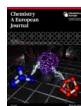


Molecular Switches

Photoswitchable Norbornadiene–Quadricyclane Interconversion Mediated by Covalently Linked C₆₀Patrick Lorenz and Andreas Hirsch*^[a]

Abstract: The synthesis and properties of various norbornadiene/quadricyclane (NBD/QC) fullerene hybrids are reported. By cyclopropanation of C₆₀ with malonates carrying the NBD scaffold a small library of NBD–fullerene monoadducts and NBD–fullerene hexakisadducts was established. The substitution pattern of the NBD scaffold, as well as the electron affinity of the fullerene core within these hybrid systems, has a pronounced impact on the properties of the corresponding energy rich QC derivatives. Based on this, the first direct photoisomerization of NBD–fullerene hybrids to their QC derivatives was achieved. Furthermore, it was possible to use


the redox-active fullerene core of a QC–fullerene monoadduct to enable the back reaction to form the corresponding NBD–fullerene monoadduct. Combining these two processes enables switching between NBD and QC simply by changing the irradiation wavelength between 310 and 400 nm. Therefore, turning this usually photo/thermal switch into a pure photoswitch. This not only simplifies the investigation of the underlying processes of the NBD–QC interconversion within the system, but also renders such hybrids interesting for applications as molecular switches.


Introduction

Towards the search of novel renewable energy technologies, molecular solar thermal (MOST) energy storage and release systems offer highly attractive opportunities. In contrast to common photovoltaics, in MOST systems the energy is not only harvested but also stored on a molecular level. Later the stored energy can be released upon demand.^[1] Therefore, the often-limiting mismatch of energy production and demand does not affect these systems. One of the most promising concepts in this regard is the valence isomerization of norbornadiene (NBD) and quadricyclane (QC). The NBD–QC interconversion holds great potential for several reasons. First, the amount of energy that is stored within the metastable framework of QC is extraordinarily high (89 kJ mol⁻¹),^[2] which in combination with the low molecular weight of only 92.14 g mol⁻¹ enables high storage capacities. Moreover, the back reaction of QC to NBD is thermally forbidden by the Woodward–Hoffmann rules for cycloadditions and therefore, QC is remarkably stable (half-life at 140 °C > 14 h).^[3] This makes it possible to store the accu-

lated energy for long time periods. Another, often underestimated advantage of the NBD–QC system is that both molecules are liquid, which is highly beneficial for practical applications. Despite these advantages, the NBD–QC valence isomerization needs further optimizations in order to approach practical applications. The main drawbacks of NBD are the absorption onset in the UV region of the spectra and the low quantum yield of the direct photoisomerization, meaning that sunlight cannot drive the isomerization directly.^[4] Hence, a triplet photosensitizer with $E_T(\text{sensitizer}) > E_T(\text{NBD})$, such as acetophenone or benzophenone, is needed to enable the isomerization of neat NBD to QC.^[5] Alternatively, it has been shown that, by functionalization of the NBD scaffold, it is possible to red-shift the absorption and simultaneously increase the quantum yield.^[6] However, functionalization of the NBD scaffold naturally is always accompanied with an increased molecular weight and, therefore, a lower energy storage density. Next to the photoisomerization, also the corresponding back reaction from QC to NBD must be considered and optimized. For practical applications it is desirable to release the stored energy catalytically. This can be achieved by various ways and some research has already been done in this regard.^[7] Possible pathways involve, for example, the catalysis through coordination of square planar transition-metal complexes,^[8,9] electrochemically induced oxidation of QC^[10] or the irradiation of charge-transfer complexes of QC and electron acceptors.^[11] It is obvious that in order to develop an efficient MOST energy storage and release system based on the NBD–QC interconversion full control over both reactions must be gained. This, however, is only possible if the underlying process of this valence isomerization are well understood. Our approach is therefore based on the design and synthesis of model systems. Analysis of the above-men-

[a] P. Lorenz, Prof. Dr. A. Hirsch
Chair of Organic Chemistry II
Friedrich-Alexander Universität Erlangen–Nürnberg
Nikolaus-Fiebiger-Strasse 10, 91058 Erlangen (Germany)
E-mail: andreas.hirsch@fau.de

 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/chem.201904679>.

 © 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of Creative Commons Attribution NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

tioned catalysts for the back reaction of QC to NBD showed that in most cases an oxidized form of QC is involved in the reaction mechanism. Based on this finding the covalent linkage of the NBD/QC moiety to electron acceptors might result in hybrid systems with interesting ground and excited state properties. For this purpose, we chose C_{60} fullerene as a building block for these hybrid systems, because C_{60} has been thoroughly investigated as both ground- and excited-state electron acceptor.^[12] Furthermore, the electron affinity of the fullerene core can be altered and tuned by changing the number of addends attached to the carbon scaffold. While monoadducts of C_{60} can easily be reduced in the ground and in the excited state, the electron affinity of C_{60} hexakisadducts is much less pronounced.^[13] During the early stage of our research, the work of Tuktarov and co-workers on the “Synthesis and Properties of Energy-Rich Methanofullerenes Containing Norbornadiene and Quadricyclane Moieties” was published; therefore, NBD/QC–fullerene monoadducts no longer presented a new class of hybrid compounds.^[14] Nevertheless, we decided to continue our investigations because some of our observations did not coincide with the reported ones. Herein, we describe the synthesis and properties of various NBD–fullerene monoadducts as well as unprecedented NBD–fullerene hexakisadducts. By careful analysis of this small library of hybrid molecules, it was possible to establish synthetic strategies towards both QC–fullerene monoadducts as well as a first QC–fullerene hexakisadduct. Even more remarkable is the development of a switchable NBD/QC interconversion system, based on NBD–fullerene monoadducts. Within this system a “push–pull” substituted NBD scaffold is covalently linked to C_{60} to give a monoadduct, direct irradiation of the “push–pull” system with 310 nm light results in the formation of the corresponding QC derivative in quantitative yield. Simply changing the irradiation wavelength to 400 nm and, therefore, excitation of the fullerene core leads to clean and quantitative back reaction. Therefore, the interconversion of such fullerene-bearing NBC–QC couples resembles the first switchable system based on NBD and QC, which uses a covalently linked excited state acceptor. This not only provides mechanistic insights into the interaction of these hybrid systems, but also renders such systems interesting for applications such as molecular switches.

Results and Discussion

Functionalization of C_{60} can be achieved by various methods,^[15] considering that the Bingel–Hirsch reaction is very reliable and uses mild reaction conditions,^[16] we believed it to be ideal for the coupling of the NBD moiety. Therefore, suitable malonates

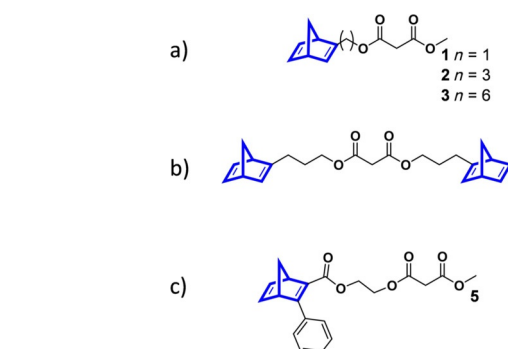
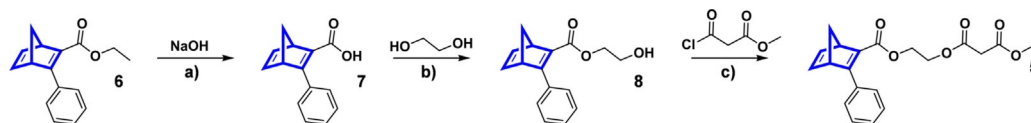


Figure 1. NBD malonates 1–5 divided into three groups: a) alkyl-mono-substituted NBD scaffold with varying linker length; b) alkyl-mono-substituted NBD bismalonate; c) malonate carrying a “push–pull” substituted NBD scaffold.

carrying the NBD scaffold were needed. In total, we designed and synthesized five different NBD malonates, which can be divided into three groups (Figure 1). To study the effect of the linker length, we synthesized malonates 1, 2 and 3 bearing a methano, propano and hexano bridge, respectively. These three malonates are easily accessible from their corresponding NBD alcohols and commercially available methyl malonyl chloride (see Supporting Information). Apart from the length of the linker also the number of NBD units might have an influence, therefore, by reacting two equivalents of the corresponding NBD alcohol with malonyl dichloride it was also possible to obtain NBD bismalonate 4 carrying two NBD moieties. For detailed information see the Supporting Information.

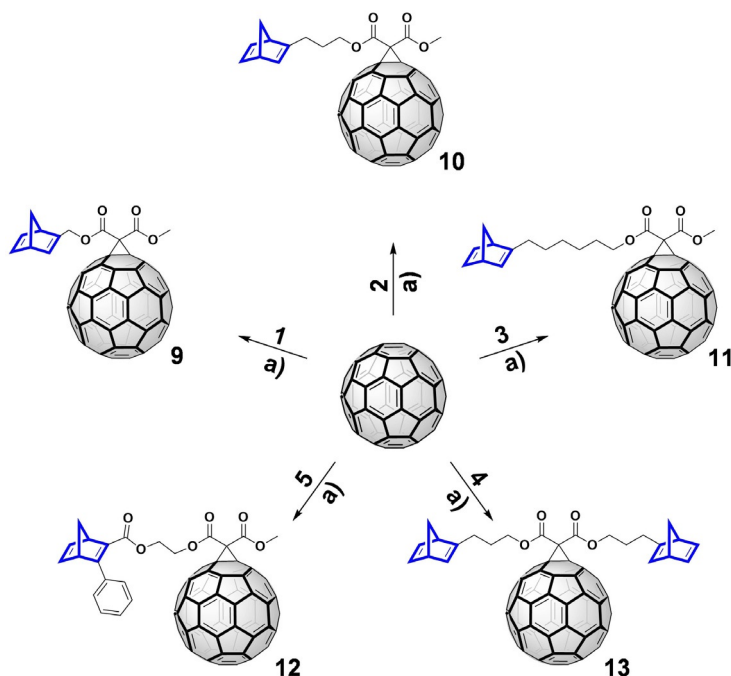
The NBD malonates of groups a) and b) carry alkyl-mono-substituted NBD scaffolds. This substitution pattern was chosen to keep the NBD scaffold as similar to the unfunctionalized parent NBD molecule as possible. It has been shown that the substitution pattern of the NBD scaffold greatly affects the photophysical properties. Especially so called “push–pull” substituted NBD derivatives, which can be obtained by attaching both an electron-donating group (EDG) and an electron-withdrawing group (EWG) to the opposite sides of one of the double bonds of NBD, show interesting and often superior photophysical properties compared to neat NBD.^[17] In course of another project, which we recently published,^[9] we investigated such a “push–pull” substituted NBD derivative NBD 6 (Scheme 1). This derivative can be readily photoisomerized to its corresponding QC isomer upon irradiation with light of a wavelength of 310 nm. Furthermore, the metastable QC isomer has a remarkably long half-life of about 450 days at room temperature in tetrachloroethane. These properties render this interconversion couple the perfect candidate for



Scheme 1. Synthesis of NBD malonate 5 starting from NBD 6; a) 9.0 equiv NaOH, THF/H₂O 1:1 v/v, reflux, 30 h; b) 2.0 equiv ethylene glycol, 1.0 equiv DCC, 0.1 equiv DMAP, CH₂Cl₂, RT, 20 h; c) 1.1 equiv triethylamine, 1.0 equiv methyl malonyl chloride, CH₂Cl₂ 0 °C to RT, overnight. DCC = *N,N*-dicyclohexylcarbodiimide; DMAP = 4-dimethylaminopyridine.

the generation of “push–pull” substituted NBD–fullerene hybrids. The synthesis of a malonate carrying the NBD **6** scaffold, without significantly altering the photochemical properties of the latter, was carried out following the reaction sequence depicted in Scheme 1. It involves saponification of the ester moiety of NBD **6** followed by a Steglich esterification with ethylene glycol to give NBD alcohol **8**. This alcohol was afterwards treated with methyl malonyl chloride to give the desired NBD malonate **5**.

Bingel–Hirsch reactions towards the desired NBD–fullerene hybrids were conducted with malonates **1–5** (Scheme 2). The reactions were carried out according to general procedure A, after purification by column chromatography and precipitation with *n*-pentane the desired NBD–fullerene monoadducts **9–13** were obtained in reasonable yields varying between 37% and 53%. Compounds **9–13** were characterized by HRMS, UV/Vis absorption spectroscopy as well as ^1H and ^{13}C NMR spectroscopy.



Scheme 2. NBD–fullerene monoadducts synthesized according to general procedure A
a) 1.0 equiv C_{60} , 1.5 equiv malonate, 1.5 equiv CBr_4 , 2.5 equiv DBU, toluene, RT, overnight.

py, for detailed information see Supporting Information. As a representative example, the ^1H and ^{13}C NMR spectra of NBD–fullerene monoadduct **12** are depicted in Figure 2 and will be briefly discussed.

All expected signals can be observed in the ^1H NMR spectrum of **12**. The detailed assignment of the protons corresponding to the NBD moiety is depicted in Figure 2. This assignment is based on a comparison with the spectra of NBD **6** which we recently published.^[9] In the ^{13}C NMR spectrum eight signals can be observed in the aliphatic region between 45–75 ppm, seven thereof originate from the malonate and the remaining signal corresponds to the sp^3 -hybridized carbon atom of C_{60} . Three of the carbon atoms of the phenyl ring give rise

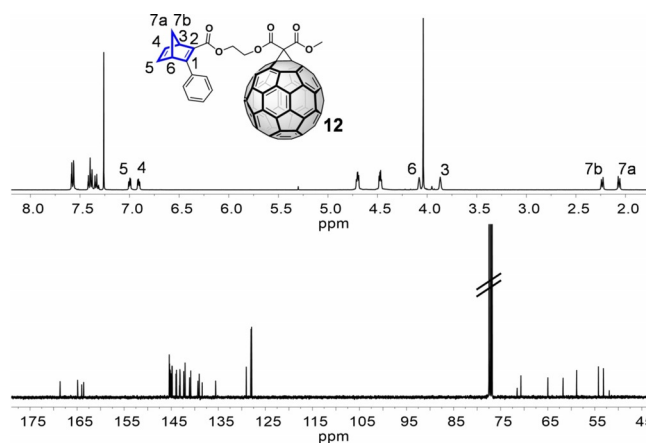
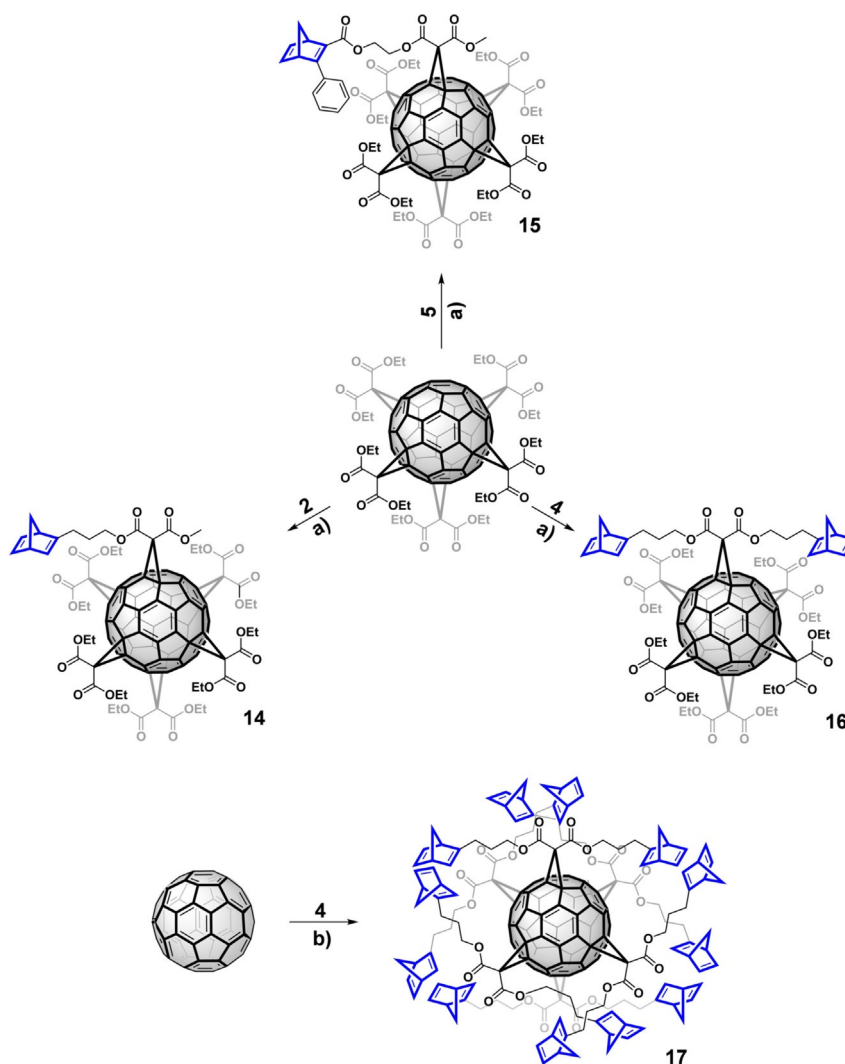


Figure 2. NMR spectra of NBD–fullerene monoadduct **12**. Top: ^1H NMR spectra with detailed assignment of the protons of the NBD scaffold (400 MHz, CDCl_3 , RT). Bottom: ^{13}C NMR spectrum of **12** (101 MHz, CDCl_3 , RT).

to the three signals located between 127.0 and 130.0 ppm. The remaining signal of the phenyl ring as well as the sp^2 hybridized carbon atoms of C_{60} and three of the olefinic carbons of the NBD scaffold can be detected between 135.0–146.0 ppm. The fourth olefinic carbon atom is strongly shifted downfield due to the conjugation of the carbonyl group and appears together with the signals of the three carbonyl groups in the region between 163.0–169.0 ppm. As evidenced, different NBDs can easily be linked to the fullerene core via their malonates in a standard Bingel–Hirsch reaction, furthermore, the purification is straightforward without the need for HPLC. Thus, NBD–fullerene monoadducts bearing a redox-active fullerene are readily available.

As already stated above, the big advantage of choosing C_{60} as an electron acceptor for our hybrid systems is that by going from a monoadduct to a hexakisadduct it is possible to significantly decrease the electron affinity of the fullerene core.^[13] Therefore, NBD–fullerene hexakisadducts would serve as the perfect reference systems, in which the electron transfer is mostly prevented, for their corresponding monoadducts. To keep the systems as similar as possible we decided to synthesize [5:1] hexakisadducts, which are readily accessible via [5:0] pentakisadducts. An efficient strategy towards these precursor molecules was developed earlier in our group.^[18] A Bingel–Hirsch reaction using the malonates **2**, **4** and **5** and a [5:0] diethyl malonate pentakisadduct gave the desired hexakisadducts in excellent yields (Scheme 3). To further expand the synthetic scope of NBD–fullerene hybrids we tested how many NBD moieties we could attach to the fullerene core. Therefore, we performed a modified Bingel–Hirsch reaction using pure C_{60} and an excess of NBD malonate **4**, CBr_4 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to obtain a [6:0] NBD–fullerene hexakisadduct **17** carrying now a total of 12 NBD moieties.



Scheme 3. Top: Synthesis of the three [5:1] hexakisadducts **14**, **15** and **16**. Conditions a) 1.0 equiv [5:0] pentakisadduct, 1.5 equiv malonate, 2.0 equiv CBr₄, 3.0 equiv DBU in toluene. Bottom: Synthesis of the [6:0] hexakisadduct **17** bearing 12 NBD moieties. Conditions b) 1.0 equiv C₆₀, 10 equiv **4**, 100 equiv CBr₄, 10 equiv DBU in toluene.

Structural characterization was done by mass spectrometry and ¹H NMR as well as ¹³C NMR spectroscopy (Figure 3). As an example, the spectra of **15** will be briefly discussed. In the MALDI-TOF mass spectrum the molecular ion peak can be detected at the expected value of *m/z* 1864.

The ¹H NMR spectrum of **15** is dominated by the two multiplets between 1.29–1.34 and 4.28–4.36 ppm which can be assigned to the CH₃ and the CH₂ groups of the five diethyl malonates, respectively. The integral ratio of these two multiplets and the remaining signals of the NBD malonate **5** confirm the formation of a [5:1] hexakisadduct. The signals corresponding to the NBD moiety are assigned in the spectrum. In the ¹³C NMR all the expected signals can be observed. The CH₃ and the CH₂ groups of the diethyl malonates give rise to two intense signals at 14.2 and 63.0 ppm, respectively. In the aliphatic region, seven signals can be assigned to the malonate carrying the NBD scaffold. The sp³-hybridized carbon atoms of the fullerene appear at around 69.0 ppm. Three of the carbon atoms of the phenyl ring give rise to signals between 127.5 to

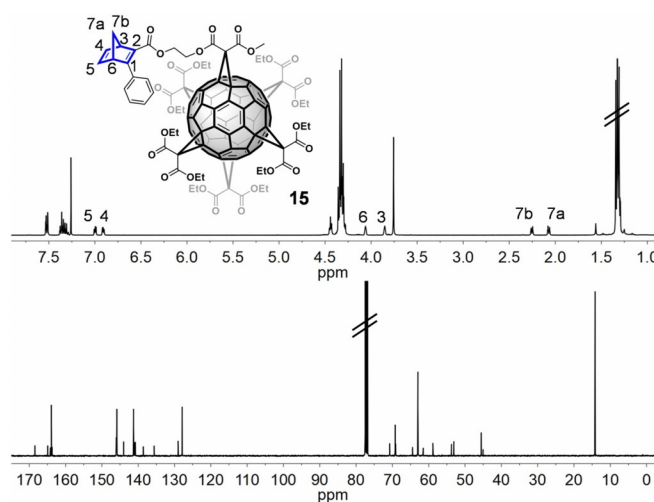


Figure 3. Top: ¹H NMR spectrum of NBD–fullerene hexakisadduct **15** (400 MHz, CDCl₃, RT) with a detailed assignment of the protons of the NBD scaffold. Bottom: ¹³C NMR spectrum of compound **15** (101 MHz, CDCl₃, RT).

129.0 ppm. The signal of the remaining carbon atom of the phenyl ring and three of the olefinic protons of the NBD scaffold are located in the region 135.0–144.0 ppm. The sp^2 -hybridized carbon atoms of the fullerene core appear in two sets of signals at 140.5–141.5 and 145.7–146.2 ppm as is typical for such [5:1] hexakisadducts (with local T_h symmetry). Signals corresponding to the carbonyl carbon atoms and of the remaining olefinic carbon atom are detected between 163.4 and 168.5 ppm.

With this small library of NBD–fullerene hybrids at hand the next step was the synthesis of their corresponding QC derivatives. In this regard, two different pathways are conceivable. First a Bingel–Hirsch reaction with the corresponding QC malonates and second the photoisomerization of the NBD–fullerene hybrid systems. Regarding the first pathway suitable malonates containing the QC scaffold were required. The simplest way towards the desired QC malonates is to photoisomerize the corresponding NBD malonates. Direct photoisomerization of the monoalkylfunctionalized NBD derivatives is not possible due to unfavorable absorption properties and low quantum yields. Therefore, an additional triplet photosensitizer is needed. According to the literature, acetophenone is ideal for this purpose.^[5] Irradiation of a mixture of malonate **2** and 5 mol% acetophenone in diethyl ether resulted in the formation of the desired QC malonate. To our surprise the successive Bingel–Hirsch reaction with this malonate did not give the expected product. Instead, NBD–fullerene hybrid **10** was obtained in small amounts as well as an inseparable mixture of side products (Scheme 4). ¹H NMR analysis suggests that side reactions occurred at the QC scaffold.

For malonates **1**, **3** and **4** it was not possible to obtain the pure corresponding QC malonates. This is most probably due to the low stability of these alkyl-monofunctionalized QC derivatives. Therefore, we pursued the second pathway via the photoisomerization of the already described NBD–fullerene hybrids. Again, acetophenone was used as a triplet photosensitizer. Tuktarov et al. reported on the formation of a poorly soluble precipitate during the irradiation of toluene solutions of NBD–fullerene hybrids and acetophenone.^[14] Although we were able to circumvent this problem by working under the strict exclusion of oxygen, we were not able to obtain the corresponding QC derivatives of compound **9**, **10**, **11**, **13**, **14** or **16**. Most likely the triplet sensitizer is more efficiently quenched by the fullerene core than by the NBD scaffold and, therefore, no isomerization can occur. Considering that our attempts towards the QC–fullerene hybrids carrying alkyl-monofunctionalized NBD scaffolds failed, we investigated the two

“push–pull” substituted NBD fullerene hybrids **12** and **15**. As described previously,^[9] the “push–pull” NBD system which is implemented in the hybrid molecules **12** and **15** undergoes clean and quantitative photoisomerization to its QC species upon direct irradiation with light of 310 nm. To test whether this also works when the system is linked to the fullerene core, a quartz glass cuvette was charged with 10 mg of compound **12** dissolved in 2.5 mL of properly degassed $CDCl_3$. The solution was irradiated by using a UV LED with an emission wavelength of 310 nm, the reaction was followed by ¹H NMR analysis (Figure 4).

The ¹H NMR spectra of **20**, depicted in Figure 4, unambiguously show that the NBD scaffold undergoes clean and com-

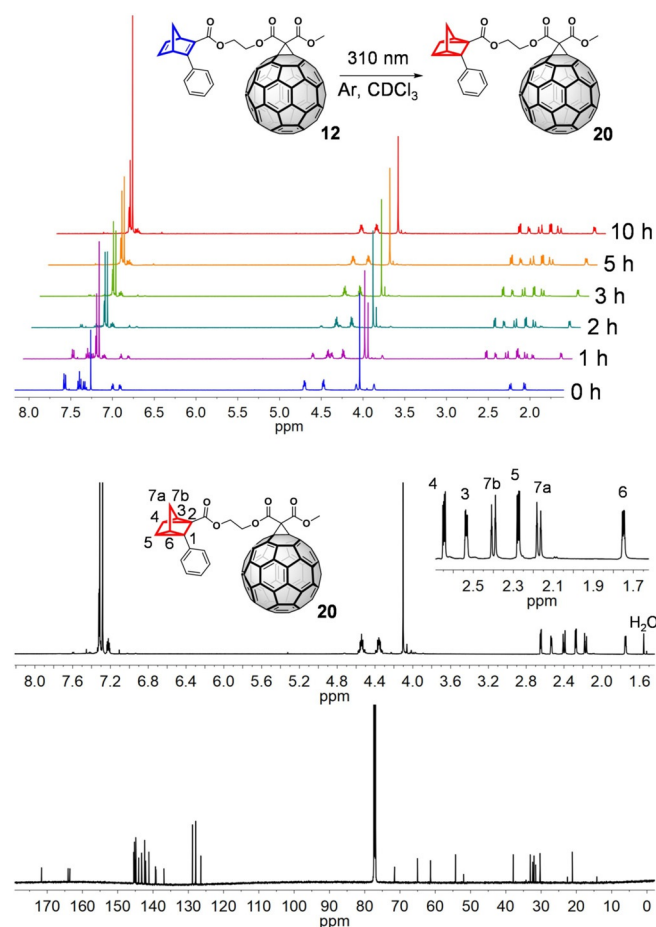
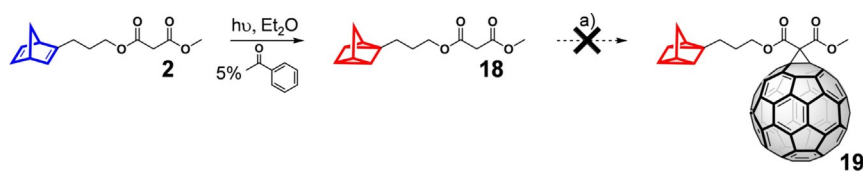


Figure 4. Top: ¹H NMR spectra of the isomerization of NBD–fullerene hybrid **12** to its QC derivative **20**. Bottom: ¹H and ¹³C NMR spectra of **20** measured in $CDCl_3$ at RT.



Scheme 4. Photoisomerization of NBD malonate **2** to QC malonate **18** (5 mol% acetophenone, diethyl ether, mercury vapor lamp); followed by the attempted synthesis of QC–fullerene monoadduct **19**. a) 1.0 equiv C_{60} , 1.0 equiv **18**, 1.2 equiv CBr_4 , 2.5 equiv DBU, toluene, RT, 4 h.

plete isomerization to its metastable QC form **20** upon irradiation. This is most obvious, when the vanishing signals of the olefinic protons of NBD located around 7.00 ppm and the new arising signals between 1.50–2.70 ppm which correspond to the QC scaffold, are taken into account. By comparing the integral ratio of the NBD and the QC signals it is possible to estimate the ratio of NBD/QC during the isomerization. Already after one hour, the reaction mixture comprises 60% QC–fullerene hybrid **20**. After two hours 80%, three hours 88%, five hours 95% and after ten hours the conversion from **12** to **20** is completed. The fact that complete isomerization to **20** can be observed is very remarkable considering that the competing absorption of the fullerene core must be considered as well, showing once more how efficient the photoisomerization of this NBD–QC couple is.

Additionally, to the ^1H NMR spectra also a ^{13}C NMR spectrum of **20** was measured to corroborate the structure of **20**. As expected, twelve signals can be detected in the aliphatic region between 20.0 and 75.0 ppm. The carbon atoms of the QC scaffold give rise to seven signals between 20.0 and 40.0 ppm. The remaining four signals corresponding to the malonate are located between 50.0 and 65.0 ppm. The sp^3 -hybridized carbon atoms of C_{60} are observed within the typical range at 71.5 ppm. As already observed for compound **12**, also in the ^{13}C NMR of **20** three signals in the range of 125.0–130.0 ppm can be assigned to the carbon atoms of the phenyl ring. The fourth carbon atom of the phenyl ring and the signals of the sp^2 -hybridized carbon atoms of the fullerene core are located between 136.0 and 146.0 ppm. As expected, three signals are observed at low field, corresponding to the three carbonyl carbon atoms of the malonate. Based on the spectral data, it can be concluded that the photoisomerization of **12** to **20** is the first successful transformation of an NBD–fullerene hybrid into its corresponding metastable QC derivative. This direct and quantitative photoisomerization of NBD–fullerene hybrids significantly simplifies the synthesis of the highly interesting QC–fullerene hybrids considering that tedious purification by HPLC is not necessary.

Encouraged by this result, the photoisomerization of the NBD–fullerene hexakisadduct **15** to the first QC–fullerene hexakisadduct **21** was attempted. According to the established method, a quartz glass cuvette was charged with 10 mg of compound **15** dissolved in 2.5 mL of properly degassed CDCl_3 . The solution was irradiated by using a UV LED with an emission wavelength of 310 nm, the reaction was followed by ^1H NMR analysis (Figure 5).

Also, in this case, a clean and complete photoisomerization of the NBD–fullerene hexakisadduct **15** to its QC derivative **21** can be observed as is evident from the ^1H NMR spectra depicted in Figure 5. Apart from the two large multiplets around 1.30 and 4.30 ppm, which correspond to the diethyl malonates, the same changes as for compound **12** can be observed during irradiation. The signal assigned to the olefinic protons of the NBD scaffold decreases, until after 10 hours it can no longer be observed. Simultaneously, the six characteristic signals corresponding to the QC scaffold of **21** arise in the region between 1.50 and 2.70 ppm. The integral ratio of NBD/QC during irradiation

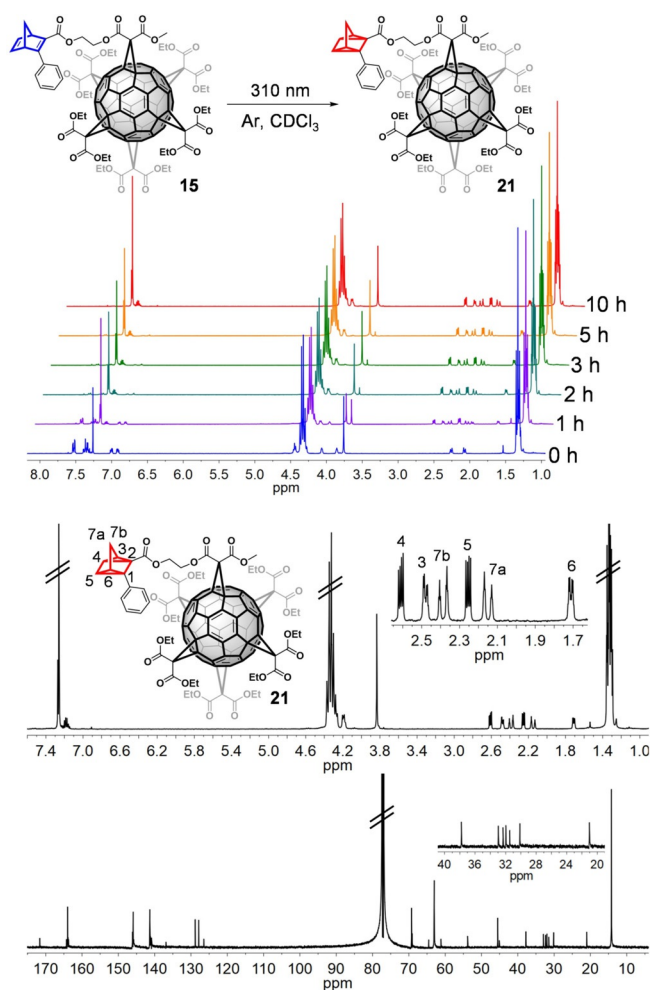
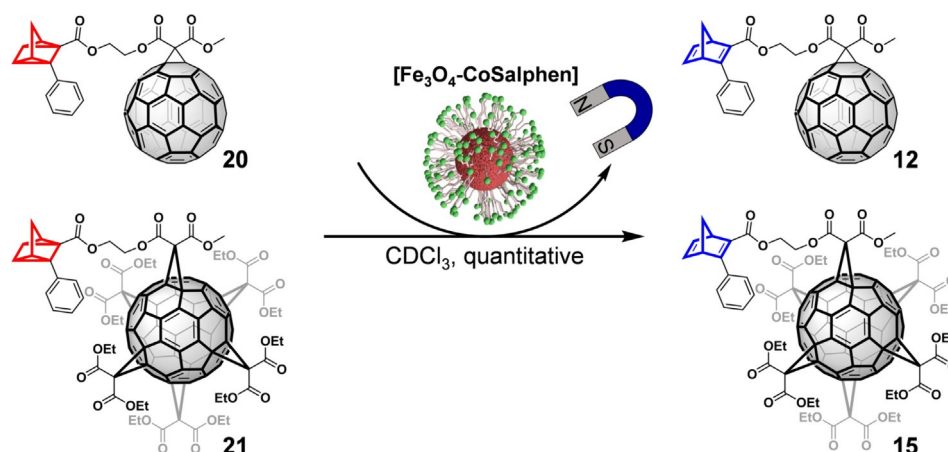


Figure 5. Top: ^1H NMR spectra of the isomerization of NBD–fullerene hybrid **15** to its QC derivative **21**. Bottom: ^1H and ^{13}C NMR spectra of **21** measured in CDCl_3 at RT.

estimates to: 1 hour 45/55%, 2 hours 13/87%, 3 hours 10/90%, 5 hours 7/93% and after 10 hours full conversion to QC–fullerene hybrid **21** was observed. Further evidence for the formation of **21** comes from the ^{13}C NMR spectrum. When comparing the ^{13}C NMR spectra of **15** and **21** this becomes most obvious, all seven signals of the NBD scaffold can no longer be observed in the spectra of **21**, instead seven new signals located in the aliphatic region between 21.0 and 38.0 ppm prove the successful isomerization to QC. The remaining signals of the malonates and C_{60} are only slightly affected by the isomerization and can be detected in the typical regions. Although the NMR spectroscopic data of **20** and **21** provides solid structural evidence, final proof for the successful photoisomerization was achieved by catalytically induced back conversion of the QC–fullerene hybrids **20** and **21** to **12** and **15**, respectively. For this purpose, we used the magnetic catalyst $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ which was recently developed in our group.^[9] The great advantage of this catalyst is that it can easily be removed from the reaction mixture by the action of an external magnet, rendering tedious purification unnecessary. Addition of the cata-



Scheme 5. Catalytic back reaction of the QC–fullerene hybrids **20** and **21** to the corresponding NBD–fullerene hybrids **12** and **15**, respectively. The magnetic nanoparticle catalyst $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$, enabled quantitative conversion in both cases, followed by the removal of the catalyst by an external magnet.

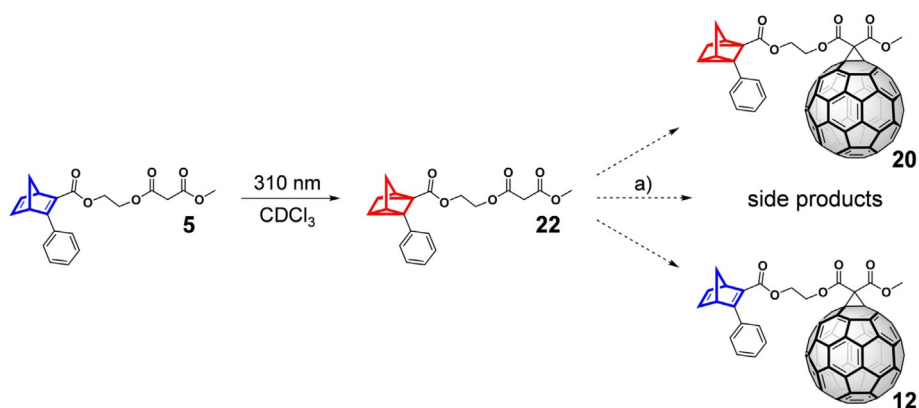
lyst $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ to solutions of **20** and **21** in CDCl_3 resulted in quantitative back conversion into **12** and **15**, respectively (Scheme 5); as apparent from ^1H NMR analysis. For more information see the Supporting Information.

As stated above, photoisomerization is only one of the two possible pathways to obtain QC–fullerene hybrids. Alternatively, it is possible to run a Bingel–Hirsch reaction with the corresponding QC malonates. Photoisomerization of NBD malonate **5** with the 310 nm UV LED proceeded smoothly in CDCl_3 and gave the corresponding QC malonate **22** in quantitative yield without further purification (Scheme 6). The synthesis of QC–fullerene monoadducts from QC malonates and C_{60} has been reported previously.^[14] Therefore, we were confident, that the Bingel–Hirsch reaction with QC malonate **22** and C_{60} would give the desired QC–fullerene hybrid **20**.

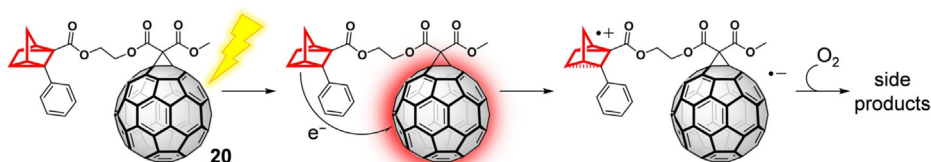
However, in direct contrast to the already published work, we observed next to the desired product, also partial formation of NBD–fullerene monoadduct **12** and inseparable side products (Scheme 6). ^1H NMR analysis (Figure S13, Supporting Information) suggests that the side reactions predominantly

occur at the QC scaffold. This, in combination with the fact that QC–fullerene hybrid **20** is known to be stable under inert conditions in the dark, makes it possible to explain the formation of side products. Although, the Bingel–Hirsch reaction is carried out under the exclusion of light and under inert atmosphere, it is inevitable that oxygen and diffuse light are present during workup and purification. Therefore, we propose that the redox active C_{60} when irradiated by diffuse light is able to oxidize QC. The thereby generated QC radical cation then undergoes side reactions (Scheme 7).

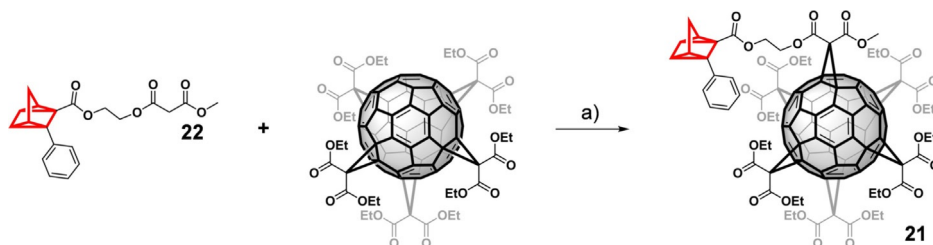
To further test this hypothesis, we also ran a Bingel–Hirsch reaction with malonate **22** and the [5:0] pentakisadduct carrying five diethyl malonates in order to obtain the QC–fullerene hexakisadduct **21**. Considering that the electron affinity of the formed hexakisadduct is much lower compared to the monoadduct **20** we expected less or no side reactions. And indeed, we were able to obtain QC–fullerene hexakisadduct **21** after purification by column chromatography (Scheme 8). The fact that C_{60} might function as an excited state electron acceptor in these QC–fullerene hybrid systems is highly interesting, consid-



Scheme 6. Photoisomerization of NBD malonate **5** to QC malonate **22**, quantitative isomerization was achieved by direct irradiation of a CDCl_3 solution of **5** with a 310 nm UV LED. The successive Bingel–Hirsch reaction with QC malonate **22** and C_{60} gave next to the desired product **20** also a small amount of NBD–fullerene monoadduct **12** and inseparable side products; a) 1.0 equiv C_{60} , 1.5 equiv **22**, 1.5 equiv CBr_4 , 2.5 equiv DBU, toluene, RT, 3 h.



Scheme 7. Proposed explanation for the formation of side products. Excitation of the fullerene core by ambient light is followed by the oxidation of QC, the generated QC⁺ is highly reactive and can undergo side reactions.

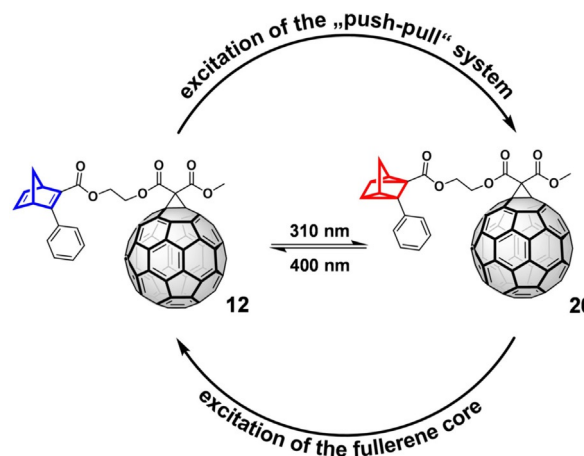


Scheme 8. Synthesis of QC–fullerene hexakisadduct **21** from QC malonate **22** and the [5:0] diethyl malonate pentakisadduct; a) 1.0 equiv [5:0] diethyl malonate pentakisadduct, 1.5 equiv **22**, 2.0 equiv CBr₄, 3.0 equiv DBU, toluene, RT, 2 d.

ering that this, in combination with the photoisomerization of the corresponding NBD–fullerene hybrids, would enable the design of switchable systems.

As a prerequisite, the back reaction from QC to NBD within the system has to be quantitative and without any side reactions. To prevent the competing irradiation and consequently the photoisomerization of the incorporated NBD “push–pull” system ($\lambda_{\text{onset}}=350$ nm) it is crucial to use a wavelength well above 350 nm to excite the fullerene core. Furthermore, to avoid side reactions caused by oxygen the used solvent was degassed thoroughly by the freeze–pump–thaw method. A cuvette was charged with 3 mg of QC–fullerene monoadduct **20** dissolved in 2.5 mL of CDCl₃ and irradiated with 400 nm light. The reaction was followed by ¹H NMR (Figures S5–S8, Supporting Information), as apparent from the NMR, excitation of the fullerene core at 400 nm results in clean and quantitative back conversion of QC–fullerene monoadduct **20** to NBD–fullerene monoadduct **12**. Thus, it is possible to switch between the NBD and the QC state in this hybrid system simply by variation of the excitation wavelength (Scheme 9).

The interconversion of NBD–fullerene monoadduct **12** and QC–fullerene monoadduct **20** resembles, to the best of our knowledge, the first switchable NBD/QC system which uses a covalently linked excited state electron acceptor to initiate the back-conversion of QC to NBD. The next subject of our experiment was to repeat the reaction with the QC–fullerene hexakisadduct **21**. Due to the weaker electron affinity of the fullerene core no or a much less efficient back-conversion of QC to NBD was expected. Under the same experimental parameters, the ratio of QC/NBD after five hours of irradiation was only about 85/15%, corroborating our previously described assumptions.



Scheme 9. The switchable NBD/QC–fullerene hybrid system. Irradiation at a wavelength of 310 nm results in the excitation of the “push–pull” system and consequently in the valence isomerization to form **20**. The reverse reaction is observed, if the fullerene core is excited at a wavelength of 400 nm. According to ¹H NMR analysis both reactions are quantitative and no side products are formed.

Conclusions

A small library of NBD–fullerene hybrid molecules, including monoadducts as well as unprecedented hexakisadducts was synthesized and investigated with regard to their corresponding QC derivatives. The tailor-made NBD scaffold incorporated into the two hybrid systems **12** and **15** made it possible to, for the first time ever, directly photoisomerize these two NBD–fullerene hybrids quantitatively to the QC–fullerene hybrids **20** and **21**, respectively. A comparison of these energy-rich methanofullerenes revealed a strong interaction of the QC moiety and the fullerene core within the monoadduct **20**; whereas the interaction in the hexakisadduct **21** is much weaker. Based on this observation, we were able to show that the fullerene core

of monoadduct **20** can be efficiently used to facilitate the back reaction from **20** to **12**. This enabled the development of the “switchable” interconversion couple **12/20** (Scheme 9) in this system it is possible to switch between the NBD and QC state simply by changing the excitation wavelength from 310 to 400 nm. This not only simplifies the investigation of the QC–NBD back reaction, but also renders such hybrid systems interesting with regard to molecular switches. The covalent linkage of the NBD/QC moiety to fullerenes has been shown to produce model systems with fascinating properties. Further investigations regarding hybrid systems featuring NBD/QC and other electron acceptors, such as rylene-dyes, are currently underway in our laboratories.

Experimental Section

General procedure A (NBD–fullerene monoadducts): Under inert atmosphere and the exclusion of light, C_{60} (1.0 equiv) was dissolved in toluene (1 mL per mg C_{60}) under sonication. The solution was degassed with nitrogen for 10 min. Afterwards 1.5 equiv of the corresponding malonate, CBr_4 (1.5 equiv) and DBU (2.5 equiv) were added. The reaction mixture was stirred overnight, concentrated and purified by column chromatography. The products were obtained after precipitation from CS_2 with *n*-pentane.

NBD–fullerene monoadduct 9: Compound **9** was prepared according to general procedure A, after purification by column chromatography (toluene, SiO_2) and precipitation from CS_2 with *n*-pentane the product was obtained as a brown solid. Yield: 102 mg, 0.108 mmol, 39%. 1H NMR (400 MHz, $CDCl_3$) δ = 6.86–6.75 (m, 3H), 5.19–5.08 (m, 2H), 4.09 (s, 3H), 3.65–3.63 (m, 1H), 3.58–3.56 (m, 1H), 2.16–2.03 ppm (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.2, 163.6, 151.5, 145.4, 145.4, 145.4, 145.3, 145.3, 145.3, 145.3, 145.1, 144.8, 144.8, 144.8, 144.0, 143.5, 143.2, 143.2, 143.2, 142.8, 142.5, 142.4, 142.1, 142.0, 142.0, 141.1, 139.2, 139.2, 74.3, 71.7, 65.8, 54.2, 52.3, 51.9, 50.7 ppm. HRMS (MALDI-TOF, dctb) $[M]^+$ m/z : 940.0730 (calcd); 940.0706 (found).

NBD–fullerene monoadduct 10: Compound **10** was prepared according to general procedure A, after purification by column chromatography (toluene, SiO_2) and precipitation from CS_2 with *n*-pentane the product was obtained as a brown solid. Yield 99 mg, 0.102 mmol, 37%. 1H NMR (400 MHz, $CDCl_3$) δ = 6.79–6.76 (m, 2H), 6.23–6.22 (m, 1H), 4.48–4.44 (m, 2H), 4.09 (s, 3H), 3.53–3.53 (m, 1H), 3.31–3.31 (m, 1H), 2.46–2.32 (m, 2H), 2.03–1.93 ppm (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.1, 163.5, 156.9, 145.3, 145.2, 145.2, 145.2, 145.1, 145.1, 145.1, 144.9, 144.7, 144.7, 144.6, 144.6, 144.6, 144.6, 144.0, 143.9, 143.9, 143.1, 143.1, 143.0, 143.0, 142.9, 142.2, 142.1, 141.9, 141.9, 140.9, 140.9, 139.1, 138.9, 134.7, 73.6, 71.5, 66.9, 54.0, 53.5, 52.1, 50.2, 27.7, 26.2 ppm. HRMS (MALDI-TOF, dctb) $[M]^+$ m/z : 968.1043 (calcd); 968.1043 (found).

NBD–fullerene monoadduct 11: Compound **11** was prepared according to general procedure A, after purification by column chromatography (toluene, SiO_2) and precipitation from CS_2 with *n*-pentane the product was obtained as a brown solid. Yield 149 mg, 0.148 mmol, 53%. 1H NMR (400 MHz, $CDCl_3$) δ = 6.74–6.71 (m, 2H), 6.11–6.10 (m, 1H), 4.49–4.46 (m, 2H), 4.08 (s, 3H), 3.47–3.47 (m, 1H), 3.25–3.25 (m, 1H), 2.25–2.14 (m, 2H), 1.99–1.94 (m, 2H), 1.87–1.80 (m, 2H), 1.52–1.34 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.7, 163.2, 158.3, 145.3, 145.3, 145.2, 145.2, 145.2, 145.2, 145.1, 145.1, 144.9, 144.7, 144.6, 143.9, 143.9, 143.8, 143.1, 143.0, 143.0, 143.0, 142.2, 142.2, 142.2, 141.9, 141.9, 141.0, 139.1, 139.0, 133.6, 73.6, 71.5, 67.3, 53.7, 53.7, 52.1, 50.3, 31.6, 29.1,

28.7, 27.3, 26.0 ppm. HRMS (MALDI-TOF, dctb) $[M]^+$ m/z : 1010.1513 (calcd); 1010.1529 (found).

NBD–fullerene monoadduct 12: Compound **12** was prepared according to general procedure A, after purification by column chromatography (toluene/ethyl acetate 95:5 v/v, SiO_2) and precipitation from CS_2 with *n*-pentane the product was obtained as a dark-brown solid. Yield 65 mg, 6.05×10^{-5} mol, 44%. 1H NMR (400 MHz, $CDCl_3$) δ = 7.59–7.56 (m, 2H), 7.42–7.31 (m, 3H), 7.01–6.90 (m, 2H), 4.71–4.69 (m, 2H), 4.49–4.46 (m, 2H), 4.09–4.08 (m, 1H), 4.04 (s, 3H), 3.87–3.87 (m, 1H), 2.25–2.05 ppm (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.6, 164.9, 164.0, 163.6, 145.4, 145.4, 145.3, 145.2, 145.2, 145.2, 145.1, 144.8, 144.8, 144.8, 144.8, 144.1, 144.0, 143.9, 143.2, 143.2, 143.2, 143.2, 143.2, 143.2, 143.1, 143.1, 142.4, 142.1, 141.1, 141.1, 140.9, 139.3, 139.1, 138.4, 135.6, 129.1, 128.1, 127.9, 71.5, 70.7, 65.0, 61.7, 58.9, 54.2, 53.2, 51.9 ppm. HRMS (MALDI-TOF, dctb) $[M]^+$ m/z : 1074.1103 (calcd), 1074.1098 (found).

NBD–fullerene monoadduct 13: Compound **13** was prepared according to general procedure A, after purification by column chromatography (toluene/ethyl acetate 95:5 v/v, SiO_2) and precipitation from CS_2 with *n*-pentane the product was obtained as a brown solid. Yield 50 mg, 4.60×10^{-5} mol, 22%. 1H NMR (400 MHz, $CDCl_3$) δ = 6.79–6.76 (m, 4H), 6.22–6.22 (m, 2H), 4.47–4.44 (m, 4H), 3.53–3.53 (m, 2H), 3.30–3.30 (m, 2H), 2.46–2.31 (m, 4H), 2.03–1.93 ppm (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.7, 157.1, 145.5, 145.4, 145.3, 145.3, 145.0, 144.8, 144.8, 144.8, 144.8, 144.1, 144.0, 143.2, 143.2, 143.1, 142.4, 142.3, 142.1, 141.1, 139.1, 134.9, 73.8, 71.8, 67.0, 53.7, 52.5, 50.3, 27.9, 26.4 ppm. HRMS (APPI, CH_2Cl_2 /toluene) $[M]^+$ m/z : 1086.1826 (calcd), 1086.1828 (found).

General procedure B (NBD–fullerene [5:1] hexakisadducts): Under inert atmosphere and the exclusion of light, [5:0] diethyl malonate pentakisadduct (1.0 equiv) was dissolved in toluene (1.5 mL per mg pentakisadduct) under sonication. The solution was degassed with nitrogen for 10 min. Afterwards 1.5 equiv of the corresponding malonate, CBr_4 (2.0 equiv) and DBU (3.0 equiv) were added. The reaction mixture was stirred for approximately 2 days. Whereas, after 1 day additional 2.0 equiv CBr_4 and 3.0 equiv DBU were added. Once TLC analysis indicated that all starting material was consumed, the solvent was evaporated, and the crude product was purified by column chromatography. The products were obtained after removal of the solvent.

NBD–fullerene hexakisadduct 14: Compound **14** was prepared according to general procedure B, after purification by column chromatography (toluene/ethyl acetate 80:20 v/v, SiO_2 ; hexanes/ethyl acetate 60:40 v/v to CH_2Cl_2 /ethyl acetate 60:40 v/v, SiO_2) and removal of the solvent in vacuo the product was obtained as a yellow solid. Yield 26 mg, 1.48×10^{-5} mol, 64%. 1H NMR (400 MHz, $CDCl_3$) δ = 6.76–6.72 (m, 2H), 6.16–6.16 (m, 1H), 4.36–4.30 (m, 20H), 4.23–4.20 (m, 2H), 3.86 (s, 3H), 3.49–3.49 (m, 1H), 3.26–3.26 (m, 1H), 2.33–2.18 (m, 2H), 1.99–1.92 (m, 2H), 1.85–1.77 (m, 2H), 1.35–1.30 ppm (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.5, 163.9, 163.9, 163.9, 157.1, 146.0, 146.0, 145.9, 145.9, 145.9, 145.9, 145.9, 144.0, 142.4, 141.3, 141.3, 141.3, 141.3, 141.2, 141.2, 134.8, 73.7, 69.3, 69.3, 69.3, 69.2, 69.2, 66.5, 63.0, 53.7, 53.6, 50.3, 45.6, 45.6, 45.5, 27.7, 26.2, 14.2 ppm. HRMS (APPI, CH_2Cl_2) $[M]^+$ m/z : 1758.3939 (calcd); 1758.3915 (found).

NBD–fullerene hexakisadduct 15: Compound **15** was prepared according to general procedure B, after purification by column chromatography (toluene/ethyl acetate 90:10 to 80:20 v/v, SiO_2) and removal of the solvent in vacuo the product was obtained as a yellow solid. Yield 26 mg, 1.42×10^{-5} mol, 71%. 1H NMR (400 MHz, $CDCl_3$) δ = 7.53–7.51 (m, 2H), 7.38–7.30 (m, 3H), 7.01–6.90 (m, 2H), 4.45–4.43 (m, 2H), 4.36–4.29 (m, 22H), 4.07–4.06 (m, 1H), 3.86–3.85 (m, 1H), 3.76 (s, 3H), 2.26–2.06 (m, 2H), 1.34–1.29 ppm (m, 30H).

^{13}C NMR (101 MHz, CDCl_3) δ = 168.4, 164.9, 164.2, 163.9, 163.9, 163.9, 163.7, 146.1, 146.0, 146.0, 146.0, 145.9, 145.9, 145.9, 145.8, 145.8, 144.0, 141.3, 141.3, 141.3, 141.3, 141.2, 141.2, 141.1, 140.9, 140.9, 140.8, 138.6, 135.6, 129.0, 127.9, 127.9, 70.7, 69.2, 69.2, 69.2, 69.2, 69.0, 64.5, 63.0, 61.5, 58.8, 53.7, 53.1, 45.5, 45.5, 45.0, 14.2 ppm. HRMS (MALDI-TOF, dctb) $[M]^+$ m/z : 1864.3999 (calcd); 1864.3993 (found).

NBD–fullerene hexakisadduct 16: Compound **16** was prepared according to general procedure B, after purification by column chromatography (toluene/ethyl acetate 90:10 v/v, SiO_2) and removal of the solvent in vacuo the product was obtained as a yellow solid. Yield 63 mg, 3.36×10^{-5} mol, 91%. ^1H NMR (400 MHz, CDCl_3) δ = 6.75–6.71 (m, 4H), 6.15–6.14 (m, 2H), 4.35–4.30 (m, 20H), 4.22–4.19 (m, 4H), 3.49–3.49 (m, 2H), 3.25–3.25 (m, 2H), 2.32–2.17 (m, 4H), 1.98–1.92 (m, 4H), 1.84–1.75 (m, 4H), 1.37–1.28 ppm (m, 30H). ^{13}C NMR (101 MHz, CDCl_3) δ = 164.0, 163.9, 163.9, 163.9, 157.0, 145.9, 145.9, 145.9, 144.0, 142.3, 141.3, 141.2, 134.7, 73.7, 69.2, 69.2, 69.2, 66.5, 63.0, 53.6, 50.3, 45.6, 45.5, 45.5, 27.7, 26.1, 14.2 ppm. HRMS (MALDI-TOF, dctb) $[M]^+$ m/z : 1876.4727 (calcd); 1876.4721 (found).

NBD–fullerene hexakisadduct 17: Under inert atmosphere and the exclusion of light, C_{60} (1.0 equiv, 6.94×10^{-5} mol, 50 mg) was dissolved in 15 mL of *ortho*-dichlorobenzene under sonication. The solution was degassed with nitrogen for 10 min. Afterwards the NBD malonate **4** (10 equiv, 6.94×10^{-4} mol, 256 mg), CBr_4 (100 equiv, 6.94 mmol, 2.30 g) and DBU (10 equiv, 6.94×10^{-4} mol, 104 μL) were added. The reaction mixture was stirred overnight and another 20 μL of DBU were added. After another day, the reaction mixture was concentrated and purified by column chromatography (hexanes/ethyl acetate, 90:10 v/v, SiO_2). The product was obtained after removal of the solvent in vacuo. Yield 21 mg, 7.23×10^{-6} mol, 10%. ^1H NMR (400 MHz, CDCl_3) δ = 6.76–6.72 (m, 24H), 6.16–6.15 (m, 12H), 4.21–4.18 (m, 24H), 3.49–3.49 (m, 12H), 3.25–3.25 (m, 12H), 2.32–2.18 (m, 24H), 1.98–1.93 (m, 24H), 1.85–1.77 ppm (m, 24H). ^{13}C NMR (101 MHz, CDCl_3) δ = 163.9, 157.1, 145.9, 144.0, 142.4, 141.3, 134.7, 73.7, 69.3, 66.6, 53.6, 50.3, 45.6, 27.8, 26.1 ppm. HRMS (APPI, CH_2Cl_2 /toluene) $[M]^+$ m/z : 2917.0981 (calcd); 2917.0954 (found).

QC–fullerene monoadduct 20: QC–fullerene monoadduct **20** was prepared by photoisomerization of the corresponding NBD–fullerene monoadduct **12**. For this purpose, 10 mg of compound **12** were dissolved in thoroughly degassed CDCl_3 (2.5 mL). The solution was transferred into a quartz cuvette which was sealed under argon atmosphere. Afterwards, the cuvette was irradiated with a 20 mW UV LED emitting light of a wavelength of 310 nm. The reaction was followed by ^1H NMR spectroscopy, which indicated full conversion after ten hours. ^1H NMR (400 MHz, CDCl_3) δ = 7.31–7.27 (m, 4H), 7.21–7.19 (m, 1H), 4.55–4.49 (m, 2H), 4.37–4.30 (m, 2H), 4.08 (s, 3H), 2.63–2.62 (m, 1H), 2.52–2.51 (m, 1H), 2.39–2.36 (m, 1H), 2.26–2.25 (m, 1H), 2.16–2.14 (m, 1H), 1.73–1.72 ppm (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ = 171.6, 164.1, 163.6, 145.5, 145.5, 145.4, 145.4, 145.3, 145.3, 145.2, 145.2, 145.2, 145.1, 144.9, 144.8, 144.8, 144.8, 144.1, 144.1, 143.3, 143.3, 143.2, 143.2, 143.2, 143.2, 143.2, 143.2, 142.4, 142.1, 142.1, 142.1, 141.2, 141.2, 139.3, 139.3, 139.1, 139.1, 136.9, 128.8, 127.9, 126.5, 71.5, 65.0, 61.3, 54.3, 51.9, 37.9, 33.1, 32.4, 32.0, 31.5, 30.3, 21.2 ppm.

QC–fullerene hexakisadduct 21: QC–fullerene hexakisadduct **19** is accessible through a Bingel–Hirsch reaction using the corresponding QC malonate **22** or by photoisomerization of the NBD–fullerene hexakisadduct **15**.

The Bingel–Hirsch reaction was carried out according to general procedure B, using the QC malonate **22**. After purification by column chromatography (toluene/ethyl acetate 90:10 v/v, SiO_2)

and removal of the solvent in vacuo the product was obtained as a yellow solid. For detailed information see supporting information. For the photoisomerization, 10 mg of NBD–fullerene hexakisadduct **15** were dissolved in 2.5 mL of properly degassed CDCl_3 . The solution was transferred into a quartz cuvette which was sealed under argon atmosphere. Afterwards, the cuvette was irradiated with a 20 mW UV LED emitting light of a wavelength of 310 nm. The reaction was followed by ^1H NMR spectroscopy, which indicated full conversion after ten hours. ^1H NMR (400 MHz, CDCl_3) δ = 7.27–7.24 (m, 4H), 7.21–7.15 (m, 1H), 4.37–4.26 (m, 22H), 4.20–4.18 (m, 2H), 3.83 (s, 3H), 2.62–2.60 (m, 1H), 2.49–2.47 (m, 1H), 2.40–2.37 (m, 1H), 2.26–2.25 (m, 1H), 2.17–2.13 (m, 1H), 1.72–1.70 (m, 1H), 1.35–1.30 ppm (m, 30H). ^{13}C NMR (101 MHz, CDCl_3) δ = 170.6, 163.3, 163.0, 163.0, 162.9, 162.9, 162.7, 145.1, 145.0, 145.0, 144.9, 144.9, 144.9, 144.8, 140.4, 140.3, 140.3, 140.3, 140.3, 140.2, 139.9, 135.9, 127.8, 126.9, 125.5, 68.3, 68.3, 68.2, 68.1, 63.5, 62.0, 62.0, 60.2, 52.8, 44.5, 44.5, 44.1, 36.8, 32.0, 31.3, 31.0, 30.5, 29.1, 20.0, 13.2 ppm.

Acknowledgements

We gratefully thank the German Research Council (DFG) for funding through the SFB 953 “Synthetic Carbon Allotropes” and the project 391585168 “Photochemisch und magnetochemisch ausgelöste Speicherung/Freisetzung von Sonnenenergie in gespannten organischen Verbindungen”.

Conflict of interest

The authors declare no conflict of interest.

Keywords: energy conversion · fullerenes · molecular switches · norbornadiene · photoswitch

- [1] K. Moth-Poulsen, D. Ćoso, K. Börjesson, N. Vinokurov, S. K. Meier, A. Majumdar, K. P. C. Vollhardt, R. A. Segalman, *Energy Environ. Sci.* **2012**, *5*, 8534–8537.
- [2] X. An, Y. Xie, *Thermochim. Acta* **1993**, *220*, 17–25.
- [3] a) G. S. Hammond, N. J. Turro, A. Fischer, *J. Am. Chem. Soc.* **1961**, *83*, 4674–4675; b) H. Hogeveen, H. C. Volger, *J. Am. Chem. Soc.* **1967**, *89*, 2486–2487.
- [4] C.-L. Sun, C. Wang, R. Boulatov, *ChemPhotoChem* **2019**, *3*, 268–283.
- [5] H. Taoda, K. Hayakawa, K. Kawase, *J. Chem. Eng. Jpn.* **1987**, *20*, 335–338.
- [6] a) A. Dreos, Z. Wang, J. Udmark, A. Ström, P. Erhart, K. Börjesson, M. B. Nielsen, K. Moth-Poulsen, *Adv. Energy Mater.* **2018**, *8*, 1703401; b) T. Toda, E. Hasegawa, T. Mukai, H. Tsuruta, T. Hagiwara, T. Yoshida, *Chem. Lett.* **1982**, *11*, 1551–1554; c) V. A. Chernov, A. D. Dubonosov, V. A. Bren, V. I. Minkin, A. N. Suslov, G. S. Borodkin, *Mol. Cryst. Liq. Cryst. Sect. A* **1997**, *297*, 239–245; d) M. Jevric, A. U. Petersen, M. Mansø, S. Kumar Singh, Z. Wang, A. Dreos, C. Sumbly, M. B. Nielsen, K. Börjesson, P. Erhart, K. Moth-Poulsen, *Chem. Eur. J.* **2018**, *24*, 12767–12772.
- [7] V. A. Bren, A. D. Dubonosov, V. I. Minkin, V. A. Chernov, *Russ. Chem. Rev.* **1991**, *60*, 451–469.
- [8] a) Z. Wang, A. Roffey, R. Losantos, A. Lennartson, M. Jevric, A. U. Petersen, M. Quant, A. Dreos, X. Wen, D. Sampedro, K. Börjesson, K. Moth-Poulsen, *Energy Environ. Sci.* **2019**, *12*, 187–193; b) J. Manassen, *J. Catal.* **1970**, *18*, 38–45; c) S. Miki, T. Ohno, H. Iwasaki, Z. Yoshida, *Tetrahedron Lett.* **1985**, *26*, 3487–3490.
- [9] T. Luchs, P. Lorenz, A. Hirsch, *ChemPhotoChem* **2019** <https://doi.org/10.1002/cptc.201900194>.
- [10] a) O. Brummel, F. Waidhas, U. Bauer, Y. Wu, S. Bochmann, H.-P. Steinrück, C. Papp, J. Bachmann, J. Libuda, *J. Phys. Chem. Lett.* **2017**, *8*, 2819–2825; b) K. Yasufuku, K. Takahashi, C. Kutal, *Tetrahedron Lett.* **1984**, *25*,

- 4893–4896; c) F. Waidhas, M. Jevric, L. Fromm, M. Bertram, A. Görling, K. Moth-Poulsen, O. Brummel, J. Libuda, *Nano Energy* **2019**, *63*, 103872.
- [11] G. Jones, W. G. Becker, *Chem. Phys. Lett.* **1982**, *85*, 271–274.
- [12] a) S. Leach, M. Vervloet, A. Desprès, E. Bréheret, J. P. Hare, T. John Dennis, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Phys.* **1992**, *160*, 451–466; b) D. M. Guldi, M. Prato, *Acc. Chem. Res.* **2000**, *33*, 695–703.
- [13] C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 1334–1344.
- [14] A. R. Tuktarov, A. R. Akhmetov, A. A. Khuzin, U. M. Dzhemilev, *J. Org. Chem.* **2018**, *83*, 4160–4166.
- [15] A. Hirsch, M. Brettreich in *Fullerenes -Chemistry and Reactions*; Wiley-VCH, Weinheim, **2004**.
- [16] a) C. Bingel, *Chem. Ber.* **1993**, *126*, 1957–1959; b) X. Camps, A. Hirsch, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1595–1596.
- [17] A. D. Dubonosov, V. A. Bren, V. A. Chernov, *Russ. Chem. Rev.* **2002**, *71*, 917–927.
- [18] a) F. Hörmann, W. Donaubauer, F. Hampel, A. Hirsch, *Chem. Eur. J.* **2012**, *18*, 3329–3337; b) M. E. Pérez-Ojeda, I. Wabra, C. Böttcher, A. Hirsch, *Chem. Eur. J.* **2018**, *24*, 14088–14100.

Manuscript received: October 14, 2019

Accepted manuscript online: November 27, 2019

Version of record online: February 19, 2020