



Efficient Cyclization of the Norbornadiene-Quadricyclane Interconversion Mediated by a Magnetic [Fe₃O₄-CoSalphen] Nanoparticle Catalyst

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We report a novel, inexpensive and effective process for the repeatable photoisomerization of norbornadiene (NBD) to its metastable isomer quadricyclane (QC), followed by catalytically induced strain energy release via back-conversion of QC to NBD. By utilization of a quasi-homogeneous catalyst based on magnetic core-shell nanoparticles, tedious purification steps are avoided. The core of this material is comprised of Fe₃O₄ and a catalytically active cobalt(II) complex is anchored on the particle surface as a self-assembled monolayer (SAM). These core-shell

nanoparticles [Fe₃O₄-CoSalphen] combine a high surface area of catalytically active molecules with straightforward separation by the action of an external magnetic field. In combination with the promising interconversion couple NBD1-QC1, which features outstanding stability ($t_{1/2}$ = 450 days at room temperature) and a high energy storage potential (88.34 kJ/mol), the nanoparticle catalyst [Fe₃O₄-CoSalphen] shows great potential for technical applications in molecular solar thermal (MOST) energy-storage systems.

1. Introduction

Within one hour, the sun provides more energy to the Earth's surface than humans consume in a whole year.^[1] However, scooping this enormous potential is not trivial, therefore, highly efficient technologies are mandatory. Next to common photovoltaic devices, molecular solar thermal (MOST) energy storage and release systems such as organometallic (fulvalene)diruthenium compounds,^[2] azobenzenes^[3] or dihydroazulene/vinylheptafulvene couples^[4] recently attracted increasing attention.^[5] In these devices the energy is harvested and transformed into a storable form on a molecular level. Afterwards, the stored energy can be released as thermal energy on demand.^[2] The big advantage of these systems is that they circumvent the problems associated with the discontinuous energy production of solar based devices. While the energy produced by common photovoltaics is only available while the sun is shining, MOST systems are not restricted to this limitation. The valence isomerization of norbornadiene (NBD) to the metastable and energy rich quadricyclane (QC) (Figure 1) is regarded a very promising concept candidate for this purpose.^[6]

In QC the energy is stored as strain energy due to the introduction of three- and four-membered rings. Overall NBD is

by about 89 kJ/mol more stable than QC in case of the parent unfunctionalized, liquid molecule.^[7] This together with the low molecular weight enables high storage capacities.

Due to the low quantum yield and lack of absorbance in the visible region of the solar spectrum a triplet photosensitizer, such as acetophenone, is needed to bring about the photoisomerization from neat NBD to QC.^[8] This can be circumvented by designing so called "push-pull" NBD derivatives (Figure 1), they show much higher quantum yields and provide a better overlap with the solar spectrum. Recently, considerable progress has been made in this field.^[9]

As stated above the main advantage of MOST systems is that the stored energy can be released on demand. Therefore, an efficient pathway to isomerize QC back to NBD is needed. Although, thermal initiation is possible it is unfavorable due to energetic reasons. From a practical point of view a catalytically induced back-reaction is desirable. Various methods have been investigated in the past; most approaches employ the catalysis of unsaturated coordination transition metal complexes,^[6] but also the use of Ag(I)^[10] or metal oxides such as MoO₃, WO₃ or V₂O₅ has been reported.^[11] In many cases the back-reaction proceeds via an oxidized form of QC. It has been shown that this intermediate can also be generated directly via electrochemistry.^[12] Only a few of the known catalysts fulfil the crucial requirements such as absence of side reactions, high turnover frequency and long-term stability. Very promising results were obtained with square planar complexes of Co(II).^[13-15] For more detailed information we refer to a review from Chernovikov and co-workers.^[6] A drawback of homogeneous catalysts is the tedious removal of the catalyst after the reaction. In most cases a purification step must be implemented which hampers cyclability of the energy storage and release process. Recently, it has been shown that it is possible to deposit catalytically active cobalt phthalocyanine on charcoal to avoid this problem, but significant leaching of the catalyst was also detected.^[16] However, beside the purification aspect, also the

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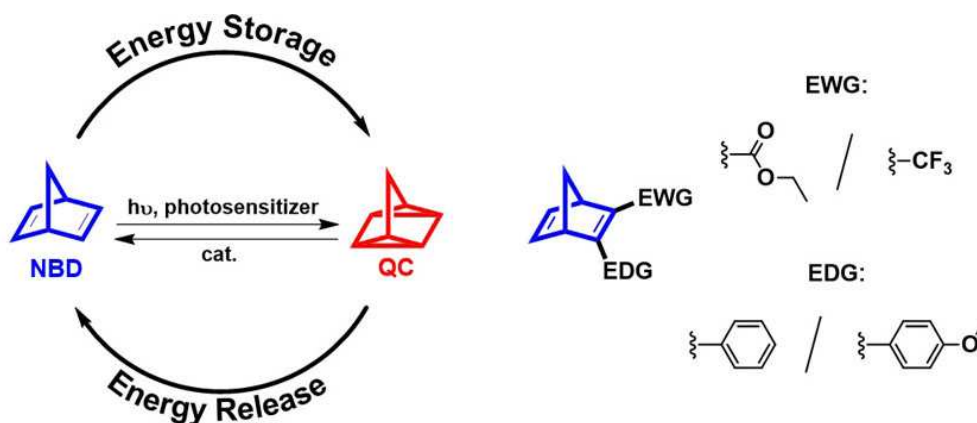


Figure 1. Left: The parent NBD-QC MOST energy storage and release system. The energy is stored as strain energy by the photochemical conversion of NBD to QC and can be released on demand with a suitable catalyst. Right: “Push-pull” substituted NBD derivative. By introducing electron-donating and electron-withdrawing groups into one of the double bonds of NBD, the photochemical properties can be significantly improved.

activity of the immobilized catalyst has to be considered. Depending on the solid support material, the accessibility of the active catalyst sites can be hindered. For a technical application of a MOST system, the development of simple, robust, inexpensive and effective methods for each step in the reversible isomerization of the NBD-QC system along with facile purification is required. Due to their high surface to volume ratio in comparison to the bulk material,^[17] the tunability of their surface properties^[18] and their facile synthesis, metal oxide nanoparticles are an excellent platform for this task.

The core of these nanoparticles provides intrinsic properties such as paramagnetism^[19] and photocatalytic activity,^[20] while the interaction with the environment can be modified by depositing self-assembled monolayers (SAMs) of active molecules on the oxide surface. The resulting core-shell materials combine the intrinsic properties of the core with the tunable properties of the shell. These include dispersibility,^[21] biocompatibility^[22] or supramolecular aggregation towards defined superstructures.^[23] In recent years magnetic core-shell nanoparticles have attracted a lot of interest as a solid support for a series of applications including water remediation,^[24] biosensing and catalytic processes.^[25] In contrast to conventional solid support materials, magnetic core-shell nanoparticles combine a high surface area with facile separation by application of a magnetic field, thus rendering filtration or centrifugation as separation methods unnecessary.

Herein we report an inexpensive, effective and repeatable process for the light induced photoisomerization of NBD to QC and the catalytic back-conversion of QC to NBD without the need for tedious purification steps. Iron oxide (Fe_3O_4) nanoparticles were covalently functionalized with a catalytically active cobalt(II) complex bearing a carboxylic acid as an anchoring group. The new core-shell material [Fe_3O_4 -CoSalphen] features the intrinsic magnetic properties of the nanoparticles, a high surface area and the catalytic properties of the surface bound ligand. Additionally, we investigated a modified NBD derivative NBD1 that combines an overlap with the solar spectrum ($\lambda_{onset} = 350$ nm), an extraordinary stability of its high energy isomer QC1 ($t_{1/2} = 450$ days at RT) and a high

energy storage capacity ($\Delta H_{storage} = 88.34$ kJ mol⁻¹). NBD1 was quantitatively converted to its high energy isomer QC1 upon irradiation at 310 nm, followed by treatment with the magnetic core-shell nanoparticles [Fe_3O_4 -CoSalphen]. This led to quantitative back-conversion to the stable NBD1 derivative. After the catalytic back-conversion the catalyst could easily be removed by the action of an outside magnet and further cycles of photochemical isomerization to QC1 and catalytic back-conversion to NBD1 could be performed without deterioration of the nanoparticle catalyst or the energy storage material NBD1-QC1. We further investigated the catalytic potential of [Fe_3O_4 -CoSalphen] together with a triplet photosensitizer and the parent NBD to show the promising potential of this magnetic core-shell nanoparticle catalyst in MOST applications, due to the facile separation by the action of an external magnetic field.

2. Results and Discussion

2.1. Synthesis and Characterization of a CoSalphen Catalyst ([Fe_3O_4 -CoSalphen]) Immobilized on Magnetic Iron Oxide NPs

For the preparation of [Fe_3O_4 -CoSalphen], commercially available Fe_3O_4 nanoparticles with a specific surface area of 100 m²/g (determined by BET analysis) were treated with the carboxylic acid bearing cobalt Salphen complex (CoSalphen) in isopropanol (Figure 2). To ensure a high degree of surface functionalization the nanoparticles were stirred with an excess of CoSalphen overnight.

After multiple washing steps by redispersion in isopropanol and magnetic separation of the nanoparticles to remove unbound ligands, the functionalized nanoparticles [Fe_3O_4 -CoSalphen] were dried at 75 °C and characterized by thermogravimetric analysis (Figure S23) and TEM (Figure S24) or transferred to chloroform for further processing or characterization by dynamic light scattering (DLS, Figure S25). After functionalization the core-shell nanoparticles [Fe_3O_4 -CoSalphen] displayed a hydrodynamic diameter of 365 nm in isopropanol, as a result of agglomeration induced by

the apolar ligand shell. After transfer to chloroform the particles showed a hydrodynamic diameter of 91 nm due to better dispersibility in the apolar solvent. From the weight loss during the TGA measurements (Figure S23) we were able to determine a CoSalphen loading of 10.7% relative to the mass of the Fe_3O_4 nanoparticles.

2.2. Synthesis and Properties of NBD1

In order to verify the successful function of our new magnetic catalyst system [Fe_3O_4 -CoSalphen], a suitable NBD-QC-interconversion couple was needed. For this purpose, we developed a robust and easily accessible push-pull conjugated NBD derivative (NBD1, Figure 3). This compound is known to readily isomerize to the corresponding QC derivative upon direct irradiation without the need of an additional triplet photosensitizer.^[26]

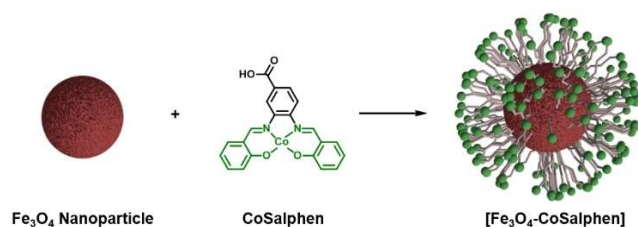


Figure 2. Functionalization of Fe_3O_4 nanoparticles with CoSalphen in isopropanol to generate the magnetic catalyst [Fe_3O_4 -CoSalphen].

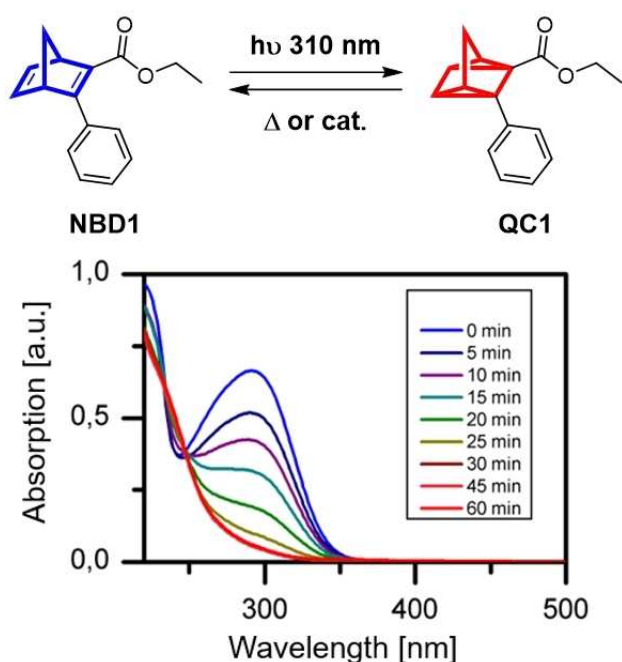


Figure 3. Top: Interconversion of NBD1 and QC1. Bottom: Photoisomerization of NBD1 to QC1 in acetonitrile monitored by UV/Vis absorption spectroscopy. Upon irradiation (310 nm) the absorption band of NBD1 centered around 300 nm decreases, until after about 30 min no further changes can be observed, indicating full conversion to QC1.

NBD1 was synthesized with slight adjustments according to a literature known procedure,^[27] it involves the Diels-Alder reaction of ethyl phenylpropiolate and cyclopentadiene (Figure S1). Surprisingly, even though NBD1 was already literature known, neither investigations on the photoisomerization, nor the generation of the corresponding quadricyclane QC1 have been described. Therefore, we studied the corresponding NBD-QC interconversion for the first time. Irradiating a solution of NBD1 in acetonitrile with a UV-LED emitting light at $\lambda_{\text{max}} = 310$ nm leads to clean and quantitative formation of QC1. This process was followed by UV/Vis absorption spectroscopy (Figure 3). Upon irradiation the intensity of the absorption band of NBD1 centered around $\lambda_{\text{max}} = 300$ nm decreases until after approximately 30 minutes no further change in the absorption profile can be detected. This indicated the completion of the photoisomerization. In view of practical applications, a highly efficient and selective photoisomerization is crucial. Remarkably, we observed no side reactions or byproduct formation during the photoisomerization of NBD1 to QC1.

Next to the photoisomerization we were also interested in the thermal stability of the metastable isomer QC1. By preparing samples of QC1 with known concentration in deuterated tetrachloroethane we were able to follow the thermally induced back reaction to NBD1 *in situ* by ^1H NMR spectroscopy (Figure S14). From the integral ratio of the QC1/NBD1 proton signals, the concentration of QC1 can be determined. This reaction follows first order kinetics. We determined the rate constants at five different temperatures (110 °C, 100 °C, 90 °C, 80 °C and 70 °C). For detailed information see the supporting information. From an Eyring plot (Figure 4) of the determined rate constants we were able to estimate $\Delta H^\ddagger_{\text{thermal}}$ (113 kJ mol⁻¹) and $\Delta S^\ddagger_{\text{thermal}}$ (-15 J mol⁻¹ K⁻¹). By extrapolating the data, it was also possible to determine the stability of QC1 at 25 °C, which shows a half-life of approximately 450 days in deuterated tetrachloroethane. Compared to similar "push-pull" substituted NBD derivatives the stability of NBD1 is outstandingly high.^[28] It has been shown before that by introducing steric bulk to the bridgehead carbon of the NBD framework or by *ortho* substitution of the adjacent phenyl ring the thermal stability can be increased, however, this is usually accompanied with a higher molecular weight and therefore, lower energy storage capacity.^[29] Although we do not have a sufficient explanation for the high stability of QC1 yet, these findings suggest that it is indeed possible to develop long lived and stable QC's without sacrificing the benefits of low molecular weight compounds. This on the other hand is highly beneficial for practical applications. Next to a high stability of the metastable isomer also the amount of energy that can be stored within QC1 is of tremendous importance. To determine this value we applied differential scanning calorimetry (DSC, Figure 5). Subsequently, three samples of QC1 were subjected to two heating cycles from 0 °C-200 °C (10 °C per minute) intermitted from a cooling cycle 200 °C-0 °C (10 °C per minute). Full conversion of QC1 to NBD1 was observed in all cases within the first heating cycle as evident from the lack of any exothermic peak in the second heating cycle. Taking the average of the three measurements, $\Delta H_{\text{storage}}$ was determined

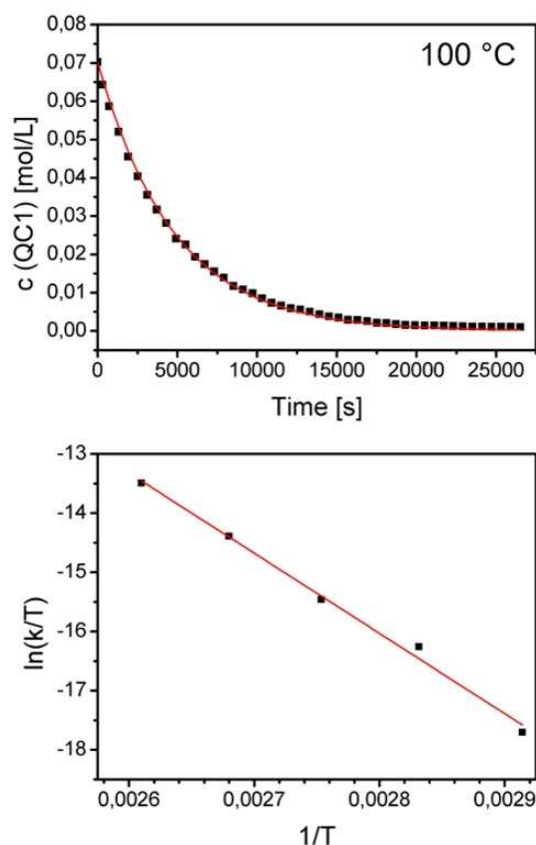


Figure 4. Top: Kinetic NMR study of the thermally induced QC1-NBD1 back-conversion at 100 °C in deuterated tetrachloroethane. Over time the concentration of QC1 decreases exponentially, indicating first-order kinetics. Bottom: Rate constants of the QC1-NBD1 back-conversion obtained at 70 °C, 80 °C, 90 °C, 100 °C and 110 °C, plotted using the Eyring equation.

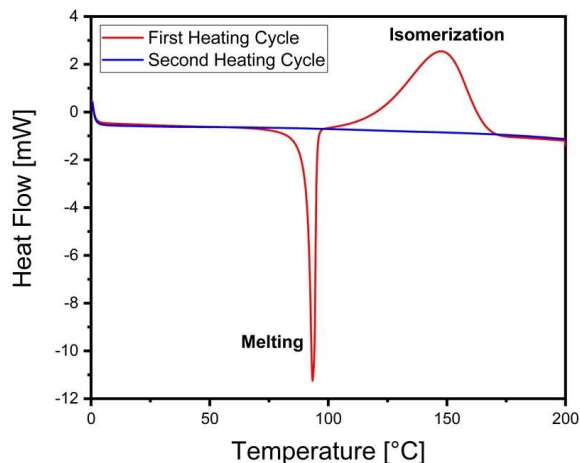


Figure 5. DSC measurement of QC1. The first peak is endothermic and is attributed to the melting of the sample whereas the second peak is exothermic and caused by the isomerization of QC1 to NBD1.

to be $\Delta H_{\text{storage}} = 88.34 \text{ kJ mol}^{-1}$. The facile and clean photoisomerization of NBD1 to QC1 combined with the enormous thermal stability and the high amount of stored energy ($\Delta H_{\text{storage}} = 88.34 \text{ kJ mol}^{-1}$) of the latter make them the ideal

model system for studying our proposed $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ -catalyst, based on energy storage and release cycles.

2.3. Back Reaction of QC1 Catalyzed by the Magnetic Catalyst System $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$

A controlled and fast release of the stored energy is of paramount importance for the operation of a solar fuel system. Apart from the thermally induced back conversion of the quadricyclane form to the corresponding norbornadiene, a cobalt(II) catalyzed back-conversion has been reported previously.^[13–16] The latter approach is more suitable for a solar fuel system since no additional thermal energy is required to trigger the release of the stored energy. To avoid tedious purification steps after the catalytical reaction we have developed a Cobalt Salphen based catalyst that is anchored onto ferromagnetic iron oxide nanoparticles via wet chemical functionalization (Figure 2). This heterogenization approach combines a high active surface area of the catalyst with the potential for facile separation by the action of an external magnetic field. To investigate the catalytic potential of $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$, a 0.0125 M solution of NBD1 in CDCl_3 was irradiated with an LED at $\lambda_{\text{max}} = 310 \text{ nm}$ for 1 h to ensure complete conversion to QC1, which was verified by ^1H NMR spectroscopy. Subsequently $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ was added and the mixture was vortexed for 1 h (560 rpm). Finally, the nanoparticles were separated by applying an external magnetic field and an aliquot of the reaction mixture was taken for NMR analysis (Figure 6).

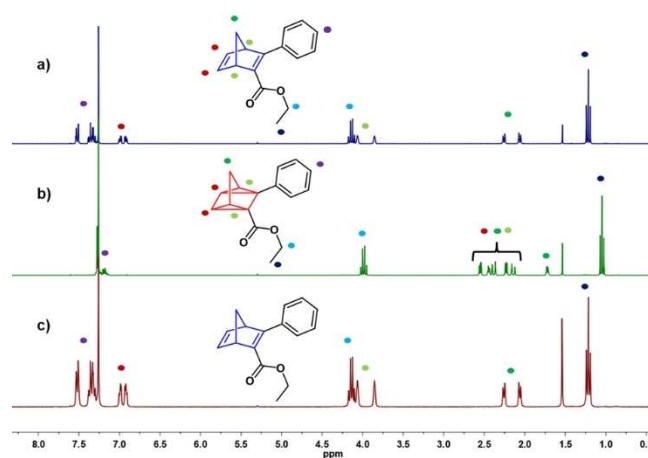


Figure 6. ^1H NMR spectra measured in CDCl_3 of: a) NBD1 before photoisomerization; b) QC1 after photoisomerization; c) NBD1 after the catalytic back-conversion using the magnetic catalyst $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$.

The ^1H NMR spectra showed that after irradiation the characteristic norbornadiene signals, especially the two alkene signals at 6.9 ppm vanished and the triplet corresponding to the CH_3 group of the ethyl ester was shifted to higher field (Figure 6b). After treatment with $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ and magnetic separation of the catalyst, the characteristic ^1H NMR spectrum of NBD1 was recovered thus indicating the complete

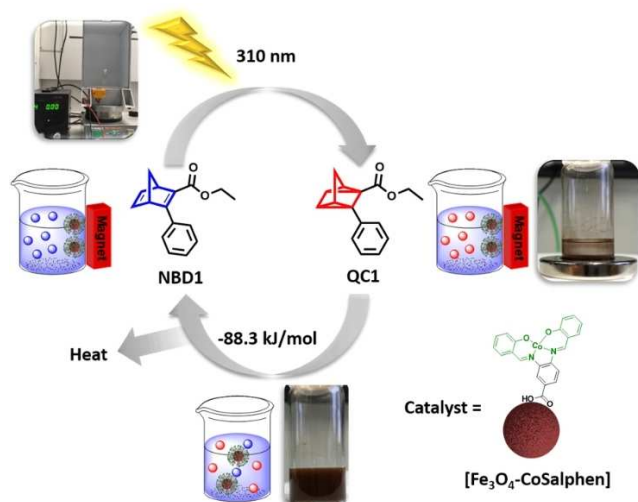


Figure 7. Full cycle of the NBD1-QC1 interconversion. NBD1 dissolved in CDCl_3 is photoisomerized to QC1 by irradiation with a UV LED (310 nm). The QC1 solution is transferred to a vial containing the magnetic catalyst $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$, after the back-conversion to NBD1 is completed the cycle is closed by facile removal of the catalyst via the application of an external magnetic field.

back conversion of the strained QC derivative to its NBD form at room temperature (Figure 6c).

Next to efficiency, the stability of the NBD-QC couple as well as the catalyst under working conditions is of great importance for a functional solar fuel system. Therefore, we subjected the system to repeated cycles of photoinduced isomerization and $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ catalyzed back-conversion (Figure 7). For this purpose, a solution of NBD1 (6 mg) in CDCl_3 (2 mL) was irradiated with an LED at 310 nm for 1 h and subsequently transferred into a vial containing the $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ catalyst. After vortexing (560 rpm) for 1 h the catalyst nanoparticles were removed by the

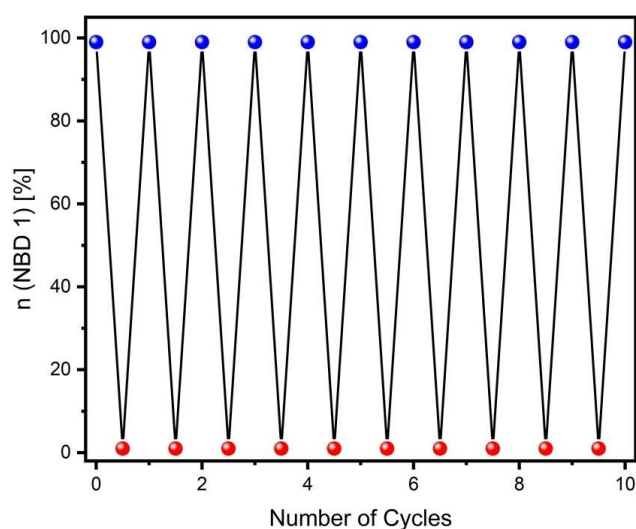


Figure 8. Repeated cycles consisting of light-induced conversion of NBD1 to QC1 and catalytic back-conversion in the presence of magnetic $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ nanoparticles, monitored by NMR spectroscopy.

action of an external magnet and the sample was transferred to a quartz glass vial for irradiation.

After each half cycle the ratio of NBD1 to QC1 was quantified by ^1H NMR spectroscopy. Figure 8 shows that each cycle led to complete conversion of NBD1 to QC1 upon irradiation and complete back conversion of QC1 to NBD1 upon treatment with $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$. During the scope of this cycling experiment no deterioration of the NBD-QC couple was observed. These findings, together with the extraordinary stability and the high amount of energy that can be stored within QC1 ($\Delta H_{\text{storage}} = 88.34 \text{ kJ mol}^{-1}$), clearly indicate that the combination of NBD1 with the magnetic catalyst $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ has great potential for a practical application as a solar fuel system.

2.4. Back Reaction of Parent QC Catalyzed by $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$

Unfunctionalized norbornadiene is a liquid at room temperature and therefore, could facilitate the technical application of a MOST system in a solvent free environment. Additionally, its low molecular weight (92.1 g/mol) leads to a high gravimetric energy storage potential. However, the major drawback of the parent norbornadiene is the low quantum yield and its lack of light absorption in the solar spectrum, which requires a photosensitizer such as acetophenone, benzophenone or Michler's ketone to facilitate the isomerization to QC. This, however, causes an additional purification step after photoisomerization to remove the photosensitizer. Therefore, we also investigated the catalytic potential of $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$ for the parent NBD and QC molecules in presence of a photosensitizer to facilitate repeated isomerization cycles without any purification steps. For this purpose, a NBD solution in CDCl_3 was irradiated with a mercury-vapor lamp in the presence of acetophenone as triplet photosensitizer to facilitate the valence isomerization to QC.

^1H NMR analysis after the irradiation (Figure 9b) showed quantitative conversion from NBD to QC, which can be clearly seen from the disappearance of the signals of the olefinic protons

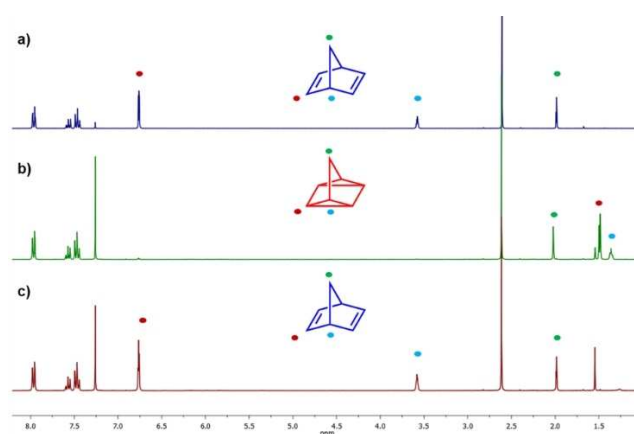


Figure 9. ^1H NMR spectra measured in CDCl_3 of: a) NBD before photoisomerization; b) QC after photoisomerization using acetophenone as a photosensitizer; c) NBD after the catalytic back-conversion using the magnetic catalyst $[\text{Fe}_3\text{O}_4\text{-CoSalphen}]$.

at 6.7 ppm and the core protons at 3.6 ppm. Subsequently, the generated QC was transferred into a vial containing the magnetic catalyst [Fe₃O₄-CoSalphen] and the mixture was vortexed at room temperature for 1 h. After vortexing the catalyst particles were removed by the action of an external magnetic field and the conversion progress was monitored by NMR spectroscopy (Figure 9c). The re-emerged signals of the olefinic protons and the core protons of the NBD form alongside with a high-field shifted bridgehead signals showed the successful back-conversion to NBD. The spectrum did not show any signal for QC, thus indicating quantitative back-conversion. Additionally, during the scope of this experiment no degradation of the photosensitizer acetophenone was observed. The combination of a triplet sensitizer with [Fe₃O₄-CoSalphen] represents a highly efficient one-pot system for the technical application of the parent NBD-QC-interconversion in a MOST device. The big advantage is that no tedious purification procedures have to be implemented after each isomerization step. The triplet photosensitizer, required for the isomerization to QC, does not interfere with the catalytic back-conversion of QC to NBD and does not cause degradation of [Fe₃O₄-CoSalphen]. After the back-conversion to NBD and release of strain energy the catalyst can easily be removed by the action of an external magnet enabling a subsequent photochemical isomerization process. This potentially enables the technical application of this isomerization cascade in a one pot system.

3. Conclusion

We introduced the promising interconversion couple NBD1-QC1 for solar thermal energy storage. Due to its remarkable stability ($t_{1/2}$: 450 days at rt), alongside with a high energy storage potential ($\Delta H_{\text{storage}} = 88.34 \text{ kJ mol}^{-1}$) this system serves as a promising candidate for MOST applications. Additionally, we prepared a novel and highly efficient catalyst system, based on magnetic core-shell nanoparticles. For this purpose, Fe₃O₄ nanoparticles were functionalized with a Co (II) complex bearing a carboxylic acid as anchoring group. The as synthesized core-shell material feature both the intrinsic properties of the core material as well as tailor made functionalities of the ligand shell. We further demonstrated the utilization of this hybrid material in the catalytic back-conversion of NBD1 to its QC derivative with facile separation by application of an external magnetic field. The combined system of NBD1-QC1 and [Fe₃O₄-CoSalphen] could undergo ten complete repeated cycles of light induced isomerization to QC1 and catalytic back-conversion to NBD1 without any signs of decomposition. Finally, we showed the successful implementation of the magnetic nanocatalyst in the isomerization cycle of unfunctionalized NBD in the presence of acetophenone as a photosensitizer. This highlighted the versatility of the catalytic system [Fe₃O₄-CoSalphen] since unfunctionalized NBD is a promising candidate in technical MOST applications due to its high gravimetric energy storage potential alongside its liquid properties. Further research into a variety of different ligands and anchoring motives alongside different particle sizes is currently under way in our laboratories.

Experimental Section

NBD1^[27]

A round-bottom pressure flask, equipped with a stirring bar, was charged with ethyl-3-phenylpropionate (28.7 mmol, 1.0 eq, 5.00 g) and freshly cracked cyclopentadiene (57.4 mmol, 2.0 eq, 3.79 g). The vessel was sealed, and the reaction mixture was heated to 180 °C overnight before it was allowed to reach room temperature. The desired product NBD1 was obtained after fractional distillation over a Vigreux column (bp = 125 °C at 0.120 mbar).

Yield 3.61 g 15.0 mmol, 52%.

¹H NMR (600 MHz, CD₂Cl₂) δ = 7.52–7.50 (m, 2H), 7.37–7.34 (m, 2H), 7.33–7.30 (m, 1H), 7.00–6.99 (m, 1H), 6.96–6.94 (m, 1H), 4.12 (qd, J = 7.1, 0.8 Hz, 2H), 4.08–4.04 (m, 1H), 3.87–3.85 (m, 1H), 2.25 (dt, J = 6.6, 1.6 Hz, 1H), 2.06 (dt, J = 6.6, 1.5 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (151 MHz, CD₂Cl₂) δ = 166.2, 165.7, 144.0, 141.3, 139.9, 136.2, 128.8, 128.2, 128.0, 71.0, 60.4, 58.9, 53.6, 14.4 ppm.

HRMS (APPI, DCM/acetonitrile) [M + H]⁺ m/z = 241.1223 (calcd.), 241.1219 (found).

QC1

QC1 was prepared from NBD1 according to general procedure A.

¹H NMR (600 MHz, CD₂Cl₂) δ = 7.28–7.24 (m, 4H), 7.20–7.16 (m, 1H), 3.96 (q, J = 7.1 Hz, 2H), 2.53 (dd, J = 4.9, 2.5 Hz, 1H), 2.44–2.42 (m, 1H), 2.38 (dt, J = 11.5, 1.4 Hz, 1H), 2.24 (dd, J = 4.9, 2.5 Hz, 1H), 2.13 (dt, J = 11.5, 1.4 Hz, 1H), 1.72–1.71 (m, 1H), 1.06 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (151 MHz, CD₂Cl₂) δ = 172.0, 137.8, 129.1, 127.9, 126.3, 60.1, 37.3, 33.4, 32.6, 32.0, 31.8, 29.2, 21.4, 14.3 ppm.

3,4-bis(((E)-2-Hydroxybenzylidene)amino)benzoic acid^[30]

In a procedure modified from the literature, salicylaldehyde (1.96 g, 16.0 mmol) and 3,4-diaminobenzoic acid (1.20 g, 7.90 mmol) were dissolved in ethanol (60 mL) under an argon atmosphere. The brown solution was stirred at rt. After stirring for 3 h the no orange suspension was filtrated, and the precipitate was washed thoroughly with ethanol and methanol to yield the title compound as an orange solid (1.69 g, 4.69 mmol, 59%).

¹H NMR (300 MHz, DMSO): δ = 13.10 (s, 1H), 12.80 (s, 1H), 12.58 (s, 1H), 9.04 (s, 1H), 8.97 (s, 1H), 7.98 (d, 4J = 1.7 Hz, 1H), 7.95 (dd, 3J = 8.2 Hz, 1H), 7.75–7.69 (m, 2H), 7.53 (d, 3J = 8.2 Hz, 1H), 7.43–7.39 (m, 2H), 6.95–7.02 (m, 4H) ppm.

CoSalphen^[30]

In a procedure modified from the literature, 3,4-bis(((E)-2-hydroxybenzylidene)amino)benzoic acid (159 mg, 0.441 mmol) was suspended in ethanol (20 mL). Cobalt acetate tetrahydrate (125 mg, 0.502 mmol) dissolved in methanol (10 mL) was added and the mixture was refluxed for 2 h. After cooling to room temperature, the brown precipitate was removed by filtration and washed extensively with ethanol and then methanol to yield the title compound as a brown solid (120 mg, 0.288 mmol, 65%).

MS (MALDI, dhb): m/z = 417 (M⁺), 418 (M + H⁺), 440 (M + Na⁺), 456 (M + K⁺).

Nanoparticle Functionalization:

In a standard procedure, the covalently coated nanoparticle-ligand systems were prepared by adding the anchor molecule dissolved in 10 mL isopropanol to 15 mg of Fe₃O₄ nanoparticles. This mixture was subjected to sonication at 21 °C for 5 min followed by stirring or vortexing (560 rpm) for 24 h. Subsequently the nanoparticles were submitted to several washing steps including redispersion in isopropanol, sonication for 5–10 min and separation by a magnetic field. For further characterization via thermogravimetric analysis (TGA) the particles were dried at 75 °C overnight or redispersed in the solvent of choice for further processing or analysis by dynamic light scattering (DLS).

Photoisomerization:

General Procedure A: For preparative photoisomerization variable amounts of NBD1 (6–100 mg) were dissolved in CDCl₃ and irradiated in a quartz glass cuvette using a 310 nm LED (Neumüller Elektronik). The quantitative conversion to the quadricyclane derivative was verified by NMR spectroscopy.

General Procedure B: For preparative photoisomerization, variable amounts of unsubstituted norbornadiene (NBD) were dissolved in CDCl₃ under argon atmosphere in the presence of acetophenone (1 eq) as a photosensitizer. The mixture was irradiated using a mercury-vapor lamp (150 W). After irradiation the quantitative conversion to QC was verified by NMR spectroscopy.

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Conflict of Interest

The authors declare no conflict of interest.

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