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Discovery and characterization of an acridine radical photoreductant

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Photoinduced electron transfer (PET) is a phenomenon whereby the absorption of light by a chemical species provides an energetic driving force for an electron-transfer reaction¹⁻⁴. This mechanism is relevant in many areas of chemistry, including the study of natural and artificial photosynthesis, photovoltaics and photosensitive materials. In recent years, research in the area of photoredox catalysis has enabled the use of PET for the catalytic generation of both neutral and charged organic freeradical species. These technologies have enabled previously inaccessible chemical transformations and have been widely used in both academic and industrial settings. Such reactions are often catalysed by visible-light-absorbing organic molecules or transition-metal complexes of ruthenium, iridium, chromium or copper^{5,6}. Although various closed-shell organic molecules have been shown to behave as competent electron-transfer catalysts in photoredox reactions, there are only limited reports of PET reactions involving neutral organic radicals as excited-state donors or acceptors. This is unsurprising because the lifetimes of doublet excited states of neutral organic radicals are typically several orders of magnitude shorter than the singlet lifetimes of known transition-metal photoredox catalysts⁷⁻¹¹. Here we document the discovery, characterization and reactivity of a neutral acridine radical with a maximum excitedstate oxidation potential of -3.36 volts versus a saturated calomel electrode, which is similarly reducing to elemental lithium, making this radical one of the most potent chemical reductants reported¹². Spectroscopic, computational and chemical studies indicate that the formation of a twisted intramolecular charge-transfer species enables the population of higher-energy doublet excited states, leading to the observed potent photoreducing behaviour. We demonstrate that this catalytically generated PET catalyst facilitates several chemical reactions that typically require alkali metal reductants and can be used in other organic transformations that require dissolving metal reductants.

Our laboratory, as well as others, has published numerous examples highlighting the diverse reactivity of acridinium salts, such as Mes-Acr⁺BF₄⁻ (Mes, mesityl; Acr, acridinium), as photooxidation catalysts in the excited state (*Mes-Acr⁺; Fig. 1a)¹³. Upon absorption of visible light, the corresponding excited state of the acridinium salt is populated and may be quenched via electron transfer from an electrochemically matched substrate, resulting in the formation of an acridine radical (Mes-Acr⁺; Fig. 1a). In past work using acridinium photoredox catalysts, this radical was typically oxidized to regenerate the parent acridinium and close a catalytic cycle. During previous mechanistic studies conducted by our laboratory, it was noted that solutions of Mes-Acr⁺ generated via reduction of Mes-Acr⁺BF₄⁻ with cobaltocene were indefinitely stable under oxygen-free conditions and possessed two major absorption features (at 350–400 nm and 450–550 nm; Fig. 1b)¹⁴. These observations led us to explore the photophysical behaviour of this

radical, with a focus on identifying potential PET behaviour. Previous studies have detailed the in situ generation and excitation of stable cation and anion radical species and their use in catalytic reactions¹⁵⁻¹⁹, indicating the potential feasibility of this strategy and prompting our studies of the photophysical behaviour of Mes-Acr^{*}.

Upon investigation of the excited-state dynamics of Mes-Acr', we found that there are two main excited states, tentatively assigned as a lower-energy doublet (D_1) and a higher-energy twisted intramolecular charge-transfer (TICT) state. The excited-state energy for the doublet excited state of Mes-Acr' is estimated by averaging the energies of the lowest-energy absorption maximum and the highest-energy emission observed upon excitation at 484 nm. The energy of the proposed higher-order excited state is estimated by averaging the energies of the emission maximum near 490 nm and the maximum of the corresponding excitation spectrum monitored at this wavelength

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Fig. 1 | **Mechanistic studies of Mes-Acr radical. a**, Reduction potential of various elemental alkali metals compared to the peak reducing potential of Mes-Acr'. E_{oxr}^* excited-state oxidation potential; E_{red}^* , excited-state reduction potential; $E_{1/2}^{red}$, half-wave reduction potential. **b**, Absorbance and emission (excitation, 400 nm) profiles for Mes-Acr' in MeCN (5 mM, 1 mm path length). **c**, SOMO and LUMO +1 visualizations for Mes-Acr'. **d**, Transient absorption spectra of Mes-Acr' (2.5 mM, THF, 1 mm path length) collected with a 250-fs

(see Supplementary Information for details of the excited-state energy calculations). Estimation of excited-state energies in this fashion gives values of 2.31 eV for the energy of the proposed D_1 excited state and 2.76 eV for the corresponding higher-energy excited state (Fig. 1e). Using the known electrochemical potential of Mes-Acr' (ref. ²⁰), the excited-state oxidation potentials of these states were estimated to be -2.91 V and -3.36 V, respectively, with respect to a saturated calomel electrode (vs SCE). To our knowledge, these values represent some of the most negative excited-state oxidation potentials reported for an organic molecule.

Before we proceed to discuss the calculated excited-state energies, we consider the key orbitals involved in the low-lying excited states. We find that the singly occupied molecular orbital (SOMO) density is

pump pulse centred at 400 nm. **e**, Excited-state energies calculated using the SRSH-PCM/TD-DFT method for Mes-Acr' (left) and frontier orbital plot showing the donor and acceptor density for the TICT excited state (right). **f**, Debromination reaction of brominated acridinium derivative giving circumstantial evidence for the TICT state. Mes, mesityl; DIPEA, *N*,*N*-diisopropylethylamine; *t*-Bu, *tert*-butyl.

localized on the acridine core, and LUMO + 1 (where LUMO is the lowest unoccupied molecular orbital) is localized on the *N*-phenyl ring of Mes-Acr' (Fig. 1c). On the basis of this observation of small spatial overlap between these two orbitals, we expect to find a relatively lowlying excitation of an intramolecular charge-transfer state. To further probe the excited-state behaviour of Mes-Acr', we performed transient absorption experiments (Fig. 1d). At early pump-probe delay times in tetrahydrofuran (THF), the ground state of Mes-Acr' is bleached (change in absorption, $\Delta A < 0$) and excited-state absorbance resonances ($\Delta A > 0$) with maxima at 550 nm and -650 nm are observed. Aromatic radical anions are known to exhibit broad absorbance peaks in the 600–800 nm range as do aqueous solvated electrons²¹⁻²⁵. The observed excited-state absorbance signal at -550 nm also matches the

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Fig. 2| **Reductive dehalogenation of aryl halides enabled by acridine radical photoredox catalysis. a**, Reaction scope. **b**, Proposed mechanism. a 0.3 M reaction concentration. b 0.5 M reaction concentration. $E_{p/2}$, half-peak potential; LEDs, light-emitting diodes; H', hydrogen atom source; hv, photon.

absorbance profile expected for a general acridine exitonic structure. Simple first-order decay to the ground state occurs after -100 ps, matching well with previously reported values for excited-state lifetimes of organic radicals. Time-dependent density functional theory (TD-DFT) calculations indicate that other red-shifted absorptions present are well matched with energies calculated for a general acridinium structure. These spectral features support the formation of a charge-transfer state possessing both aromatic radical anion and acridinium features, as expected for the proposed TICT state.

To better understand the effect of rotation of the *N*-phenyl ring on the excited-state energetics of the acridine radical, we employ the recently reported polarization-consistent TD-DFT-based framework for obtaining excited-state energies of solvated molecular systems. The approach addresses dielectric polarization consistently by invoking the same dielectric constant in the screened range-separated hybrid (SRSH) functional parameters and in the polarizable continuum mode (PCM). SRSH-PCM was benchmarked well in the calculation of charge-transfer state energies of solvated donor–acceptor complexes and in the analysis of the spectral trends of several pigments with increased accuracy, where conventional TD-DFT calculations fail to reproduce the observed trends (see Supplementary Information for full computational details)^{26–29}.

The calculated doublet excited-state energies for Mes-Acr' agree very well (within 0.1 eV) with values determined through spectroscopic measurements for both the absorption and emission spectra (Fig. 1e). The calculated lowest-energy D1 state, with an excited-state energy of 2.29 eV, agrees with the experimentally determined D₁ value of 2.31 eV. Additionally, two excited states with substantial charge-transfer character were identified and the corresponding energies were calculated to be 2.75 eV and 2.78 eV, matching closely the estimated spectroscopic values for the proposed TICT state energy of 2.76 eV. As such, the identified D_1 (2.29 eV) state is assigned as an untwisted exitonic state, whereas the calculated 2.78 eV state is assigned as a TICT state. These excited-state energies also correspond well with previously reported excited-state energies for neutral radical species9. Additionally, visualizations of the geometries of the corresponding TICT state indicate sizeable rotation of the N-phenyl ring (36°) relative to the more planarized geometry of the D₁ state, providing further evidence of the profound effects of N-phenyl rotation on excited-state energy.

With the electronic and excited-state behaviour of Mes-Acr' elucidated, we sought to use this species as a catalytic reductant in a photoredox manifold. Previous work in reductive photoredox catalysis has established the reduction of aryl halides as a common benchmark



Fig. 3 | **Scope of reductive detosylation catalysed by Mes-Acr**.¹H NMR yields obtained using DMSO or pyrazine as the internal standard. ^a48 h reaction time. ^b0.5 M reaction concentration. Ts, *p*-toluenesulfonyl.

reaction^{15,25,29,30}. Furthermore, the extremely potent reducing behaviour of the acridine radical should enable the reduction of a wide range of electronically diverse substrates. Diisopropylamine (DIPEA) was identified as a suitable single-electron reductant for the generation of Mes-Acr⁺from Mes-Acr⁺BF₄⁻ in situ. Following excitation, Mes-Acr⁺BF₄⁻ undergoes single-electron reduction via electron transfer from DIPEA, generating the desired radical Mes-Acr⁻. To chemically probe the possibility of charge transfer to the *N*-phenyl ring, brominated acridinium (1) was prepared. In the presence of 3 equiv. DIPEA, **1** was completely converted to a mixture of debrominated acridinum (1a) and hydroacridine (1b) following irradiation at 390 nm for 18 h (Fig. 1f). As aryl halide radical anions are known to quickly fragment to yield the corresponding aryl radicals, this experiment is indicative of the formation of radical anion character localized on the *N*-phenyl ring during excitation.

To evaluate the competency of this radical species as a catalytic reductant, conditions for the reductive dehalogenation of aryl halides were developed (Fig. 2a). A variety of both electron-rich (**6–13**) and electron-poor (**14, 15**) aryl bromides afforded the desired hydrodebrominated products in good to excellent yields (nuclear magnetic resonance, NMR, yields of products were taken using hexamethyldisiloxane as an internal standard). It is of note that reductively recalcitrant aryl chlorides also participated efficiently in this reaction, in contrast to previously reported methods that are only effective for electron-poor (under visible-light irradiation) or moderately electron-rich aryl chlorides (under UVA irradiation)^{31–35}. A variety of both electron-donating (**16–20**) and electron-withdrawing (**21–24**) substituents were tolerated, with only slightly reduced yields in the case of electron-poor substrates.

Substrates bearing ketone (**30**), carboxylic acid (**31**) and alcohol (**28**) functionalities all afforded the desired hydrodechlorinated products in good to excellent yield. Medicinally relevant pyridine (**25**, **26**) and aryl carbamate (**27**) derivatives were also efficient substrates for this transformation. When substrate (**23**), which bears a trifluoromethyl substituent, was subjected to the reaction conditions, partial hydrodefluorination (5%) that yielded the corresponding difluoromethyl derivative was observed in addition to hydrodechlorination. In all other examples, no Birch-type products resulting from overreduction were detected. The bis-reduction of polyhalogenated compounds (**9a**) and (**9b**) gave the corresponding bis-hydrodebromination (**9**) and bis-hydrodechlorination products in 58% and 46% yield, respectively. For compound (**9b**), 49% yield of the product resulting from mono-hydrodechlorination (**9c**) was observed in addition to the fully dechlorinated product.

On the basis of prior work in reductive dehalogenation, the following mechanism is proposed (Fig. 2b). Following excitation, Mes-Acr⁺BF₄⁻ engages in single electron transfer with the tertiary amine reductant DIPEA, generating Mes-Acr⁺ and the corresponding amine cation radical. Mes-Acr⁺ is then excited by 390-nm light, populating a combination of highly reducing D_n/TICT excited states, and undergoes electron transfer with an electronically matched aryl halide, generating an arene radical anion and reforming Mes-Acr⁺BF₄⁻. The arene radical anion then fragments, yielding an aryl radical. The resulting aryl radical abstracts a hydrogen atom from the amine cation radical, yielding the desired product as well as the corresponding iminium salt. Deuterium-labelling studies confirmed the amine cation radical as the

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primary source of hydrogen atoms in this system (see Supplementary Information section 8).

The reductive detosylation of amines was identified as another possible transformation, which may be facilitated by Mes-Acr[•] (Fig. 3). Typically, strong-acid, dissolving-metal (Li/Mg) or low-valent transition-metal reductions are employed in detosylation reactions³⁶⁻³⁸. A variety of electronically diverse tosylated aniline derivatives were smoothly converted to the desired free anilines in moderate-to-excellent yield. Interestingly, substrates containing aryl halides were tolerated under the reaction conditions. As this reaction is conducted at a much lower concentration of substrate compared to the reductive dehalogenation method (0.1 M versus 0.5 M), the observed lack of aryl halide reduction may be a function of concentration. Esters (43, 73), free carboxylic acids (44), ketones (48) and free alcohols (58) were tolerated under the reaction conditions, showing the high functionalgroup tolerance of this method relative to methods relying on harsh dissolving-metal conditions. Benzylic (52) and secondary alkyl amines (45, 53, 65-68) were efficient substrates for this transformation as well. Medicinally relevant heterocycles-including pyridines (59), indoles (58), pyrroles (62), pyrrolidines (67), indazoles (63), benzimidazoles (64) and morpholines (65)-were deprotected in good-toexcellent yields, with no reduction of the aromatic system observed in all cases. Of note is the ability of this method to chemoselectively and efficiently deprotect tosyl amines over mesyl-protected amines, as shown by the reaction of substrate 51, yielding the desired detosylation product in 61% yield with no observed cleavage of the mesyl amine. Additionally, the reaction performed well with 1.28 g of starting tosylamine, with substrate 64 giving 92% yield when the desired detosylation was conducted in a standard round-bottom flask irradiated with light-emitting diode lamps (see Supplementary Information for experimental details).

In conclusion, an acridine radical generated in situ from singleelectron reduction of an acridinium derivative may act as a potent single-electron reductant upon excitation with 390-nm light. Spectroscopic and computational investigations indicate the formation of at least two distinct excited states, one of which may be characterized as a TICT state. The development of chemoselective dehalogenation and desulfonylation reactions using Mes-Acr' complement the well known oxidative chemistry associated with acridinium salts and highlight the potential for the development of other types of reaction based on excitation of organic radicals.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-020-2131-1.

- Mattay, J. Photoinduced electron transfer in organic synthesis. Synthesis 1989, 233–252 (1989).
- Bauer, A., Westkämper, F., Grimme, S. & Bach, T. Catalytic enantioselective reactions driven by photoinduced electron transfer. *Nature* 436, 1139–1140 (2005).
- Fox, M. A. Photoinduced electron transfer. *Photochem. Photobiol.* 52, 617–627 (1990).
 Fukuzumi, S. New development of photoinduced electron-transfer catalytic systems.
- Pure Appl. Chem. 79, 981–991 (2007).
 Romero, N. A. & Nicewicz, D. A. Organic photoredox catalysis. Chem. Rev. 116,
- 10075-10166 (2016).
 Prier, C. K., Rankic, D. A. & MacMillan, D. W. C. Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. *Chem. Rev.* 113,
- 5322-5363 (2013).
 Johnston, L. J. Photochemistry of radicals and biradicals. *Chem. Rev.* 93, 251-266 (1993).
 Arradd R. P. Scienzo, J. C. & McGimpson, W. G. Electron transfer quanching of excited.
- Arnold, B. R., Scaiano, J. C. & McGimpsey, W. G. Electron-transfer quenching of excited diphenylmethyl radicals. J. Am. Chem. Soc. 114, 9978–9982 (1992).

- Scaiano, J. C., Tanner, M. & Weir, D. Exploratory study of the intermolecular reactivity of excited diphenylmethyl radicals. J. Am. Chem. Soc. 107, 4396–4403 (1985).
- Samanta, A. et al. Quenching of excited doublet states of organic radicals by stable radicals. J. Phys. Chem. 93, 3651–3656 (1989).
- Weir, D. & Scaiano, J. C. Substituent effects on the lifetime and fluorescence of excited diphenylmethyl radicals in solution. *Chem. Phys. Lett.* **128**, 156–159 (1986).
- Scordilis-Kelley, C. Alkali metal reduction potentials measured in chloroaluminate ambient-temperature molten salts. J. Electrochem. Soc. 139, 694–699 (1992).
- Margrey, K. A. & Nicewicz, D. A. A general approach to catalytic alkene anti-Markovnikov hydrofunctionalization reactions via acridinium photoredox catalysis. Acc. Chem. Res. 49, 1997–2006 (2016).
- Romero, N. A. & Nicewicz, D. A. Mechanistic insight into the photoredox catalysis of Anti-Markovnikov alkene hydrofunctionalization reactions. J. Am. Chem. Soc. 136, 17024–17035 (2014).
- Ghosh, I., Ghosh, T., Bardagi, J. I. & König, B. Reduction of aryl halides by consecutive visible light-induced electron transfer processes. Science 346, 725–728 (2014).
- Connell, T. U. et al. The tandem photoredox catalysis mechanism of [Ir(ppy)₂(dtb-bpy)]^{*} enabling access to energy demanding organic substrates. J. Am. Chem. Soc. 141, 17646–17658 (2019).
- Lu, C., Fujitsuka, M., Sugimoto, A. & Majima, T. Dual character of excited radical anions in aromatic diimide bis(radical anion)s: donor or acceptor? J. Phys. Chem. C 121, 4558–4563 (2017).
- Christensen, J. A. et al. Phenothiazine radical cation excited states as super-oxidants for energy-demanding reactions. J. Am. Chem. Soc. 140, 5290–5299 (2018).
- Gumy, J.-C. & Vauthey, E. Investigation of the excited-state dynamics of radical ions in the condensed phase using the picosecond transient grating technique. J. Phys. Chem. A 101, 8575–8580 (1997).
- Romero, N. A., Margrey, K. A., Tay, N. E. & Nicewicz, D. A. Site-selective arene C-H amination via photoredox catalysis. *Science* 349, 1326–1330 (2015).
- 21. Brancato, G. et al. Dual fluorescence through Kasha's rule breaking: an unconventional photomechanism for intracellular probe design. J. Phys. Chem. B **119**, 6144–6154 (2015).
- 22. Demchenko, A. P., Tomin, V. I. & Chou, P.-T. Breaking the Kasha rule for more efficient photochemistry. *Chem. Rev.* **117**, 13353–13381 (2017).
- 23. Peng, Z. et al. Expression of anti-Kasha's emission from amino benzothiadiazole and its utilization for fluorescent chemosensors and organic light emitting materials. J. Mater. Chem. C 6, 7864–7873 (2018).
- Scuppa, S., Orian, L., Donoli, A., Santi, S. & Meneghetti, M. Anti-Kasha's rule fluorescence emission in (2-ferrocenyl)indene generated by a twisted intramolecular charge-transfer (TICT) process. J. Phys. Chem. A **115**, 8344–8349 (2011).
- 25. Shida, T. Electronic Absorption Spectra of Radical Ions (Elsevier, 1988).
- Bhandari, S. & Dunietz, B. D. Quantitative accuracy in calculating charge transfer state energies in solvated molecular complexes using a screened range separated hybrid functional within a polarized continuum model. J. Chem. Theory Comput. 15, 4305–4311 (2019).
- Song, Y. et al. Vibronic structure of photosynthetic pigments probed by polarized twodimensional electronic spectroscopy and ab initio calculations. *Chem. Sci.* **10**, 8143–8153 (2019).
- Bhandari, S., Cheung, M. S., Geva, E., Kronik, L. & Dunietz, B. D. Fundamental gaps of condensed-phase organic semiconductors from single-molecule calculations using polarization-consistent optimally tuned screened range-separated hybrid functionals. *J. Chem. Theory Comput.* 14, 6287–6294 (2018).
- Maiti, B. et al. Enhancing charge mobilities in organic semiconductors by selective fluorination: a design approach based on a quantum mechanical perspective. *Chem. Sci.* 8, 6947–6953 (2017).
- Kerzig, C. & Goez, M. Generating hydrated electrons through photoredox catalysis with 9-anthrolate. Phys. Chem. Chem. Phys. 17, 13829–13836 (2015).
- Kerzig, C., Guo, X. & Wenger, O. S. Unexpected hydrated electron source for preparative visible-light driven photoredox catalysis. J. Am. Chem. Soc. 141, 2122–2127 (2019).
- Poelma, S. O. et al. Chemoselective radical dehalogenation and C–C bond formation on aryl halide substrates using organic photoredox catalysts. J. Org. Chem. 81, 7155–7160 (2016).
- Discekici, E. H. et al. A highly reducing metal-free photoredox catalyst: design and application in radical dehalogenations. *Chem. Commun.* 51, 11705–11708 (2015).
- Narayanam, J. M. R., Tucker, J. W. & Stephenson, C. R. J. Electron-transfer photoredox catalysis: development of a tin-free reductive dehalogenation reaction. J. Am. Chem. Soc. 131, 8756–8757 (2009).
- Yin, H. et al. The hexachlorocerate(III) anion: a potent, benchtop stable, and readily available ultraviolet A photosensitizer for aryl chlorides. J. Am. Chem. Soc. 138, 16266–16273 (2016).
- Javorskis, T. & Orentas, E. Chemoselective deprotection of sulfonamides under acidic conditions: scope, sulfonyl group migration, and synthetic applications. J. Org. Chem. 82, 13423–13439 (2017).
- Shohji, N., Kawaji, T. & Okamoto, S. Ti(O-i-Pr)_d/Me₃SiCl/Mg-mediated reductive cleavage of sulfonamides and sulfonates to amines and alcohols. Org. Lett. 13, 2626–2629 (2011).
- Alonso, E., Ramón, D. J. & Yus, M. Reductive deprotection of allyl, benzyl and sulfonyl substituted alcohols, amines and amides using a naphthalene-catalysed lithiation. *Tetrahedron* 53, 14355–14368 (1997).

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Data availability

The data supporting the findings of this study are available within the paper and its Supplementary Information.

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Author contributions I.A.M. and D.A.N. were responsible for the initial conception of the project. I.A.M., L.W. and N.P.R.O. devised and executed all experimental work. N.P.R.O., D.A.N., K.B., B.D.D., O.F.W. and I.A.M. assisted in the preparation and editing of the final manuscript. O.F.W. assisted in the collection and O.F.W. and A.M.M. performed analysis of transient absorption data. B.D.D. designed the computational approach, K.B. executed the calculations and K.B., B.D.D., N.P.R.O. and D.A.N. were responsible for the analysis of computations.

Competing interests The authors declare no competing interests.

Additional information

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