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Synthesis and photoreactivity of pyridinium-substituted norbornadienes

Julian F. M. Hebborn, Robin Schulte, Thomas Paululat, and Heiko Ihmels*

Department of Chemistry and Biology, and Research Center of Micro- and Nanochemistry and (Bio-)Technology (Cμ), University of Siegen, Adolf-Reichwein-Str. 2, Siegen 57068, Germany
Email: ihmels@chemie.uni-siegen.de

This paper dedicated to Prof. Thomas J.J. Muller on the occasion of his 60th birthday

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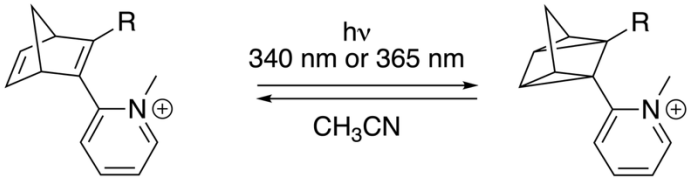
Abstract

Mono- and bispyridinium-substituted norbornadienes with different substitution pattern were synthesized in reasonable yields with Diels-Alder reactions of suitable hetaryl-substituted alkynes and cyclopentadiene, thus adding examples to the underexplored ionic norbornadiene derivatives. The photochemical properties of these compounds were investigated by absorption and NMR spectroscopy. Depending on the substitution pattern, the absorption bands extend close to the visible range. Upon direct irradiation, the norbornadiene derivatives are transformed into the corresponding quadricyclanes, but the reaction only proceeds properly with tetrafluoroborate as counter anion and in CH_3CN solution. In water and MeOH as well as with halide counter ions, significant side reactions and decomposition take place. Nevertheless, it was demonstrated exemplarily that the photoreaction can be performed in water by encapsulation of the norbornadiene and the photoproduct within a cucurbit[7]uril host molecule which protects the molecules from the solvent.



	Photostationary state
R = H	22 : 78
R = 2-*N*-methylpyridinium	33 : 67
R = 3-*N*-methylpyridinium	16 : 84
R = 3-*N*-methylpyridinium	15 : 85

Keywords: [2+2] photocycloaddition, cationic hetarenes, photochemistry, quadricyclanes

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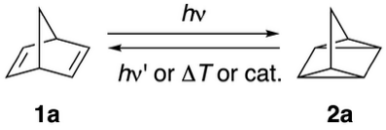
Introduction

Photochromic compounds are the paradigm of organic functional materials.[1-3] These so-called photoswitches undergo a photoinduced reversible transformation between two forms with different absorption, induced in one or both directions upon irradiation with light. Notably, these photochromic compounds may reversibly change their structure as well as their chemical and physical properties,[4,5] so that they are applied in light-responsive materials, such as, for example, self-coloring sunglasses,[6] photomechanical crystals,[7] energy storage systems (molecular solar thermal, MOST),[8,9] or even photopharmaceuticals.[10] Typical classes of photochromic compounds are azobenzene,[11] dihydroazulenes,[12] spiropyrans,[13] diarylethenes[14] and indigoids.[15] Along these lines, norbornadiene (**1**) and its derivatives represent highly robust and well-established photochromic compounds.[8,16] Upon irradiation, norbornadienes are transformed in an intramolecular [2+2] photocycloaddition in the corresponding quadricyclanes, such as **2**, and the backward cycloreversion may be triggered by light with higher energy, heat or catalysts (Scheme 1).[17,18]



Scheme 1. Photocycloaddition reaction of norbornadiene **1a** to quadricyclane **2a**.

As the quadricyclanes usually have a high energy density, namely ΔH = 966 kJ/kg for parent compound **2**,[19] and relatively long half-lives (**2**: $t_{1/2}$ >14 h at 140 °C),[20] norbornadienes are considered especially well suited as photochromic compounds that may be used for storage of light energy.[8,18,21] As a result, a large series of differently substituted and varied norbornadiene derivatives has been synthesized and thoroughly investigated.[8,9,16-21] These results contributed significantly to the knowledge about structure-property relationships with regard to the photochemical and physico-chemical properties of norbornadienes and allowed in particular to optimize their properties for the desired application.[9,16-21] However, ionic norbornadiene derivatives have been somewhat neglected in this context, even though it may be helpful to know whether cationic or anionic charges may be used to modify the photochemical properties, i.e. to introduce electron acceptor or donor properties. To add to that, ionic substrates offer the opportunity to introduce further functionalities by simple ion metathesis, thus not requiring additional covalent attachment.[22-25] To the best of our knowledge, the only cationic norbornadienes reported, so far, carry a pyrylium **3a**,[27] a pyridinium **3b**,**3c**,[26-28] a benzazolium,[29] a dimethylammonium **3d**,[30] or a phenyliodium **3e**[31,32] as ionic functionality (Figure 1). And only the pyridinium, pyrylium, benzazolium, and dimethylammonium substituted norbornadienes have been investigated with regards to their photoreactivity.[26-30] Specifically the pyrylium-containing norbornadiene **3a** exhibits a strong red-shifted absorption with zero onsets >500 nm, which is considered favorable for an application, because the photoreaction may be triggered with low-energy light, even sunlight.[27] But unfortunately, the corresponding quadricyclane was only proposed to form as an intermediate upon irradiation, which further reacts by the addition of water to the cyclopropane bond C3-C5.[27] In contrast, the absorption of the bispyridinium-substituted norbornadiene **3b** and its regioisomer still falls in the UV range, but formation of quadricyclanes has been detected upon irradiation. In this case, the absorption zero-onset strongly correlates with the substitution pattern, as the *para*-substituted norbornadiene **3b** has the most pronounced red-shifted absorption onset (≈ 430 nm) compared with the one

of the *meta*- (≈ 400 nm) and *ortho*-substituted isomers (≈ 400 nm).[26] However, the photoproduct of the norbornadiene **3b** with the most pronounced red-shifted absorption also formed an addition product with water or methanol.[26] In addition, monocationic norbornadienes, such as **3c**, have also been investigated. These compounds were obtained by protonation of the corresponding pyridiyl-substituted norbornadienes, and the protonated quadricyclanes showed an exceptionally long half-life.[28] In order to build on this preliminary work and to provide complementary data for a systematic classification of the photochemical properties of cationic derivatives, we focused our attention on 2-pyridinium-substituted norbornadienes with varied attachment of pyridinium regioisomers at position 3 of the norbornadiene scaffold. Herein, we present the synthesis of novel representatives of this class of compounds along with the investigation of their absorption and photochemical properties. In preliminary experiments, we also examined the exchange of counter anions and the influence of the latter on the photochemical properties.

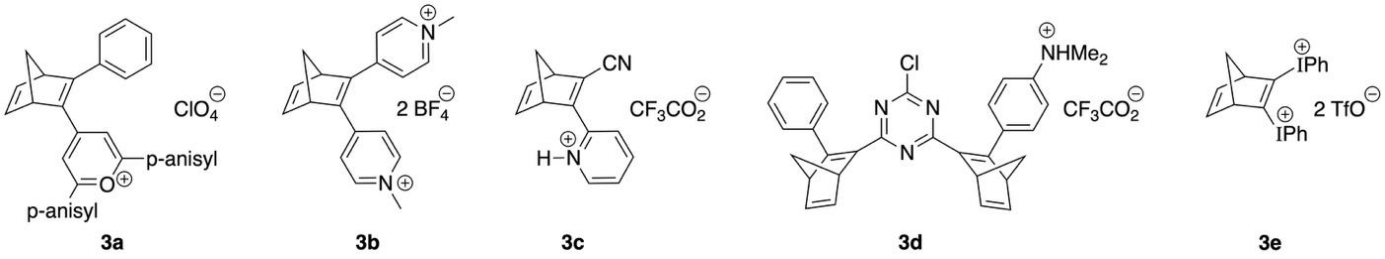
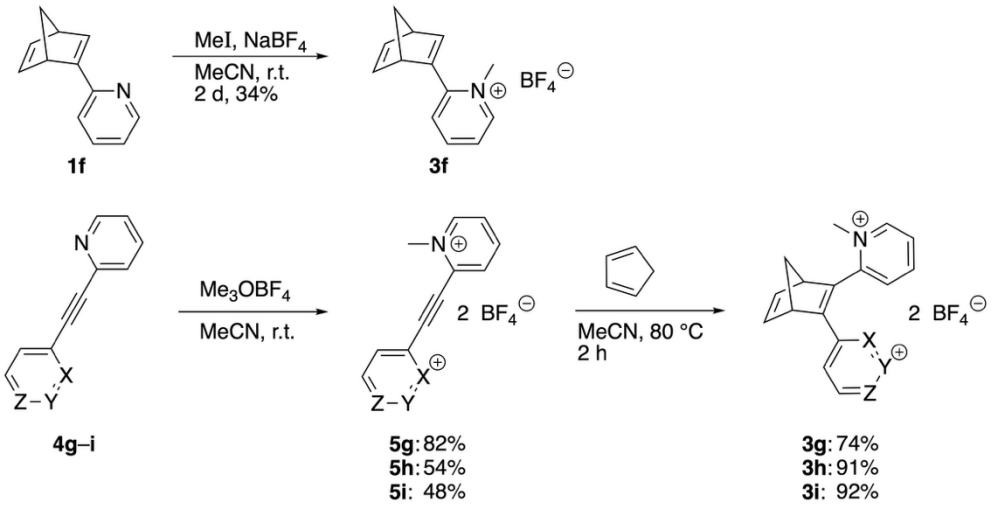


Figure 1. Representative cationic norbornadienes **3a**–**e**.

Results and Discussion

Synthesis

The monopyridinium-substituted norbornadiene **3f** was synthesized by the methylation of the known 2-norbornadienylpyridine[33] (**1f**) in 34% yield (Scheme 1). In a reversed sequence, the cationic bisarylethynes **5g**–**i** were firstly obtained by *N*-methylation of the bipyridines **4g**–**i**[34-37] with MeI or Me_3OBF_4 in moderate to good yields ranging from 42% (**5i**) to 82% (**5g**) (Scheme 2). These alkynes **5g**–**i** were then employed for the Diels–Alder reaction with cyclopentadiene to give the dicationic norbornadienes **3g**–**i** in 71–92% yield (Scheme 2). The iodide salt $\mathbf{3g^{I}}$ was obtained by Diels-Alder reaction of alkyne $\mathbf{5g^{I}}$, as obtained by methylation of **4g** with methyl iodide, and cyclopentadiene (cf. Supporting Information Scheme S1; compound number without further index implies BF_4 counter ion, whereas superscript index indicates a different counter ion). The chloride $\mathbf{3g^{Cl}}$, bromide $\mathbf{3g^{Br}}$, hexafluorophosphate $\mathbf{3g^{PF6}}$, and 2-naphthoate $\mathbf{3g^{Nap}}$ salts were obtained by ion metathesis of **3g** (cf. Supporting Information, Scheme S2). All novel compounds were identified and characterized by NMR spectroscopy (^{1}H, ^{13}C, COSY, HSQC, HMBC), melting point, and elemental analysis.



Scheme 2. Synthesis of cationic norbornadienes **3f**–**3i**.

Absorption properties

The absorption spectra of the norbornadienes **3f**–**3i, 3g^{Cl}**, **3g^{Br}**, and **3b^{I}** were recorded exemplarily in MeCN, MeOH and H_2O and did not reveal a significant dependence on the solvent (Table 1, cf. Supporting Information, Figures S1 and S2). The absorption properties of compound **3g^{PF6}** were only determined in MeCN, because it was not sufficiently soluble in protic polar solvents (Table 1, cf. Supporting Information, Figure S2 D). Within this series of compounds, a pronounced red shift of the low-energy zero-onsets was observed, the latter ranging from 362 nm (**3f**) to 431 nm (**3i**). All compounds have a broad long-wavelength absorption band with two local maxima, that may be assigned to the styrylpyridinium unit (>300 nm) and to the decoupled pyridinium fragment (<300 nm). Notably, the contribution of these bands to the overall absorption depends on the substituent at position 3. Specifically, it may be suggested that the red-shifted absorption intensity correlates with the extent of conjugation between the pyridinium unit and the alkene group. Hence, in the mono-substituted derivative **3f** the contribution of this band is the highest because in this molecule, the pyridinium experiences the least steric hindrance while accomplishing π orbital overlap. In contrast, the long-wavelength absorption of the bipyridinium-substituted derivatives is less pronounced as compared with the blue-shifted band, indicating decreased contribution of vinylpyridinium absorption, likely caused by steric repulsion between the aryl substituents. At the same time, the derivatives **3f**, **3g**, and **3h** showed essentially the same long-wavelength maximum at about 320 nm (Figure 2 A–C), that is therefore assigned to the mutual 2-vinylpyridinium unit. Nevertheless, the isomer **3i** revealed a red-shifted maximum at 336 nm (Figure 2 D), which most likely originates from the absorption of a 4-vinylpyridinium chromophore. The latter is more easily established as conjugated π system because the pyridinium substituent can rotate with less steric hinderance around the aryl-vinyl axis. A similar red shift occurs in 4-styrylpyridinium ions as compared with the 2-styrylpyridinium isomers.[38,39]

Table 1. Absorption properties of norbornadienes **3f–i** and quadricyclanes **6f–6i** in MeCN

	λ_{max} / nm[a]	λ_{max} / nm[b]	λ_{onset} / nm[c]	λ_{max} / nm[d]	λ_{onset} / nm[e]
3f	319	260	362	316	389
3g	320[i]	285	370	277	373
3h	321	n.d.[h]	375	272	363
3i	336	280	431	277	408
3g^{Cl}	320[i]	283	396	n.d.[g]	n.d.[f]
3g^{Br}	320[i]	285	375	n.d.[g]	n.d.[f]
3g^{I}	320[i]	247	584	n.d.[g]	n.d.[f]
3g^{PF6}	320[i]	283	397	278	n.d.[f]
3g^{Nap}	320[i]	280	n.d.[f]	n.d.[g]	n.d.[f]

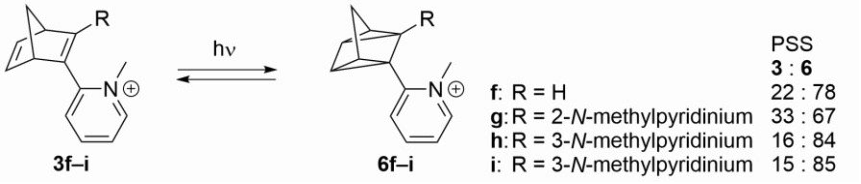
[a] = Long-wavelength absorption maximum of norbornadiene. [b] = Short-wavelength absorption maximum of norbornadiene [c] = Zero-onset of norbornadiene absorption (at ε = 500 L mol^{-1} cm^{-1}). [d] = Long-wavelength absorption maximum of quadricyclane. [e] = Zero-onset of quadricyclane absorption (at ε = 500 L mol^{-1} cm^{-1}). [f] = not determined because of rising baseline/ always above ε = 500 L mol^{-1} cm^{-1}. [g] = not determined (no clear evidence when the conversion is over). [h] = not determined (no clear short-wavelength absorption maximum). [i] = absorption shoulder.

The different counter ions of the salts **3g^{Cl}**, **3g^{Br}** and **3g^{PF6}** did not have an effect on the absorption properties of the cationic norbornadiene unit in the employed solvents. As the only exception, the absorption spectrum of the iodide salt **3g^{I}** showed a red-shifted absorption with a zero onset at 584 nm (cf. Supporting Information, Figure S2 C). The additional band was assigned to a charge transfer (CT) absorption resulting from CT complex formation between the iodide and the pyridinium unit.[40,41] The absorption of the naphthoate salt **3g^{Nap}** showed the same characteristic features as the tetrafluoroborate **3g**, along with the additional absorption band of the naphthalene chromophore (cf. Supporting Information, Figure S2 E).

Photochemical properties

The photoisomerization reactions of the norbornadienes **3f–3i** to the corresponding quadricyclanes **6f–i** (Scheme 3) were conducted by irradiation at 315 nm, 360 nm, 365 nm and 420 nm in MeCN, MeOH, and H_2O. The reactions were monitored by absorption spectroscopy. And the formation of the photoproducts was indicated by the development of the characteristic blue-shifted absorption maxima in the course of the reaction (272–316 nm). Isosbestic points were only observed during the photoreactions in MeCN solution. In water or MeOH, however, isosbestic points were not maintained, and in some instances, the absorption intensity was steadily fading, which indicated side reactions and/or decomposition (Figure 2 E, cf. Supporting Information, Figure S3 and S4). These side reactions presumably include the nucleophilic addition of water or methanol to the quadricyclane or to the pyridinium unit, as has been reported for similar cases.[26,27,42] To prevent the decomposition of the starting material and/or photoproduct in water (Figure 2 E), the photoreaction was also conducted in the presence of cucurbit[7]uril (Figure 2 F), that is, an established host system in which the organic molecules can be encapsulated and as such mainly protected from solvent.[43] Under these conditions, only minor decomposition was detected even at prolonged irradiation times (1 h). Presumably, the norbornadiene as well as the quadricyclane photoproduct are accommodated in the cavity of the cucurbit[7]uril,[43] thus shielding the photoproduct from the nucleophilic attack of water. To gain more structural information about the photoproduct and to analyze the photostationary state (PSS), samples of **3f–**

3i were irradiated in MeCN-d_3 at 340 nm or 365 nm in different time intervals, and the photoreactions were monitored by ^{1}H NMR spectroscopy. Upon irradiation of **3f** (c = 11 mM) and **3g** (c = 10 mM) with 340 nm, a photostationary state was reached with a norbornadiene to quadricyclane ratio of 22/78 and 33/67 (**3g**: 29/71 at λ_{ex} = 350 nm),[26] respectively. Furthermore, the photoreactions of the norbornadienes **3h** and **3i** were followed by in situ ^{1}H NMR spectroscopy (λ_{ex} = 365 nm, c = 10 mM), which revealed ratios of 16/84 and 15/85 in the PSS under these conditions.[44]



Scheme 3. Photoreaction of the norbornadienes **3f**–**i** (PSS: photostationary state).

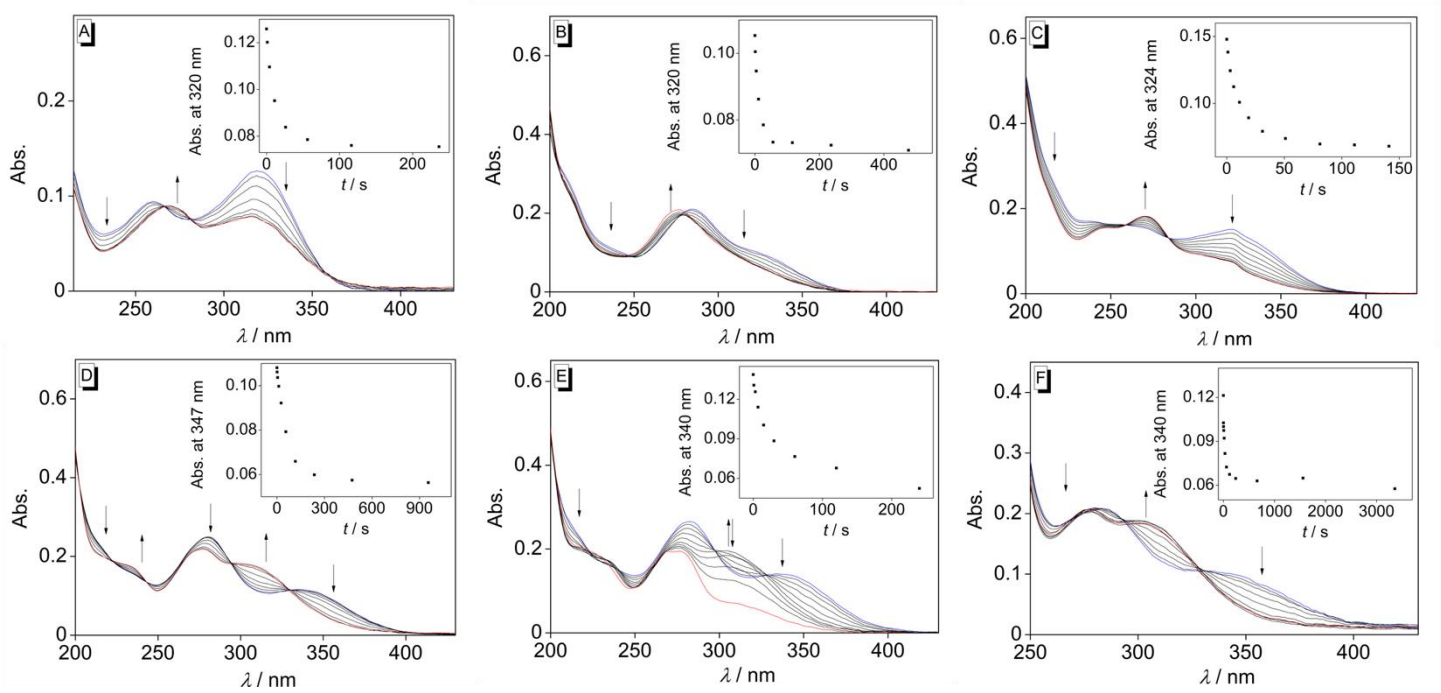


Figure 2. Photometric monitoring of the photoisomerization of **3f**–**3i** (A–D) in MeCN (c = 20 µM, T = 20 °C) and **3i** in water in the absence (E) and in the presence (F) of cucurbit[7]uril (10 eqiv. + 5% DMSO). A–B: λ_{ex} = 315 nm; C: λ_{ex} = 365 nm; D: λ_{ex} = 360 nm; E–F: λ_{ex} = 420 nm. The arrows indicate the development of the absorption bands with reaction time. Inset: Plot of absorption at fixed wavelength versus t.

The influence of different counter ions on the photoisomerization of the dicationic norbornadiene **3g** was also studied. The chloride **3g^{Cl}** and bromide **3g^{Br}** were investigated in MeCN, MeOH and water, while the iodide **3g^{I}**, hexafluorophosphate **3g^{PF6}** and 2-naphthoate **3g^{Nap}** were investigated in MeCN, either because of their insufficient solubility (**3g^{PF6}**) or because MeCN turned out to be the optimal solvent for the photoreactions (cf. Supporting Information, Figure S4–S6). In general, the low-energy absorption maximum at

285 nm decreased and a new absorption maximum developed at 277 nm, as was already observed for the tetrafluoroborate **3g^{BF4}** (Figure 2 B). However, contrary to the latter and the hexafluorophosphate **3g^{PF6}**, isosbestic points were not formed upon irradiation of the chloride and bromide salts in MeCN. Instead, the absorption decreased significantly further, indicating decomposition in the latter cases. This phenomenon was even more pronounced in MeOH and water (cf. Supporting Information, Figure S4 and S6). As this type of decomposition only occurred with the halide counter ions and not (or at least not that pronounced) with the redox-inactive tetrafluoroborate and hexafluorophosphate, it may be assumed that the decomposition reaction in the presence of the halide counterions is initiated by a photoinduced electron transfer (PET) reaction between the excited pyridinium units and the halide. This photoreaction is well known for resembling cationic hetarenes[45,46] and generates reactive radical intermediates that might subsequently lead to the decomposition. Furthermore, it should be noted that the pyridinium unit has its own photoreactivity.[47,48] Namely, upon irradiation ring-contraction, ring-opening or electron-transfer reaction may be triggered that will also lead to the formation of byproducts and eventually decomposition. Interestingly, prolonged irradiation (1 h) of the iodide salt **3g^{I}** at 520 nm did not result in a change of the absorption spectrum. Presumably, the excitation at the charge-transfer absorption band leads to a different excited state, which does not result in a photochemical reaction, as often observed for donor-acceptor-substituted chromophores. Indeed, fast relaxation (2 ps) to the ground state has been observed for resembling bispyridinium derivatives.[49]

The naphthoate salt **3g^{Nap}** was synthesized to examine whether further functionality can be introduced by the counter anion. Specifically, it was of interest whether the naphthoate accelerates the photoreaction, because the naphthalene unit may operate as photosensitizer for the photoreactions.[50] However, a significant difference in the photoreactivity of the naphthoate **3g^{Nap}** and the corresponding tetrafluoroborate **3g** was not observed, as both reactions reach the photostationary state after essentially the same time under identical conditions. This result may indicate insufficient contact between the norbornadiene unit and the sensitizer, either because the ions are well separated by solvation or because of the relatively low concentration of the substrate. For comparison, it should be noted that photosensitizers are usually employed in sufficient excess, whereas in this case, only two molar equivalents are available.

Conclusions

In summary, it was shown that pyridinium-substituted norbornadienes are readily available in reasonable yields with Diels-Alder reactions of suitable hetaryl-substituted alkynes and cyclopentadiene, thus adding more examples to the still small sample size of ionic norbornadiene derivatives. Depending on the substitution pattern, the long-wavelength absorption bands extend close to the visible range. An exceptionally red-shifted band was observed with the iodide salt as caused by an additional charge transfer (CT) absorption. Upon direct irradiation, the norbornadiene derivatives are transformed into the corresponding quadricyclanes, but the reaction only proceeds cleanly with tetrafluoroborate as counter anion and in CH_3CN solution. By contrast, side reactions and decomposition take place in water and MeOH as well as with halide counter ions. Nevertheless, it was demonstrated exemplarily that the photoreaction can be performed in water by encapsulation of the norbornadiene and the photoproduct within a cucurbit[7]uril host molecule which protects the molecules from the solvent. Overall, pyridinium-substituted norbornadienes show promising absorption properties, specifically the desired red shift towards the visible range, and photochemical

reactivity. But at the same time, it should be considered for future studies that a clean and efficient photoreaction of these compounds requires a delicate choice of counter ions and solvents.

Experimental Section

General

Equipment. NMR spectra: JEOL ECZ 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, 25 °C), Varian VNMR-S 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz, 25 °C). Reference: residual signals of DMSO-d_6 [δ(^{1}H) 2.50 ppm, δ(^{13}C) 39.5 ppm], $CDCl_3$ [δ(^{13}C) 77.16 ppm] and MeCN-d_3 [δ(^{1}H) 1.94 ppm, δ(^{13}C) 1.32 ppm], or tetramethylsilane (TMS) [δ(^{1}H) 0.00 ppm]. Melting points: BÜCHI 545 (Büchi, Flawil, CH). Elemental analysis: in-house (Organic Chemistry, University of Siegen), HEKAtech EUROEA combustion analyzer. Absorption spectra: Varian Cary 100 Bio, Analytik Jena SPECORD S, in quartz glass cuvettes (*d* 10 mm); Software: Origin (OriginPro 8.5.1) with the implemented smoothing function "adjacent averaging", factor 10. Photoreactions: 520 nm LED (Conrad electronic Nr. 181862), Thorlabs LED M340L5 (340 nm), LUMOS 43 Atlas Photonics; 275 nm, 315 nm, 360 nm, 420 nm). In situ NMR irradiations: 365 nm LEDs.[44]

Methods. Reaction mixtures were stirred with a magnetic stirring bar (400–750 rpm). Solvents were removed with a rotary evaporator at 20–40 °C under reduced pressure (360–15 mbar). Air-sensitive reactions were performed under an inert atmosphere (Ar) with Schlenk equipment. Solvents/solutions were deaerated by bubbling Argon through the solution (approx. 5 min) prior to use. Room temperature (r.t.) was 22 °C. For photometric analysis, solutions (*c* = 20 µM, *V* = 2.00 mL) of the norbornadiene **3f**–**3i**, **3g^{Cl}**, **3g^{Br}** and **3g^{I}** in MeCN, MeOH and water were prepared by the evaporation of a stock solution of the norbornadiene in MeCN (*c* = 1 mM, *V* = 40 µL) under a nitrogen stream followed by the addition of the corresponding solvent. The absorption spectra were subsequently measured (*T* = 20 °C).

Materials. Commercially available chemicals. Acros Organics: $NaBF_4$, benzyltributylammonium chloride; Alfa Aesar GmbH & Co KG: norbornadiene, iodomethane, 2-bromopyridine, 3-bromopyridine, 4-bromopyridine hydrochloride, 2-naphthoic acid, trimethyloxonium tetrafluoroborate; Bernd Kraft GmbH: K_2CO_3; Carbolution Chemicals GmbH: tetrabutylammonium bromide, $Pd(PPh_3)_2Cl_2$, 2-bromopyridine, bis(pinacolato)diborone; Fisher scientific: dicyclopentadiene, iodomethane, *t*-BuOK, *n*-BuLi (2.5 M in hexanes); Fluorochem Ltd: NH_4PF_6, 3-bromopyridine, trimethylsilylacetylene; Honeywell Specialty Chemicals Seelze GmbH: CuI; Silicycle: SiO_2 (particle size 40–63 µm).

Synthesis

General Procedure B (GP B) for the synthesis methylation of pyridines with Me_3OBF_4.[26] A mixture of bis-(pyridiyl)ethyne (500 mg, 2.77 mmol) and Me_3OBF_4 (2.10 g, 14.2 mmol, 2.5 equiv.) in anhydrous MeCN (18 mL) was stirred at r.t. for 2 d. The solution was poured into Et_2O, and the resulting precipitate was filtered and recrystallized from MeCN/EtOAc.

1-Methyl-2-((1-methylpyridinium-3-yl)ethynyl)pyridinium bis(tetrafluoroborate) (5h). A solution of **4h** (500 mg, 2.77 mmol) and Me_3OBF_4 (2.10 g, 14.2 mmol, 2.5 equiv.) were treated and purified according to GP B. The product was obtained as fine yellow crystals (571 mg, 1.49 mmol, 54%); mp 260–265 °C. – ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.40 (s, 3H, 1´-CH_3), 4.50 (s, 3H, 1-CH_3), 8.22 (ddd, ^3J 7.8 Hz, ^3J 6.1 Hz, ^4J 1.5 Hz, 1H, 5-H), 8.30 (dd,

^{3}J 8.2 Hz, ^{3}J 6.1 Hz, 1H, 5´-H), 8.44 (dd, ^{3}J 8.0 Hz, ^{4}J 1.5 Hz, 1H, 3-H), 8.68 (td, ^{3}J 7.9 Hz, ^{4}J 1.4 Hz, 1H, 4-H), 8.94 (dt, ^{3}J 8.1 Hz, ^{4}J 1.5 Hz, 1H, 4´-H), 9.14 (d, ^{3}J 6.2 Hz, 1H, 6´-H), 9.19 (dt, ^{3}J 6.2 Hz, ^{5}J 0.6 Hz, 1H, 6-H), 9.56 (s, 1H, 2´-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ 48.1 (N1CH_3), 49.0 (N1´CH_3), 85.3 (C1´´), 96.8 (C2´´), 120.3 (C3´), 128.5 (C5´), 128.7 (C5), 132.6 (C3), 136.0 (C2), 145.8 (C4), 147.7 (C6´), 148.0 (C4´), 148.6 (C6), 149.4 (C2´). – El. Anal. for $C_{14}H_{14}B_2F_8N_2$, calc. (%): C 43.80, H 3.68, N 7.30, found (%): C 43.74, H 3.51, N 7.41.

1-Methyl-2-((1-methylpyridinium-4-yl)ethynyl)pyridinium bis(tetrafluoroborate) (5i). A solution of **4i** (500 mg, 2.77 mmol) and Me_3OBF_4 (2.10 g, 14.2 mmol, 2.5 equiv.) were treated and purified according to GP B. The product was obtained as fine yellow crystals (510 mg, 1.33 mmol, 48%); mp 268–278 °C. – ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.39 (s, 3H, 1´-CH_3), 4.51 (s, 3H, 1-CH_3), 8.26 (ddd, ^{3}J 7.8 Hz, ^{3}J 6.1 Hz, ^{4}J 1.6 Hz, 1H, 5-H), 8.50 (dd, ^{3}J 5.1 Hz, ^{4}J 1.9 Hz, 2H, 3´-H, 5´-H), 8.52 (dd, ^{3}J 7.3 Hz, ^{4}J 1.4 Hz, 1H, 3-H), 8.71 (td, ^{3}J 7.9 Hz, ^{4}J 1.4 Hz, 1H, 4-H), 9.16 (dd, ^{3}J 5.3 Hz, ^{4}J 1.7 Hz, 2H, 2´-H, 6´-H), 9.22 (dt, ^{3}J 6.2 Hz, ^{5}J 0.6 Hz, 1H, 6-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ 48.2 (N1CH_3), 48.9 (N1´CH_3), 89.0 (C1´´), 97.8 (C2´´), 129.2 (C5), 130.4 (C3´, C5´), 133.3 (C3), 135.5 (C4´), 135.6 (C2), 145.8 (C4), 146.8 (C2´, C6´), 148.8 (C6). – El. Anal. for $C_{14}H_{14}B_2F_8N_2$, calc. (%): C 43.80, H 3.68, N 7.30, found (%): C 43.57, H 3.56, N 7.48.

2-(Bicyclo[2.2.1]hepta-2,5-dien-2-yl)-1-methylpyridin-1-ium tetrafluoroborate (3f). A solution of MeI (0.24 g, 0.11 mL, 0.17 mmol) and 2-(2-pyridyl)norbornadiene (96.0 mg, 567 µmol) in anhydrous MeCN (5 mL) was stirred for 24 h at room temperature. Another portion of MeI (0.24 g, 0.11 mL, 0.17 mmol) was added, and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure. The residue was suspended in water (15 mL), and $NaBF_4$ (1.00 g, 9.11 mmol) was added. The aqueous suspension was washed with hexanes (3 × 15 mL) and extracted with $MeNO_2$ (5 × 15 mL). The organic layer was separated and dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 9/1, R_f 0.31) to obtain the product as yellow needles (52.1 mg, 192 mmol, 34%); mp >105 °C (dec.). – ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.10 (d, 1H ^{2}J 6.6 Hz, 7´-H), 2.24 (dt, 1H, ^{3}J 1.7 Hz, ^{2}J 6.6 Hz, 7´-H), 3.95–3.98 (m, 1H, 4´-H), 4.03–4.06 (m, 1H, 1´-H), 4.19 (s, 3H, CH_3), 6.93 (dd, 1H, ^{3}J 3.1 Hz, ^{3}J 5.1 Hz, 5´-H), 7.15 (dd, 1H, ^{3}J 3.0 Hz, ^{3}J 5.1 Hz, 6´-H), 7.68 (d, 1H, ^{3}J 3.3 Hz, 3´-H), 7.93 (m, 2H, 4-H, 5-H), 8.48 (td, 1H, ^{4}J 1.5 Hz, ^{3}J 7.9 Hz, 3-H), 8.95 (dd, 1H, ^{4}J 1.5 Hz, ^{4}J 6.7 Hz, 6-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ 47.5 (CH_3), 52.7 (4´-C), 54.8 (C1´), 73.2 (C7´), 125.8 (C4), 127.1 (C5), 143.1 (C6´), 143.5 (C5´), 145.4 (C3), 147.2 (C6), 148.9 (C2´), 152.3 (C2), 154.9 (C3´). – El. Anal. for $C_{13}H_{14}BF_4N$, calc. (%): C 57.60, H 5.21, N 5.52, found (%) C 57.63, H 5.07, N 5.20.

General Procedure C (GP C) for the synthesis of cationic norbornadienes by Diels-Alder reactions.[26] A solution of bis(methylpyridium)ethyne bis(tetrafluoroborate) (200–495 mg, 0.52–1.29 mmol) and freshly cracked cyclopentadiene (40 equiv.) in MeCN (18–45 mL) was stirred under reflux for 18 h. After cooling to r.t., the solution was filtered and slowly added to Et_2O (200–500 mL). The precipitate was filtered off and dried in vacuum.

1-Methyl-2-(3-(1-methylpyridinium-3-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)pyridinium bis(tetrafluoroborate) (3h). A solution of **5h** (200 mg, 521 µmol) and cyclopentadiene (2.1 mL, 1.7 g, 25 mmol) were treated to GP C. The product was suspended in MeCN (30 mL). After filtration, the solvent was removed under reduced pressure, and the product was obtained as a hygroscopic yellow amorphous powder (213 mg, 473 µmol, 91%). – ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.22 (dt, ^{2}J 6.9 Hz, ^{3}J 1.6 Hz, 1H, 7´´-H), 2.58 (dt, ^{2}J 6.9 Hz, ^{3}J 1.6 Hz, 1H, 7´´-H), 4.18 (s, 3H, 1-CH_3), 4.24 (s, 1H, 1´´-H), 4.29 (s, 3H, 1´-CH_3), 4.34 (s, 1H, 4´´-H), 7.14 (s, 1H, 6´´-H), 7.19 (s, 1H, 5´´-H), 7.53 (s, 1H, 3-H), 7.93 (dd, ^{3}J 8.2 Hz, ^{3}J 6.0 Hz, 1H, 5´-H), 8.08 (ddd, ^{3}J 7.7 Hz, ^{3}J 6.1 Hz, ^{4}J 1.5 Hz, 1H, 5-H), 8.19 (d, ^{3}J 8.2 Hz, 1H, 4´-H), 8.38 (td, ^{3}J 7.7 Hz, ^{4}J 1.4 Hz, 1H, 4-H), 8.85 (d, ^{3}J 6.0 Hz, 1H, 6´-H), 9.00 (s, 1H,

2´-H), 9.18 (d, ^{3}J 6.1 Hz, 1H, 6-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ 47.3 (1-CH_3), 48.6 (1´-CH_3), 55.6 (C4´´), 57.1 (C1´´), 71.9 (C7´´), 127.4 (C5), 128.0 (C5´), 128.4 (C3), 133.8 (C3´), 143.0 (C4´), 143.1 (C6´´), 143.4 (C5´´), 144.0 (C2´), 145.2 (C6´), 146.2 (C4), 148.0 (C2´´), 148.5 (C6), 151.8 (C2), 154.8 (C3´´). – El. Anal. for $C_{19}H_{20}B_2F_8N_2$, calc. (%): C 50.71, H 4.48, N 6.23, found (%): C 50.45, H 4.13, N 6.62.

1-Methyl-2-(3-(1-methylpyridinium-4-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl)pyridinium bis(tetrafluoroborate) (3i). A solution of **5i** (200 mg, 521 µmol) and cyclopentadiene (2.1 mL, 1.7 g, 25 mmol) were treated according to GP C. The product was suspended in MeCN (30 mL). After filtration, the solvent was removed under reduced pressure, and the product was obtained as a hygroscopic yellow amorphous powder (214 mg, 476 µmol, 92%). – ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.23 (dt, ^{2}J 7.1 Hz, ^{3}J 1.6 Hz, 1H, 7´´-H), 2.61 (dt, ^{3}J 7.1 Hz, ^{3}J 1.6 Hz, 1H, 7´´-H), 4.20 (s, 3H, 1-CH_3), 4.25 (s, 3H, 1´-CH_3), 4.27 (s, 1H, 4´´-H), 4.38 (s, 1H, 1´´-H), 7.12 (s, 1H, 5´´-H), 7.24 (s, 1H, 6´´-H), 7.50 (s, 1H, 3-H), 7.87 (d, ^{3}J 6.9 Hz, 2H, 3´-H, 5´-H), 8.12 (ddd, ^{3}J 7.7 Hz, ^{3}J 6.2 Hz, ^{4}J 1.5 Hz, 1H, 5-H), 8.41 (td, ^{3}J 7.7 Hz, ^{4}J 1.5 Hz, 1H, 4-H), 8.79 (d, ^{3}J 6.9 Hz, 2H, 2´-H, 6´-H), 9.21 (d, ^{3}J 6.2 Hz, 1H, 6-H). – ^{13}C NMR (125 MHz, DMSO-d_6): δ 47.3 (1-CH_3), 47.8 (1´-CH_3), 55.2 (C1´´), 57.8 (C4´´), 71.7 (C7´´), 125.3 (C3´, C5´), 127.7 (C5), 128.1 (C3), 142.9 (C5´´), 143.6 (C6´´), 145.9 (C2´, C6´), 146.3 (C4), 148.38 (C4´), 148.6 (C6), 151.5 (C2), 152.4 (C3´´), 156.0 (C2´´). – El. Anal. for $C_{19}H_{20}B_2F_8N_2 \times 0.5\ H_2O$, calc. (%): C 49.72, H 4.61, N 6.10, found (%): C 50.12, H 4.54, N 6.26.

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Supplementary Material

Detailed experimental protocols and spectra are available as Supplementary material (SI).

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