated in process (**VI**) has an extremely high diffusivity, allowing photoreactivity to occur at greater distance from the photocatalyst and for a longer time compared to the usual timescale of ConPeT. Furthermore, these cyanoarene radical anions were found to be ideal candidates for photogenerating solvated electrons due to an inefficient back recombination of the solvated electron with the resulting neutral catalyst. Indeed, it has been shown by computational studies that the SOMO of the anions is localized on the phenyl core, so that the back electron transfer is slowed down by the limited overlap between the orbital that should host the back-transferred electron and the surrounding solvent molecules.[20]

The involvement of solvated electrons in photoredox catalysis has previously been reported in aqueous solution,[27-30] where the solvated electrons are stable and well-characterised. More recently, reports on the involvement of solvated electrons in organic solvents have appeared,[20,31] but the spectroscopic evidence of the solvated electron and the kinetic study of its interaction with the substrate are extremely rare.

In the reaction reported in ref. [13], the proposed mechanism was also supported by the following experiments: (i) quenching studies of the photocatalyst to form the corresponding radical anion, and (ii) absorption and emission spectra of the radical anion and corresponding quenching studies.

However, conclusive proofs for the involvement of the excited state of **4DPAPN**$^{\bullet-}$ are missing. The reported absorption and emission spectra (Figure 1F of the original paper[13]) attributed to **4DPAPN**$^{\bullet-}$ are likely related to decomposition products, as previously reported in the literature.[18, 19, 32] Indeed, there is no proof of reversible regeneration of the initial absorption and emission spectra of **4DPAPN** by air bubbling. Therefore, the Stern-Volmer quenching studies related to the radical anion (section 5.7 of the Supporting Information of the original paper[13]) are meaningless. Furthermore, the quenching studies of **4DPAPN** were not performed correctly: the authors plotted the ratio of the emission intensities in the presence and in the absence of the quencher (I^0/I) as a function of the quencher concentration to obtain the Stern-Volmer quenching constant. However, this simplified procedure cannot be applied to TADF chromophores because the recorded emission intensities are the convolution of the prompt and delayed components, so that the two components have to be deconvoluted or a lifetime analysis has to be performed (see SI for details).

As previously mentioned, we performed the study in acetonitrile solution to be consistent with the mechanistic analysis reported by Qiao and Jang. However, the authors screened different solvents and the reaction has been optimised in dichloromethane (experimental conditions reported in Scheme 1). We would like to point out that the photochemical mechanism might be different in different solvents. The majority of solvated electron studies have been performed in polar solvents, but excess electrons have been reported to be stabilized by aggregates of nonpolar molecules, like benzene and toluene.[33] The stability of solvated electrons in the presence of dichloromethane is significantly lower than in acetonitrile: solvated electrons produced in liquid ammonia react with dichloromethane at 296 K with a rate constant of 1.2×10^{10} M^{-1} s^{-1}, a value that is at least two orders of magnitude higher than the rate constant for the reaction with acetonitrile.[34] Similarly, it has been reported that hydrated electrons are able to reduce dichloromethane and generate chloride anions and $CH_2Cl^{\bullet}$ radicals.[35] At the present stage, the reaction mechanism in dichloromethane remains unclear, as the **4DPAPN**$^{\bullet-}$ radical anion is short-lived in dichloromethane, preventing an in-depth study with transient absorption spectroscopy.

We might hypothesise the reduction of dichloromethane, which generates strong reducing agents capable of mediating the reduction of substrate **1**. It is worth noting that the involvement of reduced solvent in a photoredox catalytic cycle has recently been hypothesized in the literature.[36]

In conclusion, we believe that, although representing a challenging task, it is of paramount importance to clarify the photochemical mechanism of a reaction in order to advance the field through a better understanding of the key factors that determine the efficiency of photocatalytic reactions. Transient absorption spectroscopy is a necessary tool when a non-emissive intermediate is involved. This technique has great potential to solve mechanistic uncertainties[37-39] and to guide the design of more efficient and sustainable photocatalytic approaches.

Supporting Information

The authors have cited additional references within the Supporting Information.[40-44]

Acknowledgements

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Keywords: solvated electron • transient absorption spectroscopy • photoinduced electron transfer • cyanoarene • photocatalysis

[1] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322-5363.

[2] P. G. Cozzi, P. Ceroni, A. Gualandi, M. Marchini, in *Photoorganocatalysis in Organic Synthesis, Vol. Volume 18*, WORLD SCIENTIFIC (EUROPE), **2018**, pp. 423-469.

[3] P. C. V. Balzani, A. Juris, *Photochemistry and Photophysics: Concepts, Research, Application*, Wiley-VCH Verlag GmbH Co. KGaA, **2014**.

[4] F. Glaser, C. Kerzig, O. S. Wenger, *Angew. Chem. Int. Ed.* **2020**, *59*, 10266-10284.

[5] M. Schmalzbauer, M. Marcon, B. König, *Angew. Chem. Int. Ed.* **2021**, *60*, 6270-6292.

[6] M. Lepori, S. Schmid, J. P. Barham, *Beilstein J. Org. Chem.* **2023**, *19*, 1055-1145.

[7] J. Xu, J. Cao, X. Wu, H. Wang, X. Yang, X. Tang, R. W. Toh, R. Zhou, E. K. L. Yeow, J. Wu, *J. Am. Chem. Soc.* **2021**, *143*, 13266-13273.

[8] A. F. Chmiel, O. P. Williams, C. P. Chernowsky, C. S. Yeung, Z. K. Wickens, *J. Am. Chem. Soc.* **2021**, *143*, 10882-10889.

[9] I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science* **2014**, *346*, 725-728.

[10] Z. Qu, T. Tian, Y. Tan, X. Ji, G.-J. Deng, H. Huang, *Green Chem.* **2022**, *24*, 7403-7409.

[11] V. J. Mayerhofer, M. Lippolis, C. J. Teskey, *Angew. Chem. Int. Ed.* **2024**, *63*, e202314870.

[12] I. A. MacKenzie, L. Wang, N. P. R. Onuska, O. F. Williams, K. Begam, A. M. Moran, B. D. Dunietz, D. A. Nicewicz, *Nature* **2020**, *580*, 76-80.

[13] W. Wei, C. Li, Y. Fan, X. Chen, X. Zhao, B. Qiao, Z. Jiang, *Angew. Chem. Int. Ed.* **2024**, *63*, e202406845.

[14] Q. Fu, S. Cao, J. Wang, X. Lv, H. Wang, X. Zhao, Z. Jiang, *J. Am. Chem. Soc.* **2024**, *146*, 8372-8380.

[15] M. Kong, Y. Tan, X. Zhao, B. Qiao, C.-H. Tan, S. Cao, Z. Jiang, *J. Am. Chem. Soc.* **2021**, *143*, 4024-4031.

[16] Y. Yin, Y. Dai, H. Jia, J. Li, L. Bu, B. Qiao, X. Zhao, Z. Jiang, *J. Am. Chem. Soc.* **2018**, *140*, 6083-6087.

[17] M. A. Bryden, E. Zysman-Colman, *Chem. Soc. Rev.* **2021**, *50*, 7587-7680.

[18] Y. Kwon, J. Lee, Y. Noh, D. Kim, Y. Lee, C. Yu, J. C. Roldao, S. Feng, J. Gierschner, R. Wannemacher, M. S. Kwon, *Nat. Commun.* **2023**, *14*, 92.

[19] E. Pinosa, E. Bassan, S. Cetin, M. Villa, S. Potenti, F. Calogero, A. Gualandi, A. Fermi, P. Ceroni, P. G. Cozzi, *J. Org. Chem.* **2023**, *88*, 6390-6400.

[20] M. Villa, A. Fermi, F. Calogero, X. Wu, A. Gualandi, P. G. Cozzi, A. Troisi, B. Ventura, P. Ceroni, *Chem. Sci.* **2024**, *15*, 14739-14745.

[21] F. Draper, E. H. Doeven, J. L. Adcock, P. S. Francis, T. U. Connell, *J. Org. Chem.* **2023**, *88*, 6445-6453.

[22] D. C. Grills, S. V. Lymar, *J. Phys. Chem. B* **2022**, *126*, 262-269.

[23] S. C. Doan, B. J. Schwartz, *J. Phys. Chem. Lett.* **2013**, *4*, 1471-1476.

[24] A. J. Rieth, M. I. Gonzalez, B. Kudisch, M. Nava, D. G. Nocera, *J. Am. Chem. Soc.* **2021**, *143*, 14352-14359.

[25] D. Gosztola, M. P. Niemczyk, W. Svec, A. S. Lukas, M. R. Wasielewski, *J. Phys. Chem. A* **2000**, *104*, 6545-6551.

[26] B. Pfund, D. Gejsnæs-Schaad, B. Lazarevski, O. S. Wenger, *Nat. Commun.* **2024**, *15*, 4738.

[27] C. Kerzig, M. Goez, *Chem. Sci.* **2016**, *7*, 3862-3868.

[28] C. Kerzig, X. Guo, O. S. Wenger, *J. Am. Chem. Soc.* **2019**, *141*, 2122-2127.

[29] F. Brandl, S. Bergwinkl, C. Allacher, B. Dick, *Chem. Eur. J.* **2020**, *26*, 7946-7954.

[30] P. Singh, N. Lal, A. C. Shaikh, *Adv. Synth. Catal.* **2024**, *366*, 1906-1921.

[31] R. Obertík, J. Chudoba, J. Šturala, J. Tarábek, L. Ludvíková, T. Slanina, B. König, R. Cibulka, *Chem. Eur. J.* **2022**, *28*, e202202487.

[32] S. Grotjahn, B. König, *Org. Lett.* **2021**, *23*, 3146-3150.

[33] R. M. Young, D. M. Neumark, *Chem. Rev*. **2012**, *112*, 5553−5577.

[34] I. Draganic, Z. Draganic, L. Petkovic, A. Nikolic, *J. Am. Chem. Soc.* **1973**, *95*, 7193–7199.

[35] T. I. Balkaş, *Int. J. Radiat. Phys. Chem.* **1972**, *4*, 199–208.

[36] A. C. Shaikh, M. M. Hossain, J. Moutet, A. Kumar, B. Thompson, V. M. Huxter, T. L. Gianetti, *Angew. Chem. Int. Ed.* **2025**, DOI 10.1002/anie.202420483.

[37] T. J. B. Zähringer, M. Wienhold, R. Gilmour, C. Kerzig, *J. Am. Chem. Soc.* **2023**, *145*, 21576-21586.

[38] B. G. Stevenson, E. H. Spielvogel, E. A. Loiaconi, V. M. Wambua, R. V. Nakhamiyayev, J. R. Swierk, *J. Am. Chem. Soc.* **2021**, *143*, 8878-8885.

[39] J. S. Beckwith, A. Aster, E. Vauthey, *Phys. Chem. Chem. Phys.* **2022**, *24*, 568-577.

[40] E. Bassan, R. Inoue, D. Fabry, F. Calogero, S. Potenti, A. Gualandi, P. G. Cozzi, K. Kamogawa, P. Ceroni, Y. Tamaki, O. Ishitani, *Sustainable Energy & Fuels* **2023**, *7*, 3454-3463.

[41] Y. Wu, Z. Chen, Y. Yang, W. Zhu, B. Zhou, *J. Am. Chem. Soc.* **2018**, *140*, 42-45.

[42] S. Bazzi, E. Schulz, M. Mellah, *Org. Lett.* **2019**, *21*, 10033-10037.

[43] J. W. Beattie, D. S. White, A. Bheemaraju, P. D. Martin, S. Groysman, *Dalton Trans.* **2014**, *43*, 7979-7986.

[44] E. Mezzina, M. Fanì, F. Ferroni, P. Franchi, M. Menna, M. Lucarini, *J. Org. Chem*. **2006**, *71*, 3773-3777.