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2,3-Diarylmaleate salts as a versatile class of diarylethenes with a full spectrum of photoactivity in water†‡

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There is incessant interest in the transfer of common chemical processes from organic solvents to water, which is vital for the development of bioinspired and green chemical technologies. Diarylethenes feature a rich photochemistry, including both irreversible and reversible reactions that are in demand in organic synthesis, materials chemistry, and photopharmacology. Herein, we introduce the first versatile class of diarylethenes, namely, potassium 2,3-diarylmaleates (DAMs), that show excellent solubility in water. DAMs obtained from highly available precursors feature a full spectrum of photoactivity in water and undergo irreversible reactions (oxidative cyclization or rearrangement) or reversible photocyclization (switching), depending on their structure. This finding paves a way towards wider application of diarylethenes in photopharmacology and bioinspired technologies that require aqueous media for photochemical reactions.

Introduction

Light is a unique energy source for chemical reactions providing the opportunity to induce them in a selected volume within the selected period of time.[1–4] Varying the properties of a molecule by its reversible or irreversible photochemical transformation is of great interest for the development of new methods and technologies in materials chemistry, biology and medicine.[5,6] Solubility of photoactive organic molecules in water is a crucial requirement in many bio-related applications.[7,8] For example, bioimaging beyond the diffraction limit with high-resolution fluorescence microscopy became possible in aqueous solutions using appropriate photoswitchable dyes as labels.[9–13] Among photoactive molecules, diarylethenes (DAEs) became one of the most powerful molecular tools for photochemical applications. There are three modes of DAE's chemical activity associated with light-induced cyclization (Scheme 1A): reversible switching between initial and closed-ring isomers,[14] irreversible oxidative cyclization towards tricyclic aromatics (Mallory reaction);[15] irreversible photorearrangement to bicyclic aromatics.[16] The classical Mallory reaction is used mainly for building polyaromatic compounds that contain a fragment of phenanthrene or its analogues (Scheme 1A(a)).[17–21] The photoswitching of DAEs finds application in the development of stimuli-responsive materials and light-controllable processes (Scheme 1A(b)).[22–27] The photorearrangement with formation of bicyclic aromatics is a recently discovered transformation (Scheme 1A(c)) that is promising for various applications, including organic synthesis,[28–30] photopharmacology[31] and click-chemistry.[32]

Water-soluble DAEs bearing solubilizing charged groups are in demand for various photopharmacological and biomedical applications (Scheme 1B). The only example of the Mallory reaction in aqueous solutions was reported for light-induced generation of a DNA/RNA intercalator by **wDAE-1** with a protonated amidine substituent.[33] Reversible switching was successfully performed for DAEs that comprised of, among others,[7] phosphate and phosphonate (**wDAE-2** (ref. 34)), pyridinium (**wDAE-3** (ref. 35 and 36), **wDAE-4** (ref. 37)), ammonium (**wDAE-5** (ref. 38)) and carboxylate groups (**wDAE-6** (ref. 39)). The corresponding dyes were successfully applied as photocontrollable enzyme inhibitors, DNA ligands, dyes for bioimaging, and agents for the control of physiological functions of living

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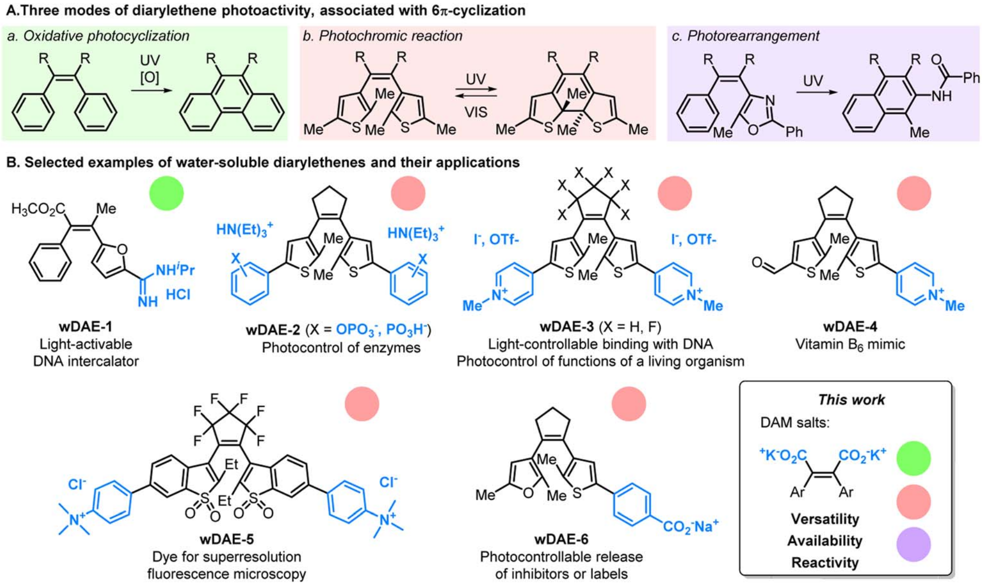


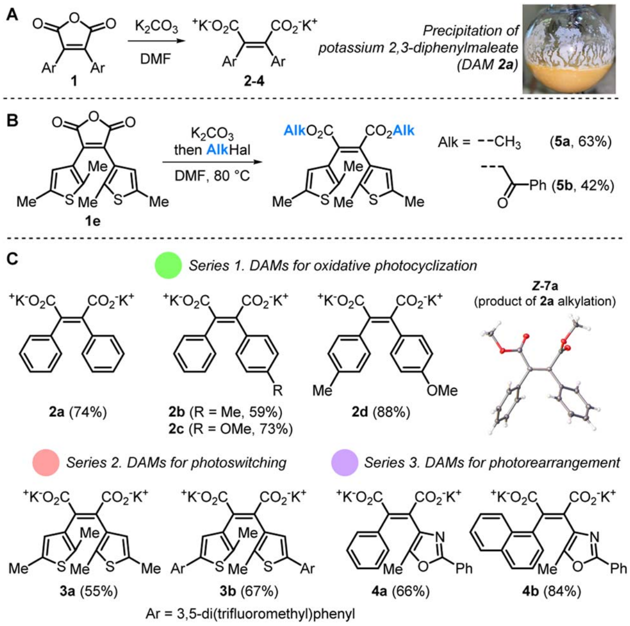
Scheme 1 Three types of DAE photoreactions (A). Water-soluble DAEs for various bio-related applications (B).

organisms. It should be noted that all examples of water-soluble DAEs contain charged groups in the pendant aromatic rings. This approach is not universal and requires a significant change in the synthesis strategy depending on the desired structure. Introduction of a solubilizing group on the central part of the molecule is an alternative approach that has never been probed for the synthesis of water-soluble DAEs. It can be expected that this method should allow the incorporation of any type of aromatic moiety "by choice" and pave a way towards the modular construction of water-soluble molecules with desired properties and functions. Herein, we introduce a first general class of water-soluble photoactive molecules – 2,3-DiArylMaleate (DAM) salts (Scheme 1B). In the structure of DAMs, two solubilizing carboxylate groups are directly attached to the central double bond and could be combined with various aromatic moieties while retaining the entire spectrum of DAE photoactivity in water.

Results and discussion

To date, DAM salts have never been considered as an individual class of organic molecules, although these entities were often involved as intermediates in the synthesis/cleavage of 3,4-di(het)arylfuran-2,5-diones **1** or related maleimides (Scheme 2).[40,41] Straightforward hydrolysis of **1** in aqueous alkali is not suitable for DAM isolation. We assumed that this problem could be overcome by cleavage of 3,4-di(het)arylfuran-2,5-diones **1** in dry DMF with potassium carbonate (K_2CO_3). First of all, we attempted trapping DAMs by *in situ* alkylation in the reaction starting from **1e** (Scheme 2). The treatment of **1e** by K_2CO_3 at the heating followed by the addition of methyl iodide or 2-bromo-1-phenylethan-1-one led to the disappearance of the starting material and formation of the corresponding dithienylmaleic acid esters **5a** and **5b**. These products were isolated with 42–63% yields. The experiments clearly showed the generation of the potassium 2,3-dithienylmaleate by cleavage of the maleic anhydride cycle of **1e**.

To synthesize a range of multipurpose water-soluble DAMs, we used eight 3,4-di(het)arylfuran-2,5-diones **1** bearing two benzene rings (towards substrates for Mallory oxidative cyclization), two thienyl rings (for photoswitchable products) and both phenyl/naphthyl and oxazolyl rings (towards photorearrangement substrates). As expected, treatment of these compounds with K_2CO_3 in dry DMF with heating results in the



Scheme 2 Synthesis of the DAM salts from accessible 3,4-diarylfuran-2,5-diones (A). Trapping of DAM salt by alkylating agents (B). Scope of the DAM salts (C).

disappearance of the starting material. To ensure complete consumption of K_2CO_3, a slight excess of **1** was exploited (for details see Section III.1 in the ESI‡). In all cases, the reaction was accompanied by abundant precipitation of DAM salts, which were isolated by filtration. The desired salts **2–4** were obtained in 55–88% yields as stable solids and were fully characterized by ^{1}H and ^{13}C NMR spectroscopy in deuterated water (D_2O). DAM **3b** bearing two lipophilic 3,5-di(trifluoromethyl)phenyl moieties was an exception. This compound was readily soluble in a 1 : 1 water/acetonitrile mixture.

The obtained DAM salts were isolated exclusively as *Z*-isomers, that is predetermined by the structure of their substrates **1**. The *Z*-configuration was additionally confirmed by NOESY NMR for **4a** (Fig. S13‡) and by X-ray crystallography data for stilbene ***Z*-7a** obtained by direct alkylation of DAM **2a** (Scheme 2). The thermodynamic stability of *Z*-stilbenes is determined by the high activation energy barrier of *Z*- to *E*-isomerization.[42,43]

It was expected that the DAMs **2a–d** as close analogues of stilbene should undergo oxidative cyclization to phenanthrene derivatives (Scheme 1A(a)).[15,44] Irradiation of **2a** by UV (λ = 365 nm) in D_2O led to new products according to NMR spectroscopy (Fig. 1B). Complete disappearance of the substrate **2a** was reached after 240 h of reaction. The major product in the reaction mixture was identified as phenanthrene derivative **6a** with characteristic doublets of $H^{1(8)}$ and $H^{4(5)}$ at 8.05 and 8.85 ppm (Fig. 1A). Two minor photoproducts with NMR signals in the 7.20–7.40 ppm range were also detected in the reaction mixture. The preparative photoreaction of **2a** in water led to a mixture with the same composition. To isolate and characterize the products, we "transferred" the products from the aqueous phase to the organic one by trapping potassium salts with methyl iodide and separation by column chromatography (Fig. 1A). Two products where obtained: the expected phenanthrene **8a** (57% yield) and methyl diphenylmaleate **7a** in the *E*-configuration (31% yield). A similar reaction outcome was obtained for DAM salts **2b–d** (yields 55–66% for phenanthrenes **8b–d**; Fig. S4–S6‡). The structures of DAM **4b** photoproducts ***E*-7b** and **8b** were supported by X-ray crystallography (Fig. 1A). In addition, the molecular structures were obtained for photoproducts ***E*-7c** and **8d** (for details, see Section IV in the ESI‡).

The main photoproducts of photolysis of DAM salts **2a–d** were found to be expected phenanthrenes **6**, formed by 6π-photocyclization followed by oxidation by oxygen species.[45] The side process is *Z*-/*E*-isomerization, that is *quasi*-irreversible probably due to a low quantum yield. Photolysis of **2a** in the buffer solution (pH = 7.00) allowed us to detect the elusive 4*a*,4*b*-dihydrophenanthrene intermediate of the Mallory reaction,[45,46] a closed-ring isomer **2a-B** (Fig. 1A). These species are usually highly unstable and could be isolated in specific cases only.[46,47] This entity has absorbance maxima at 459 nm due to a conjugated system of π-bonds (Fig. 1B). Simulation of the spectrum by DFT calculations gave the value of 490 nm for this species (Table S3‡). The intermediate **2a-B** was thermally unstable and underwent fast bleaching in the dark. In the presence of air, the half-life of these species was *ca.* 200 s, while in nitrogen-saturated water, $t_{1/2}$(**2a-B**) = 300 s (Fig. S17‡). According to the literature data,[47,48] the product of unsubstituted stilbene photocyclization (4*a*,4*b*-dihydrophenanthrene) features a similar stability, suggesting that the effect of carboxylate anions on the stability of **2a-B** is minor.

The next probed photochemical reaction was the reversible switching of thiophene-derived DAMs **3a,b** between initial and closed-ring isomers (Scheme 1Ab).[14] Irradiation of **3a** with UV (254 nm) for 4.5 h in D_2O resulted in the formation of the

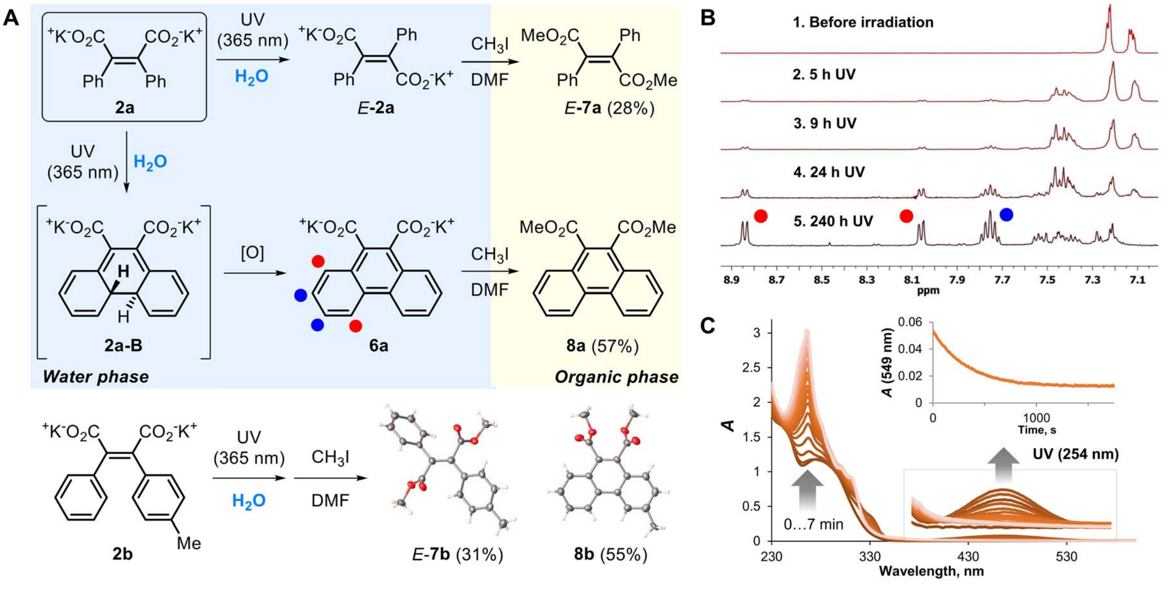


Fig. 1 Photoreactions of DAM **2a** and **2b** in water. Molecular structures of trapped photoproducts of DAM **2b** (A). ^{1}H NMR spectra under irradiation of **2a** with UV (365 nm) in D_2O (B). UV-Vis spectra under irradiation with UV (254 nm) in H_2O (buffer pH = 7.00) and thermal decay of colored intermediate **2a-B** (C).

closed-ring isomer **3a-B** (Fig. 2A) with an absorbance maximum at 450 nm (Fig. S21‡) with conversion ≈ 40%, that was clearly observed by the shift of thiophene protons in the NMR spectra (Fig. 2C). Subsequent irradiation with blue light resulted in the restoration of the initial spectrum. However, prolonged irradiation with UV to reach higher conversion results in two products: a $2a^1$,5*a*-dihydro-5,6-dithiaacenaphthylene derivative **9** and the *E*-isomer of **3a** (see Section III.4 in the ESI‡). The first one is the result of formal 1,2-dyotropic rearrangement, limiting the photoswitching of thiophene-based diarylethenes.[49,50]

The structures of both products were proved again by transferring the preparative reaction mixture to the organic phase followed by isolation of products **10** and ***E*-5a**. After 23 h of preparative photolysis of **3a** with subsequent methylation, the yields of **10** and ***E*-5a** were 58% and 24%, respectively.

Similarly to the diphenyl-substituted DAMs **2a–d**, dithienylethene derivative **3a** undergoes *Z*-/*E*-isomerization as well as irreversible phototransformation. These side reactions are highly undesirable for photoswitch applications. To bypass the 1,2-dyotropic rearrangement, we incorporated additional 3,5-di(trifluoromethyl)phenyl groups[50] to the thiophene rings in **3a** (DAM **3b**, Fig. 1B). As expected, **3b** displayed an enhanced light-induced switching between the initial state and the closed-ring isomer **3b-B**, which was tracked by UV-Vis and NMR spectroscopy. The open-ring form **3b** is colorless with an intense band at 315 nm ($\varepsilon = 24\,500$ M^{-1} cm^{-1}) (Fig. 2D). Upon UV irradiation, a prominent band of the closed-ring isomer **3b-B** at 545 nm ($\varepsilon = 10\,900$ M^{-1} cm^{-1}) emerges, which completely disappears upon green light irradiation. According to NMR spectroscopy, the conversion of **3b** to **3b-B** in the photostationary state was 84% (Fig. S10‡). The cyclization (Φ_{OC}) and cycloreversion (Φ_{CO}) quantum yields were 0.083 and 0.004, respectively. These values suggest that incorporation of carboxylate groups into the chromophore system reduces the efficiency of photoreactions in comparison with typical cyclopentene and perfluorocyclopentene diarylethenes.[50]

In contrast to **3a**, **3b** revealed switching between two isomers accompanied by a minor impact of side processes (Fig. 2E). In particular, the *Z*-/*E*-isomerization of **3b** was suppressed significantly. After two cycles, no signs of the *E*-product were found in NMR spectra (Fig. S10‡). In absorbance studies, only a minor contribution of the *E*-isomer (the shoulder at 370–380 nm) was detected after 7 cycles (Fig. S24‡) in contrast to **3a** (Fig. S22‡). Although diarylethenes with a completely suppressed cyclization pathway were described previously,[51,52] the effect of incorporating aryl groups on the *E*-/*Z*-isomerization is unknown to the best of our knowledge. We suggest that the difference in **3a**/**3b** performance is a result of the twofold increase in the extinction coefficients in the UVA region, a 10-fold decrease in Φ_{CO}, and an enhancement of Φ_{OC} in the case of **3b** (Table S1‡).

The drawback of the **3b** photoswitch is the decreased hydrophilicity due to the presence of four CF_3 groups. It is poorly soluble in water, so the experiments were performed in water/acetonitrile solutions (1 : 1). According to the previous results by Hecht *et al.*,[50] the number of lipophilic electron-withdrawing groups in the diarylethene molecule could be reduced without loss of fatigue resistance. This should be taken into account in the future design of DAM photoswitches.

Finally, we studied the DAMs **4a,b** as analogues of DAEs that undergo irreversible photorearrangement with formal cycloreversion of the oxazole ring (Scheme 1A(c)).[16,28] ^{1}H NMR monitoring of **4a** photolysis disclosed an almost quantitative

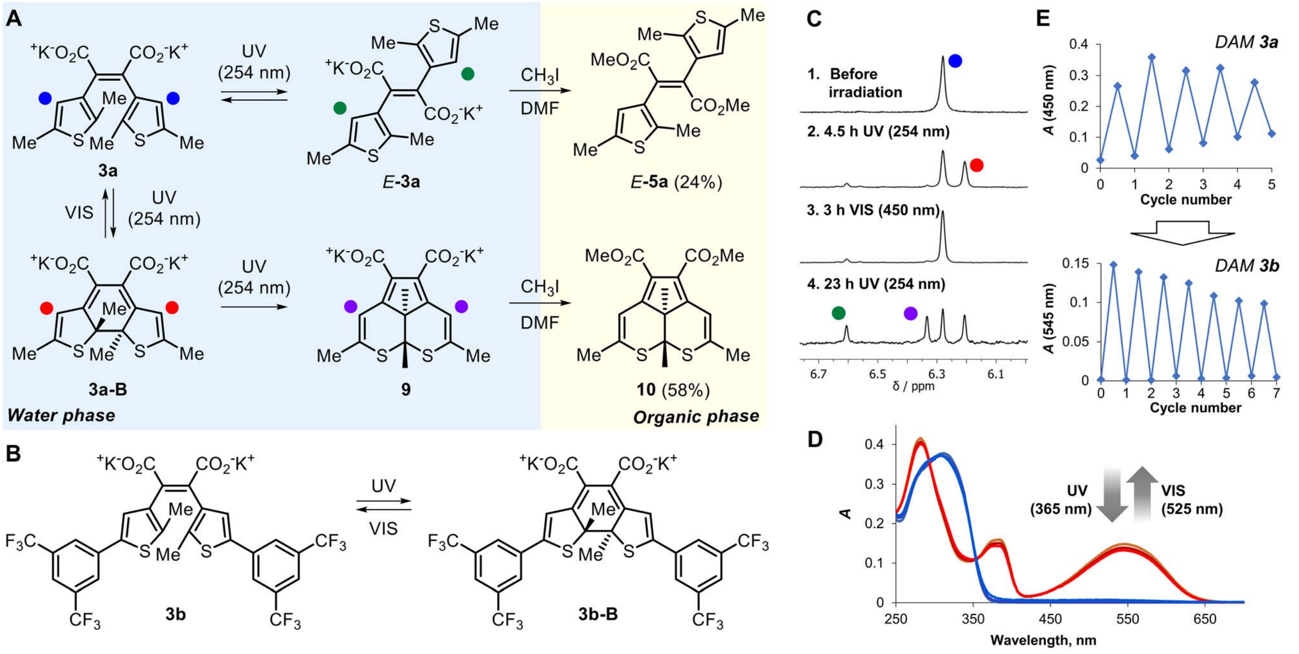


Fig. 2 Photoreactions of DAMs **3a** (A) and **3b** (B). ^{1}H NMR spectra of **3a** under irradiation with UV and visible light in D_2O (C). Changes in UV-Vis spectra of **3b** during three cycles of cyclization–cycloreversion in 1 : 1 MeCN/H_2O (D). Multiple photoswitching of DAMs **3a** and **3b** in H_2O and MeCN/H_2O (buffer pH = 7.00), respectively (E).

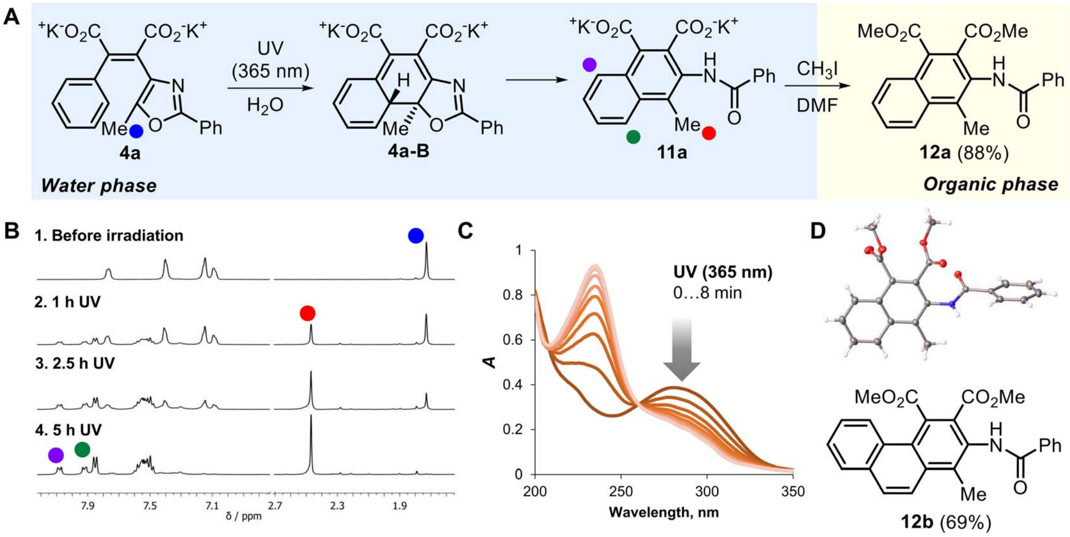


Fig. 3 Photochemical rearrangement of DAM **4a** in water (A). ^{1}H NMR spectra under irradiation with UV (365 nm) in D_2O (B). UV-Vis spectra under irradiation with UV (365 nm) in H_2O (C). Molecular structure of **12a** and structure of product **12b** (D).

conversion to a new product with characteristic doublets at 7.95 and 8.05 ppm, showing the formation of the naphthalene system of **11a** (Fig. 3A and B). The side *Z*-/*E*-isomerization was negligible, unlike DAMs **2a–d** and **3a** and similarly to **3b**. UV-Vis spectroscopy also disclosed the nearly quantitative conversion to a sole product accompanied by the isosbestic point at 260 nm (Fig. 3C).

Similarly to the related diarylethenes,[28,53] a key intermediate of the photorearrangement **4a-B** was not observed during photolysis due to a fast aromatization-driven migration of hydrogen, which triggers the irreversible process. Unexpectedly, the quantum yield of the irreversible rearrangement was relatively high, $\Phi = 0.33$. This value is comparable to quantum yields of the related DAEs, measured in acetonitrile ($\Phi = 0.34$ for the furanone derivative[54] and 0.15 for the cyclopentenone derivative[53]). The significant increase of the cyclization efficiency in comparison with photochromic DAMs **3a,b** ($\Phi_{OC} = 0.051–0.083$) could be explained by the stabilization of the photoactive conformation of diarylethene[55–57] (a possible approach is a fixation of the oxazole ring by non-covalent interactions of water with a nitrogen atom and carboxylate group[58]).

Preparative photolysis of **4a** with subsequent alkylation by methyl iodide afforded naphthalene derivative **12a** with 88% yield (the structure was proved by X-ray crystallography, Fig. 3D). The related result was obtained for DAM **4b** (Fig. S12‡), which formed the corresponding phenanthrene in the irreversible photorearrangement with good yield (alkylated product **12b** was isolated with 69% yield). It should be noted that intermediate **4b-B** is relatively stable[59] and was detected by its prominent absorbance band at 427 nm (Fig. S26‡).

Conclusions

In conclusion, we introduce the first versatile class of water-soluble diarylethenes, namely, potassium 2,3-diarylmaleates (DAMs). A technologically simple method for their synthesis from accessible 3,4-di(het)arylfuran-2,5-diones was suggested. Three types of efficient photochemical reactions of DAM salts in water were demonstrated. The first one is the Mallory reaction of diphenyl-substituted DAMs, leading to the phenanthrene derivatives with good yields. The second photoreaction is the reversible cyclization/cycloreversion, which was performed for thiophene-based DAMs. Finally, photolysis of DAMs bearing phenyl/naphthyl and oxazolyl groups resulted in rearrangement products. Such a combination of various modes of photoactivity in water is unique for diarylethenes. Due to availability and versatility, DAMs could be considered as promising photoactive agents for the development of new bioinspired and photopharmacological applications that require solubility in water.†

Data availability

The data related to this study are available from the corresponding author upon reasonable request.

Author contributions

I. A. B., A. O. U., E. S. S., A. A. F., Y. H., and A. V. S. synthesized 3,4-di(het)arylfuran-2,5-diones and DAM salts. I. A. B. and A. O. U. studied the photochemical properties of DAM salts. I. A. U. performed NMR spectroscopy. K. A. L. performed X-ray crystallography. A. G. L. performed DFT calculations. L. Y. and A. G. L. supervised the project and supported writing of the manuscript. All authors read and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 R. S. Stoll and S. Hecht, *Angew. Chem., Int. Ed.*, 2010, **49**, 5054–5075.
2 A. J. Teator, D. N. Lastovickova and C. W. Bielawski, *Chem. Rev.*, 2016, **116**, 1969–1992.
3 W. Szymański, J. M. Beierle, H. A. V. Kistemaker, W. A. Velema and B. L. Feringa, *Chem. Rev.*, 2013, **113**, 6114–6178.
4 V. M. Lechner, M. Nappi, P. J. Deneny, S. Folliet, J. C. K. Chu and M. J. Gaunt, *Chem. Rev.*, 2022, **122**, 1752–1829.
5 A. Goulet-Hanssens, F. Eisenreich and S. Hecht, *Adv. Mater.*, 2020, **32**, 1905966.
6 V. García-López, D. Liu and J. M. Tour, *Chem. Rev.*, 2020, **120**, 79–124.
7 J. Volarić, W. Szymanski, N. A. Simeth and B. L. Feringa, *Chem. Soc. Rev.*, 2021, **50**, 12377–12449.
8 R. Weinstain, T. Slanina, D. Kand and P. Klán, *Chem. Rev.*, 2020, **120**, 13135–13272.
9 B. Roubinet, M. L. Bossi, P. Alt, M. Leutenegger, H. Shojaei, S. Schnorrenberg, S. Nizamov, M. Irie, V. N. Belov and S. W. Hell, *Angew. Chem., Int. Ed.*, 2016, **55**, 15429–15433.
10 X. Chai, H.-H. Han, A. C. Sedgwick, N. Li, Y. Zang, T. D. James, J. Zhang, X.-L. Hu, Y. Yu, Y. Li, Y. Wang, J. Li, X.-P. He and H. Tian, *J. Am. Chem. Soc.*, 2020, **142**, 18005–18013.
11 K. Uno, A. Aktalay, M. L. Bossi, M. Irie, V. N. Belov and S. W. Hell, *Proc. Natl. Acad. Sci. U. S. A.*, 2021, **118**, e2100165118.
12 B. Roubinet, M. Weber, H. Shojaei, M. Bates, M. L. Bossi, V. N. Belov, M. Irie and S. W. Hell, *J. Am. Chem. Soc.*, 2017, **139**, 6611–6620.
13 K. Uno, M. L. Bossi, M. Irie, V. N. Belov and S. W. Hell, *J. Am. Chem. Soc.*, 2019, **141**, 16471–16478.
14 M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.*, 2014, **114**, 12174–12277.
15 K. B. Jørgensen, *Molecules*, 2010, **15**, 4334–4358.
16 A. G. Lvov, *J. Org. Chem.*, 2020, **85**, 8749–8759.
17 F. Saal, F. Zhang, M. Holzapfel, M. Stolte, E. Michail, M. Moos, A. Schmiedel, A.-M. Krause, C. Lambert, F. Würthner and P. Ravat, *J. Am. Chem. Soc.*, 2020, **142**, 21298–21303.
18 J. Tomada, T. Dienel, F. Hampel, R. Fasel and K. Amsharov, *Nat. Commun.*, 2019, **10**, 3278.
19 R. K. Mohamed, S. Mondal, J. V. Guerrera, T. M. Eaton, T. E. Albrecht-Schmitt, M. Shatruk and I. V. Alabugin, *Angew. Chem., Int. Ed.*, 2016, **55**, 12054–12058.
20 A. T. Turley, P. K. Saha, A. Danos, A. N. Bismillah, A. P. Monkman, D. S. Yufit, B. F. E. Curchod, M. K. Etherington and P. R. McGonigal, *Angew. Chem., Int. Ed.*, 2022, **61**, e202202193.
21 M. Krzeszewski, H. Ito and K. Itami, *J. Am. Chem. Soc.*, 2022, **144**, 862–871.
22 Y. Hai, H. Ye, Z. Li, H. Zou, H. Lu and L. You, *J. Am. Chem. Soc.*, 2021, **143**, 20368–20376.
23 F. Eisenreich, M. Kathan, A. Dallmann, S. P. Ihrig, T. Schwaar, B. M. Schmidt and S. Hecht, *Nat. Catal.*, 2018, **1**, 516–522.
24 S. M. Büllmann, T. Kolmar, N. F. Zorn, J. Zaumseil and A. Jäschke, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117735.
25 A. G. Lvov, A. V. Yadykov, K. A. Lyssenko, F. W. Heinemann, V. Z. Shirinian and M. M. Khusniyarov, *Org. Lett.*, 2020, **22**, 604–609.
26 C. Jurissek, F. Berger, F. Eisenreich, M. Kathan and S. Hecht, *Angew. Chem., Int. Ed.*, 2019, **58**, 1945–1949.
27 O. Babii, S. Afonin, C. Diel, M. Huhn, J. Dommermuth, T. Schober, S. Koniev, A. Hrebonkin, A. Nesterov-Mueller, I. V. Komarov and A. S. Ulrich, *Angew. Chem., Int. Ed.*, 2021, **60**, 21789–21794.
28 A. G. Lvov, V. Z. Shirinian, V. V. Kachala, A. M. Kavun, I. V. Zavarzin and M. M. Krayushkin, *Org. Lett.*, 2014, **16**, 4532–4535.
29 A. G. Lvov, A. M. Kavun, V. V. Kachala, K. A. Lyssenko and V. Z. Shirinian, *Org. Biomol. Chem.*, 2019, **17**, 4990–5000.
30 J. Fan, T. Wang, C. Li, R. Wang, X. Lei, Y. Liang and Z. Zhang, *Org. Lett.*, 2017, **19**, 5984–5987.
31 A. V. Yadykov, A. M. Scherbakov, V. V. Trofimova, A. G. Lvov, A. I. Markosyan, I. V. Zavarzin and V. Z. Shirinian, *Org. Lett.*, 2019, **21**, 9608–9612.
32 F. Zhang, Z. Zhang, L. Deng, H. Guo, T. Xia, W. Mao and J. Zhang, *Org. Lett.*, 2023, **25**, 872–876.
33 K. Starčević, G. Karminski-Zamola, I. Piantanida, M. Žinić, L. Šuman and M. Kralj, *J. Am. Chem. Soc.*, 2005, **127**, 1074–1075.
34 B. Reisinger, N. Kuzmanovic, P. Löffler, R. Merkl, B. König and R. Sterner, *Angew. Chem., Int. Ed.*, 2014, **53**, 595–598.
35 M. P. O'Hagan, J. Ramos-Soriano, S. Haldar, S. Sheikh, J. C. Morales, A. J. Mulholland and M. C. Galan, *Chem. Commun.*, 2020, **56**, 5186–5189.
36 U. Al-Atar, R. Fernandes, B. Johnsen, D. Baillie and N. R. Branda, *J. Am. Chem. Soc.*, 2009, **131**, 15966–15967.
37 D. Wilson and N. R. Branda, *Angew. Chem., Int. Ed.*, 2012, **51**, 5431–5434.
38 D. Kim, A. Aktalay, N. Jensen, K. Uno, M. L. Bossi, V. N. Belov and S. W. Hell, *J. Am. Chem. Soc.*, 2022, **144**, 14235–14247.
39 R. Göstl and S. Hecht, *Chem.–Eur. J.*, 2015, **21**, 4422–4427.
40 M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 803–808.
41 X. Mei, J. Wang, Z. Zhou, S. Wu, L. Huang, Z. Lin and Q. Ling, *J. Mater. Chem. C*, 2017, **5**, 2135–2141.
42 G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, 1934, **56**, 638–642.
43 K. Imato, A. Sasaki, A. Ishii, T. Hino, N. Kaneda, K. Ohira, I. Imae and Y. Ooyama, *J. Org. Chem.*, 2022, **87**, 15762–15770.
44 C. O. Parker and P. E. Spoerri, *Nature*, 1950, **166**, 603.
45 F. B. Mallory and C. W. Mallory, *Org. React.*, 1984, 1–456.

46 Y. Shi, S. K. Mellerup, K. Yuan, G.-F. Hu, F. Sauriol, T. Peng, N. Wang, P. Chen and S. Wang, *Chem. Sci.*, 2018, **9**, 3844–3855.

47 K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 1967, 662–678.

48 W. M. Moore, D. D. Morgan and F. R. Stermitz, *J. Am. Chem. Soc.*, 1963, **85**, 829–830.

49 M. Irie, T. Lifka, K. Uchida, S. Kobatake and Y. Shindo, *Chem. Commun.*, 1999, 747–750.

50 M. Herder, B. M. Schmidt, L. Grubert, M. Pätzel, J. Schwarz and S. Hecht, *J. Am. Chem. Soc.*, 2015, **137**, 2738–2747.

51 M. Takeshita, T. Hirowatari and A. Takedomi, *Tetrahedron Lett.*, 2016, **57**, 3565–3567.

52 X. Guo, J. Zhou, M. A. Siegler, A. E. Bragg and H. E. Katz, *Angew. Chem., Int. Ed.*, 2015, **54**, 4782–4786.

53 E. M. Glebov, N. V. Ruban, I. P. Pozdnyakov, V. P. Grivin, V. F. Plyusnin, A. G. Lvov, A. V. Zakharov and V. Z. Shirinian, *J. Phys. Chem. A*, 2018, **122**, 7107–7117.

54 A. V. Zakharov, E. B. Gaeva, A. G. Lvov, A. V. Metelitsa and V. Z. Shirinian, *J. Org. Chem.*, 2017, **82**, 8651–8661.

55 S. Fukumoto, T. Nakashima and T. Kawai, *Angew. Chem., Int. Ed.*, 2011, **50**, 1565–1568.

56 H. Ogawa, K. Takagi, T. Ubukata, A. Okamoto, N. Yonezawa, S. Delbaere and Y. Yokoyama, *Chem. Commun.*, 2012, **48**, 11838–11840.

57 V. Z. Shirinian, A. G. Lvov, M. M. Krayushkin, E. D. Lubuzh and B. V. Nabatov, *J. Org. Chem.*, 2014, **79**, 3440–3451.

58 T. Nakashima, R. Fujii and T. Kawai, *Chem.–Eur. J.*, 2011, **17**, 10951–10957.

59 A. V. Zakharov, A. V. Yadykov, A. G. Lvov, E. A. Mitina and V. Z. Shirinian, *Org. Biomol. Chem.*, 2020, **18**, 3098–3103.