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**Authors** Roland Löw, Tobias Moje, Fynn Röhricht and Rainer Herges

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**ORCID® iDs** Fynn Röhricht - <https://orcid.org/0000-0001-9935-9256>; Rainer Herges - <https://orcid.org/0000-0002-6396-6991>

# Norbornadiene functionalized triaza-triangulenium and trioxa-triangulium platforms

Roland Löw, Tobias Moje, Fynn Röhricht, Rainer Herges\*

Otto Diels Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, 24118 Kiel, Germany

Email: rherges@oc.uni-kiel.de

## Abstract

Triazatriangulenium (TATA) and trioxatriangulenium (TOTA) ions are among the most efficient systems to mount functional molecules onto atomically flat surfaces such as Au(111). The TATA and TOTA units serve as platforms that adsorb onto the surface and form ordered monolayers, while the functional groups are protruding upright and freestanding from the central carbon atoms. Azobenzene derivatized TATA's are known to exhibit extremely fast *cis*→*trans* isomerizations on metal surfaces, via a peculiar non-adiabatic singlet→triplet→singlet mechanism. We now prepared norbornadienes (NBD) and quadricyclanes (QC) attached to TATA and TOTA platforms to check if these accelerated rates and the spin change mechanism also apply to [2+2]cycloreversions (QC→NBD).

## Keywords

Norbornadiene, quadricyclane, TATA platform, TOTA platform, photochemical isomerization, thermal isomerization, [2+2] cycloaddition, [2+2] cycloreversion

## Introduction

The storage of solar energy is one of the main challenges for the supply of consumers with renewable energy.<sup>[1]</sup> Photoisomerization reactions in principle allow the direct conversion of solar energy to chemical energy if the photoproduct has a higher strain energy than the reactant.<sup>[2]</sup> The stored energy is released on demand by catalytical back-isomerization. One of the most promising molecular solar-thermal energy storage systems is norbornadiene (NBD) which upon irradiation reacts through triplet state<sup>[3,4]</sup> by an intramolecular [2+2] cycloaddition to the metastable, energy-rich quadricyclane (QC),<sup>[5-8]</sup> first described half a century ago.<sup>[9]</sup> The cycloreversion of QC back to the NBD (activation energy 140 kJ mol<sup>-1</sup>) releases 89 kJ mol<sup>-1</sup> of strain energy as heat.<sup>[10-14]</sup> The [2+2] cycloreversion is a thermochemically forbidden reaction and proceeds slowly under ambient conditions over a radical mechanism.<sup>[15,16]</sup> However, catalysts such as Co<sup>2+</sup> or Rh<sup>2+</sup> complexes very efficiently convert the QC back to the NBD and release the strain energy stored in the QC compound.<sup>[17]</sup> For practical solar energy storage applications, it is essential to use heterogenic catalysis (immobilized catalysts) because the reaction can be controlled by addition and removal of the catalyst.<sup>[2]</sup> Besides transition metal complexes, metal surfaces were found to be effective. The decomposition of desorbed norbornadiene on Pt(111) was proven by MUETTERTIES and co-workers at around 500 K.<sup>[18]</sup> The catalyzed cycloreversion of unsubstituted quadricyclane to norbornadiene was investigated on Pt(111) and Ni(111) surfaces at low temperatures.<sup>[2,19]</sup> The cycloreversion starts at 175 K. Furthermore at 190 K to 220 K the decomposition to a norbornadienyl intermediate was detected

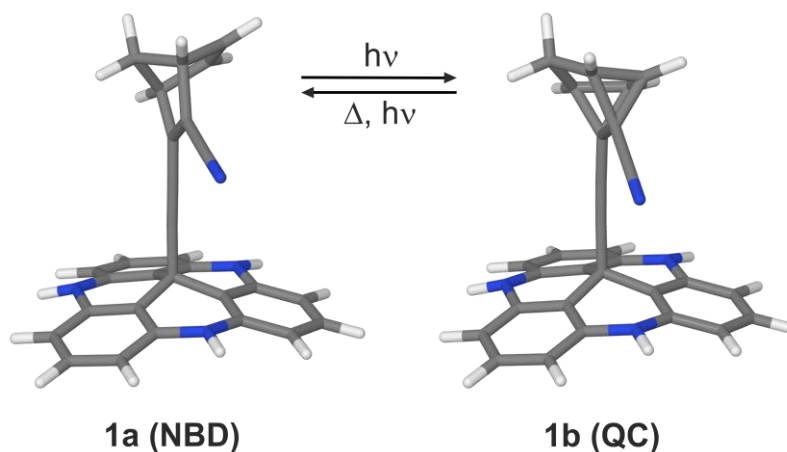
which further dehydrogenates and decomposes at 380 K into carbonaceous fragments which confirms the results of MUETTERTIES.<sup>[2,18]</sup>

Recently, we discovered that the thermochemically forbidden *cis-trans* isomerization of azobenzenes can be efficiently catalyzed by a completely different mechanism on bulk gold.<sup>[20]</sup> In contrast to conventional surface catalysis, where the surface is chemically involved in the reaction, electronic coupling to the conducting band of a bulk metal is sufficient to accelerate the rate of isomerization by three orders of magnitude.<sup>[21-23]</sup> The reacting azobenzene molecule is not directly absorbed onto the surface but mounted on a carefully designed molecular framework. This approach was coined the platform approach.<sup>[24]</sup> Three molecular units are combined in a modular way to achieve a controlled absorption on the surface: the platform, a spacer and the functional molecule. Triazatriangulenium (TATA) and trioxatriangulenium (TOTA) units are used as molecular platforms. They adsorb on the surface and form ordered monolayers. A linear spacer (e.g. an ethynyl unit) is attached to the central carbon atom and the functional molecule is mounted on top. This architecture allows investigating molecules on surfaces under controlled conditions. The size of the platforms determine the intermolecular distances and enforce an upright orientation of the free standing functional groups.<sup>[25]</sup> The length and the nature of the spacer is used to tune the distance and electronic coupling of the functional system on top.<sup>[20]</sup>

Preliminary experiments proved that the electronic coupling to the surface is the decisive parameter controlling the *cis-trans* rate acceleration of azobenzenes and not the length of the spacer.<sup>[20]</sup> A full conjugation path from the azobenzene on top through the ethynyl spacer and the platform to a bulk gold surface shortens the half-life of the metastable *cis* isomer from days to seconds even though the azo N=N group is 11 bonds and 14 Å away from the surface. A singlet→triplet→singlet pathway was suggested to explain the dramatic rate acceleration.

To obtain further insight into this unusual mechanism and to explore scope and limitation of the general concept, we are aiming at the extension from simple *cis*→*trans* isomerizations to other thermochemically forbidden reactions. Moreover, a deeper understanding of the non-adiabatic, catalytic process and successful application of the concept to the QC→NBD isomerization could open new ways to optimize the molecular solar thermal energy systems.

Towards this end, and following the “platform concept”, we designed a cyano-substituted norbornadiene, which is functionalized with an acetylene spacer on a TATA platform to investigate an eventual “spin-catalyzed” [2+2] cycloreversion on bulk gold of quadricyclane **1b** to norbornadiene **1a** (Figure 1).



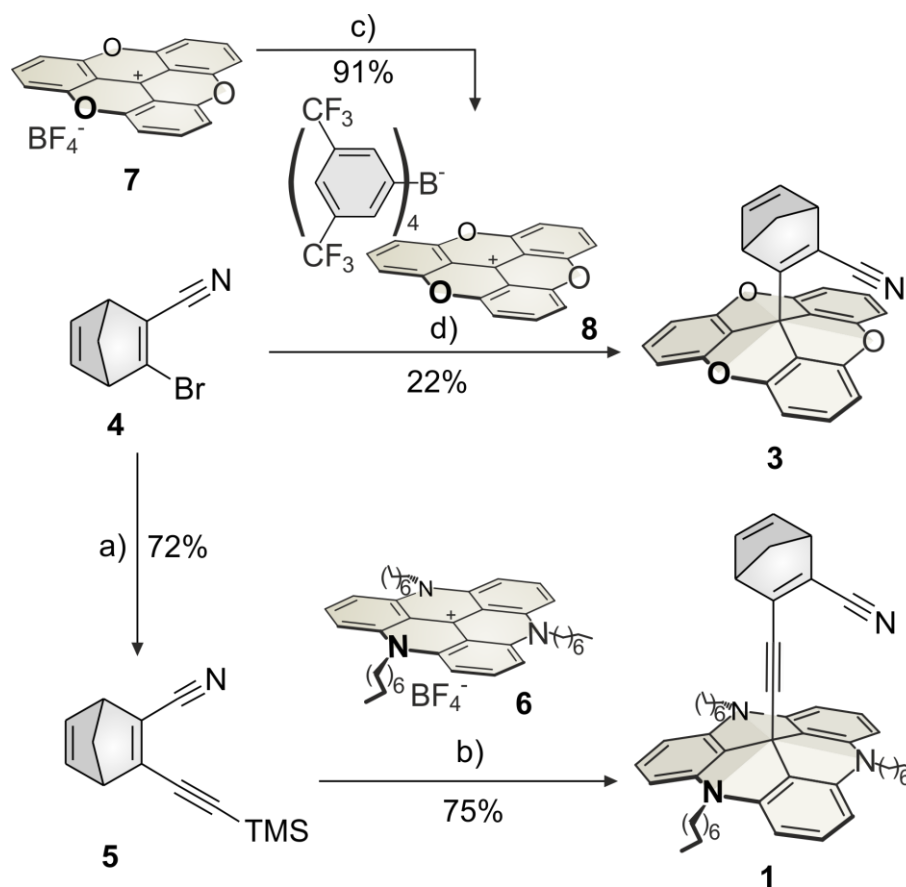
**Figure 1:** Theoretically calculated (M062x-D3/def2TZVPP) structures of the norbornadiene platform **1a** and the quadricyclane platform **1b**. The alkyl side chains at the bridge N atoms of the TATA platforms are omitted for clarity (for geometry coordinates and further details see supporting information). The norbornadiene isomerizes upon irradiation with 385 nm to the quadricyclane **1b**, and with 311 nm or thermochemically back to the norbornadiene **1a**.

The cycloreversion of most norbornadiene system proceeds smoothly in solution upon irradiation in the presence of triplet sensitizers.<sup>[26]</sup> If **1b** is adsorbed on a gold surface the bulk gold could take the role of a triplet sensitizer, mediate the spin change (which otherwise is forbidden) and accelerate the cycloreversion. Substitution in the 2 and 3 positions shifts the bathochromic absorption to 375 nm which is in agreement with similar systems.<sup>[27]</sup> Furthermore the cyano and ethynyl group provide a complete conjugation path across the double bond of norbornadiene to the metal. Additionally, it is known that electron withdrawing groups in 2 or 3 position change the triplet energy hypersurface in such a way that a triplet excited quadricyclane **1b** decays into the ground state of the norbornadiene **1a**,<sup>[28]</sup> which is a precondition for an efficient QC→NBD isomerization via our postulated non-adiabatic singlet→triplet→singlet mechanism.

If our proposed spin change mechanism, mediated by the conducting electrons in bulk gold were correct, interruption of the conjugation path and decoupling from the surface should restore the properties of the system (half-life of the metastable quadricyclane) in solution. According to this line of thought, we synthesized molecule **2** with a methyl-phenyl group inserted into the spacer unit. The methyl group prevents a planar arrangement of the phenyl group and the double bond of the NBD unit and thus lowers the conjugation.

We also synthesized the corresponding system directly connected to a TOTA platform **3**. Functionalized TOTA molecules are more stable than the corresponding TATA systems and usually can be sublimed without decomposition, which is a necessary precondition for ultra-high vacuum STM investigations.

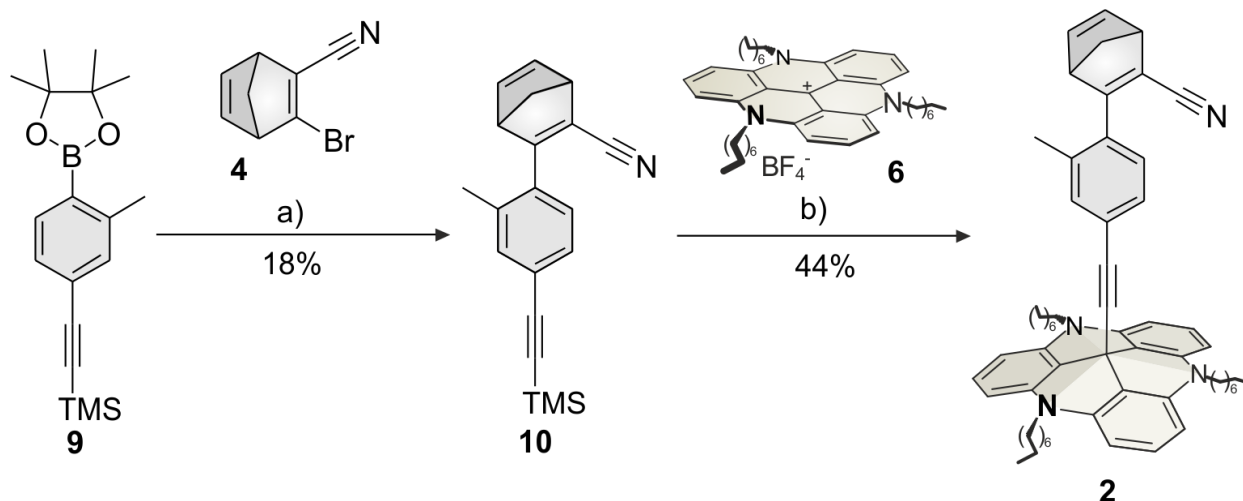
The cyano norbornadiene **4** was synthesized as described in literature (Scheme 1).<sup>[29-31]</sup>



**Scheme 1:** Syntheses of the norbornadiene TATA platform **1** and TOTA platform **3**. a) TMS-acetylene, Pd(PPh<sub>3</sub>)<sub>4</sub>, Cu(I)I, Et<sub>3</sub>N, N<sub>2</sub>, 100 °C, 1.3 h; b) KOH, THF, N<sub>2</sub>, reflux, 5 h; c) sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAR<sup>F<sub>4</sub></sup>), DCM, rt, 2 h; d) *n*-BuLi, THF, N<sub>2</sub>, -78 °C to rt, 20 h.

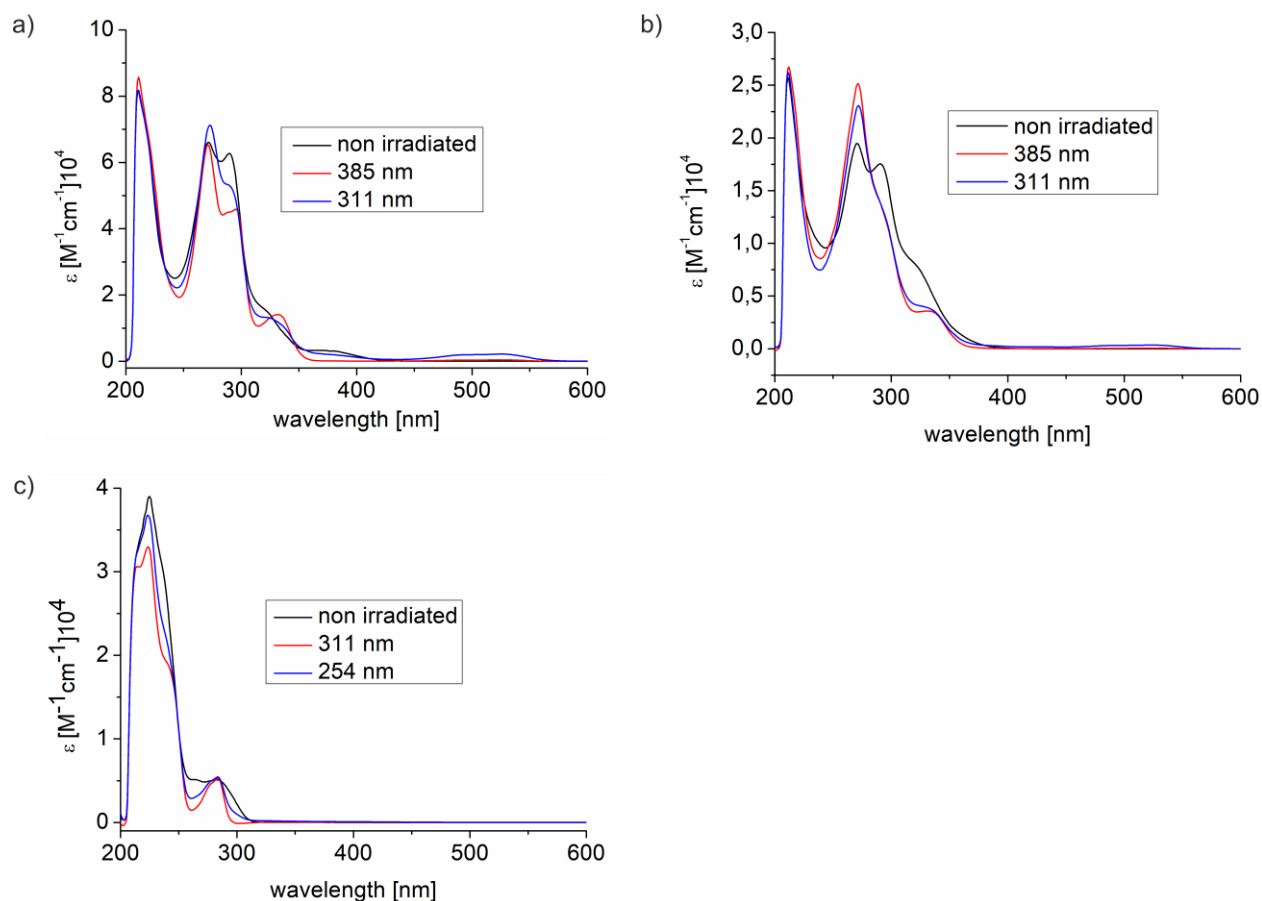
The bromine compound **4** was converted into the product **5** with a trimethylsilyl protected acetylene substituent (72%) in a SONOGASHIRA cross coupling reaction. The triazatriangulenium ion **6** was synthesized according to a procedure of LAURSEN and KREBS.<sup>[32]</sup> The platform **6** was functionalized with the norbornadiene **5** by deprotection of the acetylene with potassium hydroxide and in situ formation of the C-C bond between the acetylene and the central C atom of the platform **6** to yield the norbornadiene substituted platform **1** (75%).

The TOTA cation with the tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TOTA<sup>+</sup>[BAR<sup>F<sub>4</sub></sup>]) anion **8** was obtained by ion exchange of the TOTA tetrafluoroborate **7** (TOTA<sup>+</sup> BF<sub>4</sub><sup>-</sup>) to achieve a high solubility in organic solvents.<sup>[33]</sup> 3-Bromo-2-cyano norbornadiene **4** was subjected to halogen-metal exchange with *n*-BuLi and coupled with the central atom of the TOTA platform **8** to obtain the norbornadiene functionalized TOTA platform **3** (22%, Scheme 1). The synthesis of the corresponding TATA platform including an additional ethynyl spacer **2** was obtained in a convergent synthesis (Scheme 2). Boronic ester **9** was synthesized as described in the literature.<sup>[34]</sup> In a SUZUKI cross coupling reaction norbornadiene **4** was coupled with **9** to the extended norbornadiene **10** (18%), which was attached to the TATA platform **6** to yield the extended norbornadiene platform **2** (44%).



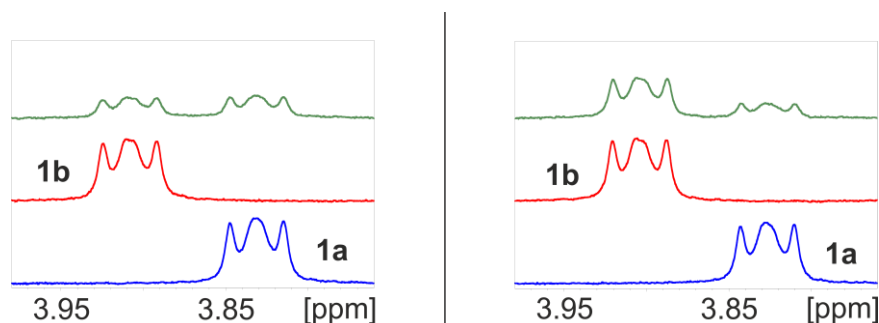
**Scheme 2:** Syntheses of methylphenyl norbornadiene platform **2**. a)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{Na}_2\text{CO}_3$ , toluene, EtOH,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $90\text{ }^\circ\text{C}$ , 5 h; b) KOH, THF,  $\text{N}_2$ , reflux, 1 h.

The photophysical properties and the switching behaviour of **1** were determined in solution (THF). The UV-vis spectra of **1**, **2** and **3** as NBD, QC and after irradiation of QC with 311 nm or 254 nm are shown in Figure 2. The bathochromic absorption maximum of norbornadiene **1a** is at 375 nm (as compared to  $<300\text{ nm}$  in parent norbornadiene).<sup>[35,36]</sup> The absorption maximum of quadricyclane **1b** is at 336 nm. The weak and broad absorption band with a maximum at 524 nm is due to the TATA cation generated by decomposition during irradiation with 311 nm.



**Figure 2:** UV-vis spectra of platform **1** (a), **2** (b) and **3** (c) (in tetrahydrofuran at room temperature): Norbornadiene (black), quadricyclane (red) and after 2.5 min irradiation with 311 nm and 254 nm (blue).

The photostationary states were determined in oxygen containing deuterated benzene and degassed deuterated benzene in  $^1\text{H}$  NMR measurements (Figure 3). Norbornadiene **1a** isomerizes quantitatively to quadricyclane **1b** by irradiation with 385 nm. Upon irradiation with 311 nm of **1b** under nitrogen, the cycloreversion yields 28% norbornadiene (Table 1).

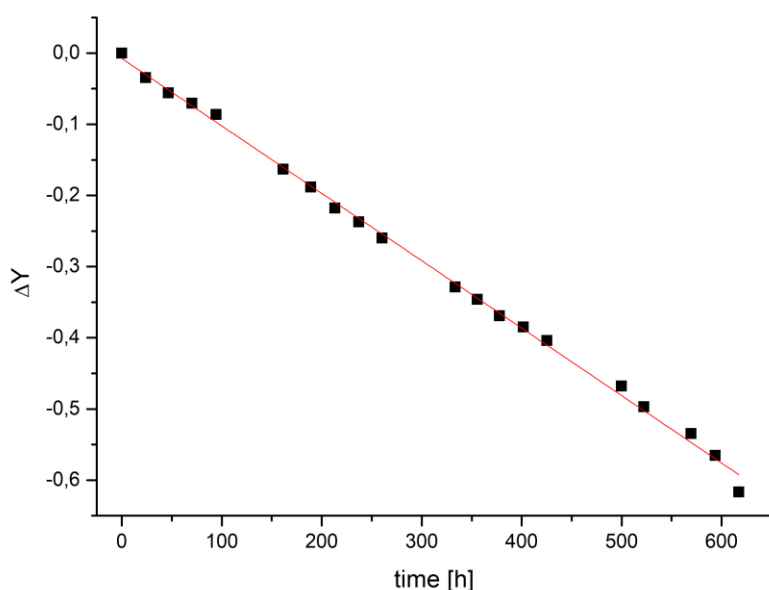


**Figure 3:**  $^1\text{H}$  NMR spectra of **1** in deuterated oxygen containing benzene (left) and degassed deuterated benzene (right). Shown are the signals of the  $\text{CH}_2$  groups of the alkyl side chains next to the nitrogen atoms in the TATA platforms, which are indicative of the isomerization. *Left bottom* (blue): non-irradiated NBD **1a**; *left middle* (red): pure QC **1b** obtained after irradiation of

**1b** with 385 nm for one minute; and *left top* (green): photostationary state of **1a** and **1b** after 1 h irradiation with 311 nm under air (52% **1a** / 48% **1b**). *Right bottom* (blue): pure NBD **1a**; *right middle* (red): pure QC **1b** obtained after irradiation of **1a** with 385 nm for one minute and *right top* (green): photostationary state of **1a** and **1b** after 2 h irradiation with 311 nm under nitrogen atmosphere (28% **1a** / 72% **1b**).

The efficiency of the cycloreversion is higher under air (52%), however, slow decomposition was observed (cleavage of the TATA<sup>+</sup> platform). Obviously, in the presence of oxygen, the photochemical cycloreversion proceeds via a triplet radical mechanism. This agrees with observations described in the literature.<sup>[16]</sup> In degassed benzene neither **1a** nor **1b** exhibits decomposition upon repeated irradiation with 385 nm and 311 nm.

The thermal isomerization of QC **1b** back to NBD **1a** was investigated by <sup>1</sup>H NMR measurements (Figure 4).



**Figure 4:** Determination of the thermal isomerization rate  $k$  of **1b** (QC) by <sup>1</sup>H NMR spectroscopy (toluene, 293.5 K, 800 μmol/L, under nitrogen).  $\Delta Y$ :  $\ln \{ [QC]_t / [QC]_0 \}$ ,  $[QC]_t$ : <sup>1</sup>H NMR integral of the CH<sub>2</sub> group neighbouring the N bridge atom of the TATA platform in QC **1b** at time  $t$ ,  $[QC]_0$  corresponding <sup>1</sup>H integral at  $t = 0$ . A rate constant of  $k = 0.95 \cdot 10^{-3} \text{ s}^{-1}$  was determined from a linear fit of the  $\Delta Y/t$  curve.

The cycloreversion follows a first order reaction, the rate constant could be determined by logarithmic fitting of the integrals of the CH<sub>2</sub> signals next to the nitrogen atoms of the platform as  $k = 1.06 \cdot 10^{-3} \text{ s}^{-1}$  under air and  $0.95 \cdot 10^{-3} \text{ s}^{-1}$  under nitrogen. Hence, the thermal reaction (in contrast to the photochemical reaction) is not largely affected by oxygen. The half-life of the metastable quadricyclane is  $t_{1/2} = 655 \text{ h}$  in benzene under air at 293 K (Table 1). Minor amounts of degradation products (<1%) after following the cycloreversion within a period of one month are visible in the <sup>1</sup>H NMR spectrum. Under nitrogen atmosphere the half-life of the cycloreversion is  $t_{1/2} = 732 \text{ h}$  (294 K).



**Table 1:** Photo stationary states (PSS) of norbornadiene platforms **1**, **2** and **3** upon irradiation with light of the wavelengths  $\lambda_{\text{irrad}}$ : 385 nm (**1a**, **2a**) or 311 nm (**3a**) and 311 nm (**1b**, **2b**) or 254 nm (**3b**) and the thermal isomerization half-life  $t_{1/2}$  determined by  $^1\text{H}$  NMR spectroscopy (deuterated benzene under air / degassed deuterated benzene).

	atmos- phere	PSS % QC ( $\lambda_{\text{irrad}}$ )	PSS (% NBD)	$t_{1/2}$ (h)	EA KJ/mol
<b>1</b>	air	~100 (385 nm)	52 (311 nm)	655 (293 K)	/
<b>1</b>	N <sub>2</sub>	~100 (385 nm)	28 (311 nm)	732 (294 K)	111
<b>2</b>	N <sub>2</sub>	~100 (385 nm)	48 (311 nm)	/	/
<b>3</b>	N <sub>2</sub>	91 (311 nm)	33 (254 nm)	/	/

The rate constant as a function of the temperature follows an Arrhenius-type relationship. The activation energy for the cycloreversion was determined by linear fit of  $\ln(k)$  as a function of  $1/T$ . The cycloreversion of QC **1b** to NBD **1a** has an activation energy of 111 KJ mol<sup>-1</sup> (degassed deuterated benzene). The switching efficiency of NBD **2a** to QC **2b** is quantitative (~100%) after irradiation with 385 nm, whereas the photostationary state of NBD **3a** to QC **3b** is lower with 91%.

No thermal cycloreversion of the quadricyclanes **2b** and **3b** was observed at room temperature within a period of one month. Obviously, a cyano as well as a neighboring ethynyl substituent are necessary to induce the back-isomerisation at ambient conditions as realized in compound **1**. Consequently, future surface chemistry investigations will be performed with compound **1** including the TATA platform and an ethynyl spacer.

## Conclusions

In summary, we present the syntheses of three different norbornadiene functionalized platform molecules (**1-3**). The photochemical switching between the norbornadiene and quadricyclane isomers with two different wavelengths was investigated. Norbornadienes **1** and **2** are quantitatively converted to the corresponding quadricyclanes upon irradiation with light of 385 nm. Back-isomerization with 311 nm to the norbornadiene isomer is less efficient (52%). The high energy quadricyclane isomer is thermochemically unstable at room temperature (half-life 31 d at 21 °C in benzene) only if a cyano as well as an ethynyl substituent are present. No thermal conversion under ambient conditions was observed for **2** and **3**, lacking ethynyl substitution. Further studies will be devoted to the surface chemistry of these compounds.

## Experimental Section

**General Experimental Methods.** All compounds were characterized using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The signals were assigned using 2D spectroscopy. For  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignment we performed HSQC and HMBC NMR experiments in deuterated solvents (Deutero). Analytic measurements were performed by the following instruments: Bruker CABAV 500neo ( $^1\text{H}$  NMR: 500 MHz,  $^{13}\text{C}$  NMR: 125 MHz,  $^{11}\text{B}$  NMR: 160 MHz,  $^{19}\text{F}$  NMR: 470 MHz,  $^{29}\text{Si}$  NMR: 99 MHz) and Bruker AV 600 ( $^1\text{H}$  NMR: 600 MHz,  $^{13}\text{C}$  NMR: 150 MHz). Infrared

spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer with an A531-G Golden-Gate-Diamon-ATR-unit. The high-resolution (HR) mass spectra were measured with an APEX 3 FT-ICR with a 7.05 T magnet by co. Bruker Daltonics. Electron impact (EI).

**3-[2-Trimethylsilyl-ethynyl]-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (5).** In toluene (24 mL), 3-bromo-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile **4**<sup>31</sup> (600 mg, 3.06 mmol) was dissolved under nitrogen atmosphere, trimethylsilylacetylene (522  $\mu$ L, 3.67 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (106 mg, 91.8  $\mu$ mol), copper(I)iodide (58.3 mg, 306  $\mu$ mol) and triethylamine (1.06 mL, 7.65 mmol) were added and the mixture was stirred for 80 min at 60 °C. The mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (silica gel, cyclohexane/ ethyl acetate, 4/1) to obtain a yellow liquid (468 mg, 2.19 mmol, 72%).

**<sup>1</sup>H NMR** (500.1 MHz, CDCl<sub>3</sub>, 298 K, TMS):  $\delta$  = 6.85-6.81 (m, 2H, *H*-5, *H*-6), 3.86-3.83 (m, 1H, *H*-1), 3.77-3.73 (m, 1H, *H*-4), 2.27 (dt, <sup>3</sup>*J* = 7.0 Hz, <sup>4</sup>*J* = 1.6 Hz, 1H, *H*-7<sub>a</sub>), 2.18 (dt, <sup>3</sup>*J* = 7.0 Hz, <sup>4</sup>*J* = 1.6 Hz, 1H, *H*-7<sub>b</sub>), 0.24 (s, 9H, *H*-11) ppm. **<sup>13</sup>C NMR** (125.8 MHz, CDCl<sub>3</sub>, 298 K, CHCl<sub>3</sub>):  $\delta$  = 154.09 (s, *C*-2), 142.02 (s, *C*-5), 141.49 (s, *C*-6), 129.79 (s, *C*-3), 115.04 (s, *C*-9), 97.63 (s, *C*-8), 73.10 (s, *C*-7), 57.32 (s, *C*-4), 54.19 (s, *C*-1), -0.22 (s, *C*-11) ppm. **<sup>29</sup>Si NMR** (99.4 MHz, CDCl<sub>3</sub>, 298 K, TMS):  $\delta$  = -16.23 ppm. **MS** (EI, 70eV): *m/z* = 213.1 [M]<sup>+</sup>. **IR** (ATR):  $\tilde{\nu}$  = 2927 (w), 2852 (w), 2207 (m), 2139 (w), 1576 (w), 1557 (w), 1450 (w), 1302 (m), 1251 (m), 1132 (w), 1068 (w), 1019 (w), 840 (vs), 760 (m), 733 (s), 702 (w), 626 (m), 534 (m) cm<sup>-1</sup>. **HRMS** (EI, 70 eV): *m/z* [M]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>15</sub>NSi: 213.09738, found: 213.09724.

**12c-Bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile-ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (1).** In tetrahydrofuran (abs., 60 mL) 3-[2-trimethylsilyl-ethynyl]-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile **5** (100 mg, 469  $\mu$ mol) was dissolved under nitrogen atmosphere, octyl-TATA-BF<sub>4</sub> **6**<sup>32</sup> (397 mg, 562  $\mu$ mol) and powdered potassium hydroxide (263 mg, 3.69 mmol) were added and the mixture was refluxed for 5 h. The mixture was poured onto saturated sodium chloride solution (50 mL) and the aqueous phase extracted with diethyl ether (3x 50 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (aluminium oxide basic, diethyl ether) and recrystallized from ethanol to obtain an orange solid (222 mg, 292  $\mu$ mol, 62%). **<sup>1</sup>H NMR** (600.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  = 7.21 (t, <sup>3</sup>*J* = 8.2 Hz, 3H, *H*-15), 6.61 (m, 6H, *H*-14), 5.91-5.86 (m, 1H, *H*-5), 5.76-5.73 (m, 1H, *H*-6), 3.86-3.80 (ps. t, 6H, *H*-16), 2.89-2.86 (m, 1H, *H*-4), 2.82-2.79 (m, 1H, *H*-1), 1.86-1.77 (m, 6H, *H*-17), 1.34-1.20 (m, 32H, *H*-7<sub>a</sub>, *H*-7<sub>b</sub>, *H*-18, *H*-19, *H*-20, *H*-21, *H*-22), 0.94-0.90 (ps. t, 9H, *H*-23) ppm. **<sup>13</sup>C NMR** (150.9 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  = 153.78 (s, *C*-2), 141.34 (s, *C*-5), 141.11 (s, *C*-13), 140.83 (s, *C*-6), 129.37 (s, *C*-3), 129.09 (s, *C*-15), 109.44 (s, *C*-12), 105.55 (s, *C*-14), 79.48 (s, *C*-10), 72.23 (s, *C*), 56.36 (s, *C*-1), 53.57 (s, *C*-4), 47.08 (s, *C*-16), 32.22 (s, *C*), 30.17 (s, *C*-11), 29.76 (s, *C*), 29.69 (s, *C*-7), 27.24 (s, *C*), 25.93 (s, *C*-17), 23.09 (s, *C*-18), 14.40 (s, *C*-22) ppm. **MS** (MALDI-TOF): *m/z* = 759.1 [M]<sup>+</sup>. **IR** (ATR):  $\tilde{\nu}$  = 2953 (m), 2922 (m), 2851 (m), 2207 (w), 1617 (s), 1579 (vs), 1481 (s), 1456 (vs), 1394 (vs), 1372 (m), 1267 (m), 1246 (m), 1207 (w), 1167 (s), 1147 (m), 908 (w), 766 (vs), 731 (vs), 657 (w), 637 (m), 609 (w) cm<sup>-1</sup>. **m.p.** = 101.7 °C. **Elemental analysis** calcd. (%) for C<sub>53</sub>H<sub>66</sub>N<sub>4</sub>: C 83.86; H 8.76; N 7.38; found: C 83.538; H 8.649; N 7.322.

**3-[2-Methyl-4-trimethylsilylethynylphenyl]-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile (10).**

In a solution of toluene (15 mL), ethanol (3.75 mL) and H<sub>2</sub>O (750  $\mu$ L) 2-[2-methyl-4-[2-(trimethylsilyl)ethynyl]phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **9**<sup>34</sup> (402 mg, 1.28 mmol), 3-bromo-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile **4** (250 mg, 1.28 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (73.9 mg, 64.0  $\mu$ mol) and sodium carbonate (339 mg, 3.20 mmol) were suspended under nitrogen atmosphere and refluxed for 19 h. To the mixture H<sub>2</sub>O (10 mL) was added and the layers were separated. The water layer was extracted with dichloromethane (3x 30 mL) and the combined organic layers were dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate, 1/1) to obtain a yellow oil (59.0 mg, 194  $\mu$ mol, 38%).

**<sup>1</sup>H NMR** (500.1 MHz, acetone-d<sub>6</sub>, 298 K, TMS):  $\delta$  = 7.39 (s, 1H, *H*-11), 7.33 (dd, <sup>3</sup>*J* = 8.0 Hz, <sup>4</sup>*J* = 1.0 Hz, 1H, *H*-13), 7.19 (d, <sup>3</sup>*J* = 8.0 Hz, 1H, *H*-14), 7.11-7.04 (m, 2H, *H*-5, *H*-6), 3.99-3.96 (m, 2H, *H*-1, *H*-4), 2.45 (td, <sup>3</sup>*J* = 6.9 Hz, <sup>4</sup>*J* = 1.6 Hz, 1H, *H*-7<sub>a</sub>), 2.32 (s, 3H, *H*-9), 2.21 (td, <sup>3</sup>*J* = 6.9 Hz, <sup>4</sup>*J* = 1.6 Hz, 1H, *H*-7<sub>b</sub>), 0.24 (s, 9H, *H*-18) ppm. **<sup>13</sup>C NMR** (125.8 MHz, acetone-d<sub>6</sub>, 298 K, TMS):  $\delta$  = 174.06 (s, C-3), 143.99 (s, C), 142.56 (s, C), 136.95 (s, C-10), 135.87 (s, C-9), 134.81 (s, C-11), 130.03 (s, C-13), 128.20 (s, C-14), 124.68 (s, C-12), 123.58 (s, C-2), 105.54 (s, C-16), 95.69 (s, C-17), 73.68 (s, C-7), 58.28 (s, C), 55.42 (s, C), 20.36 (s, C-9), 0.00 (s, C-18) ppm. **<sup>29</sup>Si NMR** (99.4 MHz, acetone-d<sub>6</sub>, 298 K, TMS):  $\delta$  = -17.48 ppm. **MS** (EI, 70 eV): *m/z* = 303.14 [M]<sup>+</sup>. **IR** (ATR):  $\tilde{\nu}$  = 2958 (br, w), 2204 (m), 2151 (w), 1606 (w), 1560 (w), 1493 (w), 1450 (w), 1310 (w), 1295 (m), 1233 (w), 1004 (w), 949 (w), 899 (w), 834 (vs), 814 (s), 759 (m), 723 (vs), 658 (m) cm<sup>-1</sup>. **HRMS** (EI, 70 eV): *m/z* [M]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>21</sub>NSi: 303.14433, found: 303.14410.

**12c-(4-(Bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile)3-methylphenyl)ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (2).**

In tetrahydrofuran (abs., 40 mL) 3-[2-methyl-4-trimethylsilylethynylphenyl]-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile **10** (65.0 mg, 214  $\mu$ mol) was dissolved under nitrogen atmosphere and octyl-TATA-BF<sub>4</sub> **6** (181 mg, 257  $\mu$ mol) and powdered potassium hydroxide (95.9 mg, 1.71 mmol) were added and the mixture was refluxed for 1 h. The mixture was poured onto sat. sodium chloride solution (30 mL) and extracted with diethylether (3x 50 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (aluminium oxide basic, diethyl ether) and recrystallized from ethanol to obtain a grey solid (80.0 mg, 94.2  $\mu$ mol, 44%).

**<sup>1</sup>H NMR** (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  = 7.25 (t, <sup>3</sup>*J* = 8.3 Hz, 3H, *H*-22), 6.85 (dd, <sup>3</sup>*J* = 8.1 Hz, <sup>4</sup>*J* = 1.1 Hz, 1H, *H*-13), 6.82 (s, 1H, *H*-11), 6.66-6.61 (m, 7H, *H*-21, *H*-14), 6.33 (dd, <sup>3</sup>*J* = 5.1 Hz, <sup>3</sup>*J* = 3.0 Hz, 1H, *H*-5), 6.19 (dd, <sup>3</sup>*J* = 5.1 Hz, <sup>3</sup>*J* = 3.0 Hz, 1H, *H*-6), 3.84-3.78 (ps. t, 6H, *H*-23), 3.24-3.21 (m, 1H, *H*-4), 3.02-2.99 (m, 1H, *H*-1), 1.85-1.77 (m, 6H, *H*-24), 1.76 (s, 3H, *H*-9), 1.64 (td, <sup>3</sup>*J* = 6.8 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H, *H*-7<sub>a</sub>), 1.54 (td, <sup>3</sup>*J* = 6.8 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H, *H*-7<sub>b</sub>), 1.31-1.15 (m, 30H, *H*-25, *H*-26, *H*-27, *H*-28, *H*-29), 0.91 (ps. t, 9H, *H*-30) ppm. **<sup>13</sup>C NMR** (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  = 172.34 (s, C-3), 142.91 (s, C-5), 141.17 (s, C-20), 140.99 (s, C-6), 135.03 (s, C-10), 134.48 (s, C-11), 133.48 (s, C-15), 129.42 (s, C-13), 128.69 (s, C-22), 126.68 (s, C-14), 125.00 (s, C-12), 122.16 (s, C-2), 111.07 (s, C-19), 105.67 (s, C-21), 95.63 (s, C-16), 84.11 (s, C-17), 72.37 (s, C-7), 57.20 (s, C-1), 54.46 (s, C-4), 46.71 (s, C-23), 32.21 (s, C-27), 29.74 (s, C-28), 29.69 (s, C-29), 29.08 (s, C-18), 27.23 (s, C-25), 26.19 (s, C-24), 23.04 (s, C-26), 19.96 (s, C-9), 14.37 (s, C-30) ppm. **MS** (MALDI-TOF): *m/z* = 849.4 [M]<sup>+</sup>. **IR** (ATR):  $\tilde{\nu}$  = 2922 (s), 2852 (m), 2204 (w), 1615 (s), 1579 (vs), 1482 (vs), 1456 (vs), 1393 (cs), 1373 (m),

1293 (w), 1267 (m), 1244 (m), 1167 (s), 1022 (w), 911 (w), 886 (w), 828 (w),, 816 (w), 789 (w), 772 (m), 748 (m), 724 (s), 696 (vs), 657 (w), 608 (w) cm<sup>-1</sup>. **m.p.** =73.6 °C. **Elemental analysis** calcd. (%) for C<sub>60</sub>H<sub>72</sub>N<sub>4</sub>: C 84.86; H 8.55; N 6.60; found: C 84.634; H 8.476; N 6.571.

**4,8,12-Trioxatrianguleniumtetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (8).** In dichloro methane (200 mL) 4,8,12-trioxatrianguleniumtetrafluoroborate **7**<sup>33</sup> (636 mg, 1.71 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1.89 g, 2.10 mmol) were suspended and stirred at room temperature for 2 h. The mixture was filtered and the solution was washed with water (3x 150 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was dissolved in 25 mL ethyl acetate and precipitated by adding 400 mL cyclohexane. Filtration gave 1.77 g (1.54 mmol, 91%) of a yellowish solid.

**<sup>1</sup>H NMR** (500.1 MHz, acetone-d<sub>6</sub>, 298 K, TMS): δ = 8.66 (t, <sup>3</sup>J = 8.5 Hz, 3H, *H*-5), 7.99 (d, <sup>3</sup>J = 8.5 Hz, 6H, *H*-4), 7.79 (t, <sup>4</sup>J = 2.5 Hz, 8H, *H*-7), 7.67 (s, 4H, *H*-9) ppm. **<sup>13</sup>C NMR** (125.8 MHz, acetone-d<sub>6</sub>, 298 K, TMS): δ = 162.6 (q, C-6), 154.7 (s, C-3), 144.7 (m, C-5), 135.5 (m, C-7), 130.0 (m, C-10), 125.4 (d, C-8), 118.4 (m, C-9), 113.6 (s, C-4), 107.3 (s, C-2) ppm. **<sup>19</sup>F NMR** (470 MHz, acetone-d<sub>6</sub>, 298 K, TMS): δ = -62.2 ppm. **<sup>11</sup>B NMR** (160 MHz, acetone-d<sub>6</sub>, 298 K, TMS): δ = -5.86 ppm. **IR** (ATR):  $\tilde{\nu}$  = 2311 (w), 2164 (w), 1635 (s), 1552 (m), 1467 (m), 1355 (s), 1275 (s), 1143 (s), 1112 (s), 1063 (s), 1021 (s), 900 (m), 887 (m), 776 (s), 681 (s), 558 (s), 412 (m) cm<sup>-1</sup>. **MS** (ESI, pos): m/z = 285.05 [C<sub>19</sub>H<sub>9</sub>O<sub>3</sub>]<sup>+</sup>. **MS** (ESI, neg): m/z = 863.07 [C<sub>32</sub>H<sub>12</sub>BF<sub>24</sub>]<sup>-</sup>. **m.p.** = 202 °C.

**12c-Bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile-4,8,12-trioxatriangulene (3).** In tetrahydrofuran (abs., 15 mL), 3-bromo-bicyclo[2.2.1]hepta-2,5-diene-2-carbonitrile **4** (213 mg, 1.09 mmol) was dissolved under nitrogen atmosphere und the solution was cooled to -78 °C. To the solution *n*-BuLi (436 μL, 1.09 mmol, 2.5 M in *n*-hexane) was added slowly and stirred for 45 min. 4,8,12-trioxatrianguleniumtetrakis-[3,5-bis(trifluormethyl)phenyl]borate **8** (1.38 g, 1.20 mmol), dissolved in tetrahydrofuran (abs., 30 mL), was added slowly and stirred for 45 min at -78 °C and further for 20 h at room temperature. To the solution, diethylether (30 mL) was added and the solution was washed with water (3x 50 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (alox basic, diethylether) and recrystallized from methanol to obtain a colorless solid (147 mg, 367 μmol, 42%).

**<sup>1</sup>H NMR** (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ = 6.93 (t, <sup>3</sup>J = 8.3 Hz, 3H, *H*-13), 6.87-6.81 (m, 6H, *H*-12), 6.01 (dd, <sup>3</sup>J = 5.0 Hz, <sup>3</sup>J = 3.1 Hz, 1H, *H*-5), 5.83 (dd, <sup>3</sup>J = 5.0 Hz, <sup>3</sup>J = 3.1 Hz, 1H, *H*-6), 3.55-3.53 (m, 1H, *H*-4), 3.03-3.00 (m, 1H, *H*-1), 1.25-1.20 (m, 2H, *H*-7) ppm. **<sup>13</sup>C NMR** (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ = 173.68 (s, C-3), 153.31 (d, C-11), 142.32 (s, C-5), 140.30 (s, C-6), 129.90 (s, C-13), 120.43 (s, C-2), 111.92 (d, C-12), 109.93 (s, C-10), 70.67 (s, C-7), 55.41 (s, C-1), 52.55 (s, C-4), 31.28 (s, C-9) ppm. **MS** (EI, 70eV): m/z = 401.07 [M]<sup>+</sup>. **IR** (ATR):  $\tilde{\nu}$  = 2946 (w), 2202 (w), 1743 (w), 1612 (s), 1481 (m), 1456 (s), 1306 (w), 1260 (vs), 1065 (m), 1041 (m), 1010 (vs), 934 (w), 903 (m), 877 (m), 786 (m), 773 (m), 688 (m), 597 (w), 576 (w) cm<sup>-1</sup>., **m.p.** = 197.5 °C., **HRMS** (EI, 70 eV): m/z [M]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>15</sub>NO<sub>3</sub>: 401.10519, found: 401.10515.

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

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## References

- [1] Cook, T.; Dogutan, D.; Reece, S.; Surendranath, Y.; Teets, T.; Nocera., D. *Chem. Rev.* **2010**, *110*, 6474-6502.
- [2] Bauer, U.; Mohr, S.; Döpfer, T.; Bachmann, P.; Späth, F.; Düll, F.; Schwarz, M.; Brummel, O.; Fromm, L.; Pinkert, U.; Görling, A.; Hirsch, A.; Bachmann, J.; Steinrück, H.-P.; Libuda, J.; Papp., C. *Chem. Eur. J.* **2017**, *23*, 1613-1622.
- [3] Murov, S.; Hammond, G. *J. Phys. Chem.* **1968**, *72*, 3797-3801.
- [4] Turro, N.; Cherry, W.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7388-7390.
- [5] Moth-Poulsen, K.; Coso, D.; Börjesson, K.; Vinokurov, N.; Meier, S. K.; Majumdar, A.; Vollhardt, K.; Segalman., R. *Energy environ. Sci.* **2012**, *5*, 8534-8537.
- [6] Börjesson, K.; Lennartson, A.; Moth-Poulsen., K. *Sustainable Chem. Eng.* **2013**, *1*, 585-590.
- [7] Lennartson, A.; Roffey, A.; Moth-Poulsen, K. *Tetrahedron Lett.* **2015**, *56*, 1457-1465.
- [8] Kucharski, T.; Tian, Y.; Akbulatov, S.; Boulatov, R. *Energy Environ. Sci.* **2011**, *4*, 4449-4472.
- [9] Hammond, G.; Wyatt, P.; De Boer, C.; Turro., N. *J. Am. Chem. Soc.* **1964**, *86*, 2532-2533.
- [10] Frey, H. M. *J. Am. Chem. Soc.* **1964**, 365-367.
- [11] Kabakoff, D. B.; Binzli, J. C. G.; Oth, J. F. M.; Hammond, W. B.; Berson., J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3197-3201.
- [12] Kotal, C.; Schwendiman, D. P.; Grutsch., P. *Solar Energy* **1977**, *19*, 651-655.
- [13] Maruyama K.; Tamiaki, H.; Kawabata, S. *J. Chem. Soc., Perkin Trans.* **1986**, *0*, 543-549.
- [14] Winkler, T.; Dix, I.; Jones, P. G.; Herges., R. *Angew. Chem.* **2003**, *42*, 3541-3544.
- [15] Hammond, G. S.; Turro, N. J.; Fischer., A. J. *J. Am. Chem. Soc.* **1961**, *83*, 4674-4675.
- [16] Herges, R.; Starck, F.; Winkler, T.; Schmittel., M. *Chem. Eur. J.* **1999**, *5*, 2965-2970.
- [17] Herges, R.; Reif., W. *Liebigs Ann. Chem.* **1996**, *5*, 761-768.
- [18] Tsai, M.-C.; Stein, J.; Friend, C.; Muetterties., E. *J. Am. Chem. Soc.* **1982**, *104*, 3533-3534.
- [19] Bauer, U.; Fromm, L.; Weiß, C.; Bachmann, P.; Späth, F.; Düll, F.; Steinhauer, J.; Hieringer, W.; Görling, A.; Hirsch, A.; Steinrück, H.-P.; Papp., C. *J. Phys. Chem. C* **2019**, *123*, 7654-7664.
- [20] Schlimm, A.; Löw, R.; Rusch, T.; Röhrich, F.; Strunskus, T.; Tellkamp, T.; Sönnichsen, F.; Manthe, U.; Magnussen, O.; Tuczek, F.; Herges., R. *Angew. Chem. Int. Ed.* [10.1002/anie.201814342](https://doi.org/10.1002/anie.201814342).
- [21] Jung, U.; Schütt, C.; Filinova, O.; Kubitschke, J.; Herges, R.; Magnussen., O. *J. Phys. Chem. C* **2012**, *116*, 25943-25948.
- [22] Jacob, H.; Ulrich, S.; Jung, U.; Lemke, S.; Rusch, T.; Schütt, C.; Petersen, F.; Strunskus, T.; Magnussen, O.; Herges, R.; Tuczek., F. *Phys. Chem. Chem. Phys.* **2014**, *16*, 22643-22650.
- [23] Bronner, C.; Tegeder, P. *New Journal of Physics* **2014**, *16*, 053004.
- [24] Baisch, B.; Raffa, D.; Jung, U.; Magnussen, O. M.; Nicolas, C.; Lacour, J.; Kubitschke, J.; Herges, R. *J. Am. Chem. Soc.* **2009**, *131*, 442-443.
- [25] Ulrich, S.; Jung, U.; Strunskus, T.; Schütt, C.; Bloedorn, A.; Lemke, S.; Ludwig, E.; Kipp, L.; Faupel, F.; Magnussen, O. M.; Herges., R. *Phys. Chem. Chem. Phys.* **2015**, *17*, 17053-17062.
- [26] Nishino, H.; Toki, S.; Takamuku., S. *J. Am. Chem. Soc.* **1986**, *108*, 5030-5032.
- [27] Quant, M.; Lennartson, A.; Dreos, A.; Kuisma, M.; Erhart, P.; Börjesson, K.; Poulsen, K. M. *Chem. Eur. J.* **2016**, *22*, 13265-13274.

- [28] Ikezawa, H.; Kutal, C.; Yasufuku, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 1589-1594.
- [29] Kennedoff, J.; Polborn, K.; Szeimies, G. *J. Am. Chem. Soc.* **1990**, *112*, 6117-6118.
- [30] Tranmer, G. K.; Yip, C.; Handerson, S.; Jordan, R. W.; Tam, W. *Can. J. Chem.* **2000**, *78*, 527-535.
- [31] Gunes, Y.; Arcelik, N.; Sahin, E.; Fleming, F. F.; Altundas, R. *Eur. J. Org. Chem.* **2015**, 6679-6686.
- [32] Laursen, B. W.; Krebs, F. C. *Chem. Eur. J.* **2001**, *7*, 1773-1783.
- [33] Martin, J. C.; Smith, R. G. *J. Am. Chem. Soc.* **1964**, *11*, 2252-2256.
- [34] Browne, D. L.; Baumann, M.; Harji, B. H.; Baxendale, I. R.; Ley, S. V. *Org. Lett.* **2011**, *13*, 3312-3315.
- [35] Gray, V.; Lennartson, A.; Ratanalert, P.; Börjesson, K.; Moth-Poulsen, K. *Chem. Commun.* **2013**, *50*, 5330-5332.
- [36] Dilling, W. L. *Chem. Rev.* **1966**, *66*, 373-393.