

Communication

Electrochemically controlled energy storage in a norbornadiene-based solar fuel with 99% reversibility

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ABSTRACT

Solar fuels based on molecular photoswitches hold the potential to combine solar energy conversion, storage, and release in an extremely simple one-photon one-molecule process. In this work we demonstrate electrochemically controlled solar energy storage and release with high reversibility in a tailor-made norbornadiene photoswitch. We investigated the photochemical conversion of the energy-lean 2-cyano-3-(3,4-dimethoxyphenyl)-norbornadiene (NBD') to its energy-rich counterpart 2-cyano-3-(3,4-dimethoxyphenyl)-quadricyclane (QC') and the electrochemically triggered reconversion. Characteristic bands of NBD' and QC' were identified by density functional theory (DFT) and monitored in-situ during the energy storage and release process by photoelectrochemical infrared reflection absorption spectroscopy (PEC-IRRAS). We identified the stable regions of both isomers at a Pt(111) electrode and tested the stability of the NBD'/QC' couple over 1000 storage and release cycles. It is shown that reversibilities of more than 99% per cycle can be achieved in this electrochemically triggered energy storage system.

1. Introduction

Sunlight is a renewable but intermittent source of energy. Its use requires conversion, storage, and release steps to be combined with a high level of efficiency and control. Besides the conventional photo-voltaic and photo(electro)chemical technologies, there are alternative chemical methods that provide particularly simple solutions to combine the three steps of solar energy conversion, storage, and release. Among these methods is energy storage in molecular photoswitches [1–4], such as the valence couple norbornadiene/quadricyclane (NBD/QC) [5–19]. In an extremely simple one-photon one-electron process, the energy-poor NBD is converted into the energy-rich QC, thereby storing solar energy in form of chemical strain (see Fig. 1a). Noteworthy, the energy density of the solar fuel QC is 0.97 MJ/kg [20–22], a value that is comparable to state-of-the-art batteries.

Typically, the process of energy release is triggered by adding mild oxidizing agents [21,23,24], which initiate the formation of QC^{•+} and lead to reconversion in a radical chain reaction. Homogeneous oxidizing agents, however, provide a low level of control so that it is preferable to use heterogeneous catalysts instead. Recently, some of the authors demonstrated macroscopic heat release from a NBD/QC-based

molecular solar thermal (MOST) storage device with a reversibility of more than 99.8% per storage cycle [25]. In this device, the energy release was triggered heterogeneously by a carbon-supported cobalt phthalocyanine catalyst [25].

A particularly fascinating concept is the electrochemically triggered energy release from the NBD/QC storage couple. In an electrochemical system, the energy release can be controlled via the electrode potential [26–29]. A QC^{•+} radical is formed electrochemically, which converts into NBD by an autocatalytic reaction [28]. Moreover, it might be feasible to release part of the energy in form of electricity [28]. This would enable the design of an 'energy storing solar cell', similar to a dye-sensitized solar cell but replacing the excited state by a stable energy-rich molecule [28]. Recently, we demonstrated that it is indeed possible to trigger the energy release from NBD electrochemically via an applied potential [28]. In a newly developed photoelectrochemical infrared reflection absorption spectroscopy (PEC-IRRAS) setup, which allows fast in-situ studies, we were able to monitor both the photochemical conversion and the electrochemically triggered energy release [29]. We showed that both the photochemical reaction and the electrochemically triggered reconversion have selectivities of around 95%.

However, the photoconversion of pristine NBD comes with a major

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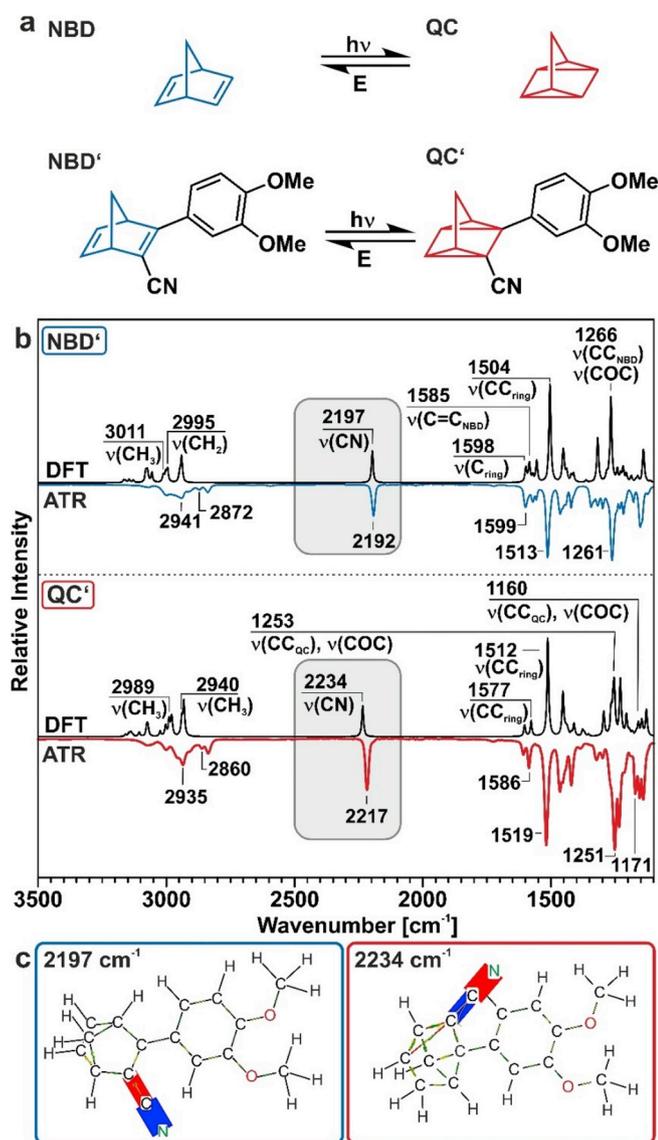


Fig. 1. (a) Energy storage and release in the valence couple norbornadiene (NBD) - quadricyclane (QC) and in the derivatives 2-cyano-3-(3,4-dimethoxyphenyl)-norbornadiene (NBD') and 2-cyano-3-(3,4-dimethoxyphenyl)-quadricyclane (QC'); (b) Experimental IR spectra (ATR-FTIR) and IR spectra calculated by DFT for NBD' and QC' including the assignment of the most prominent bands; (c) For analysis in this work we used the CN stretch modes of NBD' and QC'. The modes as calculated by DFT are visualized using QVibeplot [43].

drawback: The reaction requires an additional photosensitizer such as Michler's ketone (MK, 4,4'-bis(dimethylamino)benzophenone) to shift the absorption into the near visible region. In our previous work, we showed that the photosensitizer is the main factor that limits the cyclability of the storage system: [29] During the energy storage step, a slow follow-up reaction with photoexcited MK leads to degradation of QC. During the energy release step, partial oxidation of MK occurs at potentials at which the reconversion is initiated [29].

In this work, we demonstrate how this limitation can be circumvented by molecular design. A variety of different NBD derivatives are described in the literature. For a detailed summary we refer to review articles [4,10,30]. The absorption maximum of these derivatives is shifted to the near visible or visible region, thereby allowing solar energy storage without additional photosensitizer. [9,15,31–34] Shifting the absorption maximum, however, also decreases unfavourably the barrier for thermal reconversion and shortens the metastable storage time of QC. We use the NBD derivative NBD' (2-cyano-3-(3,4-

dimethoxyphenyl)-norbornadiene) and its counterpart QC' (see Fig. 1a) [35]. The push-pull ligands at the NBD unit redshift the absorption maximum to a value of 340 nm, so that light absorption in the near UV region is possible directly in the NBD' molecule. The derivative shows excellent absorption properties and the substituents in the ortho position of the aryl group interfere sterically with the reconversion reaction, which improves the stability of the QC', overcomes the correlation between absorption maximum and reconversion barrier, and increases the half-life of the molecule to 29 days (at 25 °C) [35]. Based on this photoactive NBD'/QC' couple we demonstrate that a high selectivity of 99% and above can be achieved by triggering the energy storage system electrochemically.

2. Material and methods

Cleaning of the equipment: For the electrochemical measurements, all glass and Teflon equipment as well as all noble metal wires were stored in a solution of NOCHROMIX (Sigma Aldrich) and concentrated sulfuric acid (Merck, Emsure, 98%) overnight. Before use, the equipment was rinsed with ultra-pure water (MilliQ Synergy UV, 18.2 M Ω ·cm at 25 °C, TOC < 5 ppm) 5 times, boiled in Milli-Q water for at least 15 min 3 times, and finally dried under vacuum.

PEC-IRRAS: The PEC-IRRAS experiments were performed with a vacuum-based FT-IR spectrometer (Bruker, Vertex 80v) with evacuated optics and a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. For the photochemical experiments the spectrometer was equipped with a UV LED (Seoul Viosys, CUD4AF1B, 340 nm, 55 mW) underneath a CaF₂ hemisphere (Korth, d = 25 mm) which serves as IR and UV transparent window. All experiments were conducted in reflection mode and in thin layer configuration. For more details of the setup we refer to our previous work [29,36]. The acquisition of the IR spectra was performed with a resolution of 2 cm⁻¹ and 128 scans (acquisition time: 57 s) for each spectrum. For the time-resolved measurements, the scanner velocity was increased from 40 to 320 kHz lowering the acquisition time to 47 ms per spectrum and using a resolution of 8 cm⁻¹. All IR measurements were performed with a solution of 10 mM NBD' and 0.1 M tetrabutylammoniumperchlorate (Sigma Aldrich 99.0%) in dichloromethane (DCM) (Sigma-Aldrich, \geq 99.8%). The potential was controlled by a commercial potentiostat (Gamry, Reference 600+) using a three-electrode configuration. As working electrode (WE) a hat-shaped Pt(111) single crystal (MaTech, 99.99%, d = 10 mm, roughness < 10 nm, accuracy < 0.4°) was used with a Pt wire (Hauner, 99.95%) serving as counter electrode (CE). Both, WE and CE were annealed in the flame of a Bunsen burner and cooled under Ar atmosphere (Linde, 5.0) before each measurement. As a reference electrode (RE), a saturated Ag/Ag⁺ electrode (AgNO₃ with 0.1 M tetrabutylammoniumperchlorate in DCM) was used. For its calibration, we recorded a cyclic voltammogram of 10 mM ferrocene (Alfa Aesar, 99.5%) in DCM in a separate cell before and after each measurement. Note, that in this work all potentials are referred to ferrocene (V_{fc}).

Cyclic voltammetry (CV): CV was measured in a homebuilt electrochemical cell in hanging meniscus configuration using a commercial potentiostat (Gamry reference 600). A Pt(111) bead-type electrode (icryst, surface area 4.5 mm², depth of roughness < 0.05 μ m, accuracy of orientation < 0.5°), a Pt wire (Hauner 99.95%), and an Ag/Ag⁺ (AgNO₃ with 0.1 M tetrabutylammoniumperchlorate in DCM) were used as working (WE), counter (CE), and reference electrode (RE), respectively. During the complete measurements a potential was applied and controlled. Voltammograms were measured with different scan rates ranging from 5 to 500 mV·s⁻¹. The potentials were calibrated with respect to the ferrocene couple.

Ex-Situ X-ray photoelectron spectroscopy (XPS): The Pt(111) surface was characterized by ex-situ XPS after 1000 conversion cycles. A depth profile was measured using Ar⁺ sputtering (2 kV, 10 nm·min⁻¹) and spectra were measured before sputtering and after 30s sputtering steps up to 360s. The XPS setup (PHI, Quantera II) was equipped with a

monochromated Al K α X-ray source (1486.6 eV) and a multichannel energy analyzer. Survey scans and scans of the O 1s, N 1s, C 1s, and Pt 4f regions were measured.

DFT: To simulate vibrational spectra the Turbomole program suite (v. 7.2) [37] was used. DFT calculations using the PBE exchange-correlation functional by Perdew, Burke, and Ernzerhof [38] were performed with the def2-TZVP basis set of Wiegend and Ahlrichs [39]. For modeling van-der-Waals interactions the Grimme D3 correction scheme with Becke-Johnson damping [40] was adopted. The calculations were accelerated using the RI-J [41] and MARI-J [42] approximations. Frequency calculations were done analytically within the harmonic approximation.

Synthesis of 2-Cyano-3-(3,4-dimethoxyphenyl)norbornadiene (NBD⁺): Cyclopentadiene (7 mL, 83 mmol), 3-(3,4-dimethoxyphenyl)propionitrile (6.31 g, 33.7 mmol), butylated hydroxytoluene (20 mg) and chlorobenzene (7 mL) were heated in a sealed vial to 130 °C for 20 h using a microwave reactor. The mixture was purified using flash column chromatography (CH₂Cl₂) and recrystallization (Et₂O/*n*-heptane – 18 °C) to give NBD⁺ as a white crystalline powder (yield: 6.83 g, 80%). For further details on the synthesis we refer to literature [35].

¹H NMR (CDCl₃, 400 MHz): δ = 7.46 (d, J = 2.1 Hz, 1H), 7.23 (dd, J = 8.4, 2.1 Hz, 1H), 6.92 (br dd, J = 5.1, 3.0 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.82 (br dd, J = 5.1, 3.1 Hz, 1H), 4.11 (ddtd, J = 3.1, 2.5, 1.6, 0.7 Hz, 1H), 3.93 (s, 3H), 3.92–3.90 (m, 4H), 2.25 (dt, J = 6.8, 1.6 Hz, 1H), 2.17 (dt, J = 6.8, 1.6 Hz, 1H) ppm.

¹³C NMR (CDCl₃, 100 MHz): δ = 170.6, 150.9, 149.2, 143.3, 140.1, 126.3, 120.0, 119.2, 114.0, 110.9, 109.4, 70.8, 56.1, 54.8, 53.9 ppm.

Synthesis of 2-Cyano-3-(3,4-dimethoxyphenyl)quadricyclane (QC⁺): NBD⁺ dissolved in toluene was irradiated with 365 nm UV light. QC⁺ was formed with total conversion as colorless oil.

¹H NMR (CDCl₃, 400 MHz): δ = 6.81 (d, J = 8.2 Hz, 1H), 6.80 (d, J = 2.1 Hz, 1H), 6.74 (dd, J = 8.2, 2.1 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.63 (dd, J = 4.9, 2.6 Hz, 1H), 2.44 (dt, J = 11.8, 1.4 Hz, 1H), 2.37 (dq, J = 4.9, 1.4 Hz, 1H), 2.23–2.19 (m, 2H), 1.87 (dq, J = 5.1, 1.4 Hz, 1H) ppm.

¹³C NMR (CDCl₃, 100 MHz): δ = 149.1, 148.0, 128.2, 119.7, 118.7, 111.5, 110.1,

56.1, 56.0, 35.3, 32.4, 31.3, 30.8, 26.7, 21.8, 14.6 ppm.

3. Results and discussion

In a first step, we analyzed the IR spectra of NBD⁺ and QC⁺. In Fig. 1b we compare the experimental spectra measured by attenuated total reflection (ATR) IR spectroscopy with calculated spectra from DFT (see Materials and Methods part for details). The calculated spectra were analyzed using the software QVibplot [43] and the experimental bands were assigned accordingly. For NBD⁺, we observe dominant bands at 2942 (ν (CH₃)), 2872 (ν (CH₂)_{NBD}), 2192 (ν (CN)), 1599 (ν (CC)_{ring}), ν (C=C)_{NBD}, 1514 (ν (CC)_{ring}), ν (CO), ν (C=C)_{NBD}, and 1261 cm⁻¹ (ν (COC), ν (CC)). For QC⁺ the strongest bands appear at 2936 (ν (CH₃)), 2860 (ν (CH₃)), 2217 (ν (CN)), 1586 (ν (CC)_{ring}), 1519 (ν (CC)_{ring}), 1251 (ν (CC)_{QC}, ν (COC)), and 1171 cm⁻¹ (ν (CC)_{QC}, ν (COC), ν (CH₃)). A more detailed analysis of the spectra is provided in the Supporting Information (Chapter 1, Tables S1 and S2 and Figs. S1 and S2).

In the present work, we used the CN stretching bands of NBD⁺ at 2192 cm⁻¹ and of QC⁺ at 2217 cm⁻¹ as a spectroscopic marker for a successful conversion. The spectral shift of 25 cm⁻¹ is sufficient to follow the interconversion during the storage cycle by in-situ IR spectroscopy. To perform the experiments, we used the previously mentioned PEC-IRRAS setup with a light source that fits to the absorption maximum of NBD⁺ [35] (emission wavelength λ_{max} = 340 nm, 55 mW) and a Pt(111) single crystal as a working electrode (see Fig. 2). In preparatory experiments we showed that the electrochemically triggered conversion is negligible at an electrode potential of –0.88 V_{fc} (see Supporting Information Chapter 2 for details) and that the complete photochemical conversion in the thin layer occurs within an

irradiation time of ~2 s (see Supporting Information Chapter 3 for details). Note that the photochemical conversion of NBD⁺ to QC⁺ is highly efficient with a quantum yield of 68% [44]. In the next step, we investigated the electrochemically triggered reconversion using the experimental procedure illustrated in Fig. 2a. At the beginning of the experiment, we recorded a reference spectrum at –0.88 V_{fc} and, subsequently, recorded spectra before and after irradiation (3 s) at –0.88 V_{fc}. The spectrum before irradiation (red) does not show any feature except for a positive band at 1264 cm⁻¹, which is assigned to the HCH rocking mode of the solvent DCM [45]. The spectrum after irradiation shows complete conversion of NBD⁺ to QC⁺, as indicated by the difference bands in the ν (CN) region. Next, the electrode potential was ramped from –0.88 to 1.62 V_{fc} in steps of 0.1 V and an IR spectrum was recorded at every potential (see Fig. 2b). In the CN stretching region we observe the disappearance of the negative ν (CN)_{QC} band at 2220 cm⁻¹ (indicating consumption of QC⁺) and the disappearance of the positive ν (CN)_{NBD} band at 2195 cm⁻¹ (indicating formation of NBD⁺). Note that in the PEC-IRRAS experiment we record difference spectra, in which positive bands correspond to species consumed and negative bands correspond to species formed with respect to the reference). The quantitative analysis derived from the band intensities is shown in Fig. 2d (see Supporting Information Chapter 4 for details). We conclude that QC⁺ is fully reconverted to NBD⁺ at a potential of 0.32 V_{fc}. In the cyclic voltammograms measured at different scan rates (see Supporting Information Chapter 5, Fig. S6) we did not observe any features which we assign to the oxidation of QC⁺. This indicates that the conversion is mainly driven autocatalytically by just a low amount of electrochemically formed QC⁺. This is in contrast to unfunctionalized NBD which shows clear oxidation peaks for QC in the CV [28]. The reaction is fully selective at the accuracy level of the experiment (\pm 5%). A more accurate assessment of the reversibility will be given below. In comparison with the unfunctionalized NBD [28,29], we conclude that the conversion potential of the functionalized QC⁺ is at ~0.2 V lower potential and that the reaction is driven autocatalytically.

Two additional observations are noteworthy. First, we observe a slow reconversion over a broad potential region from –0.88 to –0.08 V_{fc} at a rate which increases slowly with increasing potential. We assign this effect to the catalytic activity of the pristine Pt(111) surface, which is capable of triggering the reconversion due to a low activation barrier [46]. Secondly, we observe the reappearance of a positive ν (CN)_{NBD} band at potentials above 0.92 V_{fc} (consumption of NBD⁺). We attribute this observation to the electrooxidation of NBD⁺ which leads to an irreversible consumption. We conclude that the potential window suitable for selective electrochemically triggered reconversion of QC⁺ to NBD⁺ is between 0.32 and 0.82 V_{fc}.

Finally, we investigated the reversibility of the energy storage and release cycle in the NBD⁺-QC⁺ system in a specially designed PEC-IRRAS experiment. In this experiment we took advantage of the push and pull ligands of NBD⁺ which redshift the absorption maximum in comparison to unfunctionalized NBD. As a result, we can avoid the use of an additional photosensitizer, which would limit the cyclability [29]. The experimental procedure is illustrated in Fig. 3a. After recording the reference spectrum at –0.88 V_{fc}, 1000 storage and release cycles were performed. Each cycle consisted of an irradiation step (3 s irradiation at –0.88 V_{fc}) and a subsequent electrochemically triggered reconversion (at 0.42 V_{fc} for 30 s).

IR spectra were recorded after both steps at –0.88 V_{fc} to quantify the fraction of NBD⁺ that is converted and reconverted, respectively. The complete experiment was performed in thin layer configuration, which suppresses reactant exchange between the thin layer and the bulk solution (diffusion into and out of the thin layer requires several hours, see Supporting Information Chapter 6, Fig. S7) [47].

In Fig. 3b, the IR spectra are displayed after irradiation. The reference spectrum (S_{R-P}) was taken before irradiation, i.e. in the presence of NBD. We observe a positive band at 2195 cm⁻¹ (indicating the consumption of NBD⁺) and negative band at 2220 cm⁻¹ (indicating the

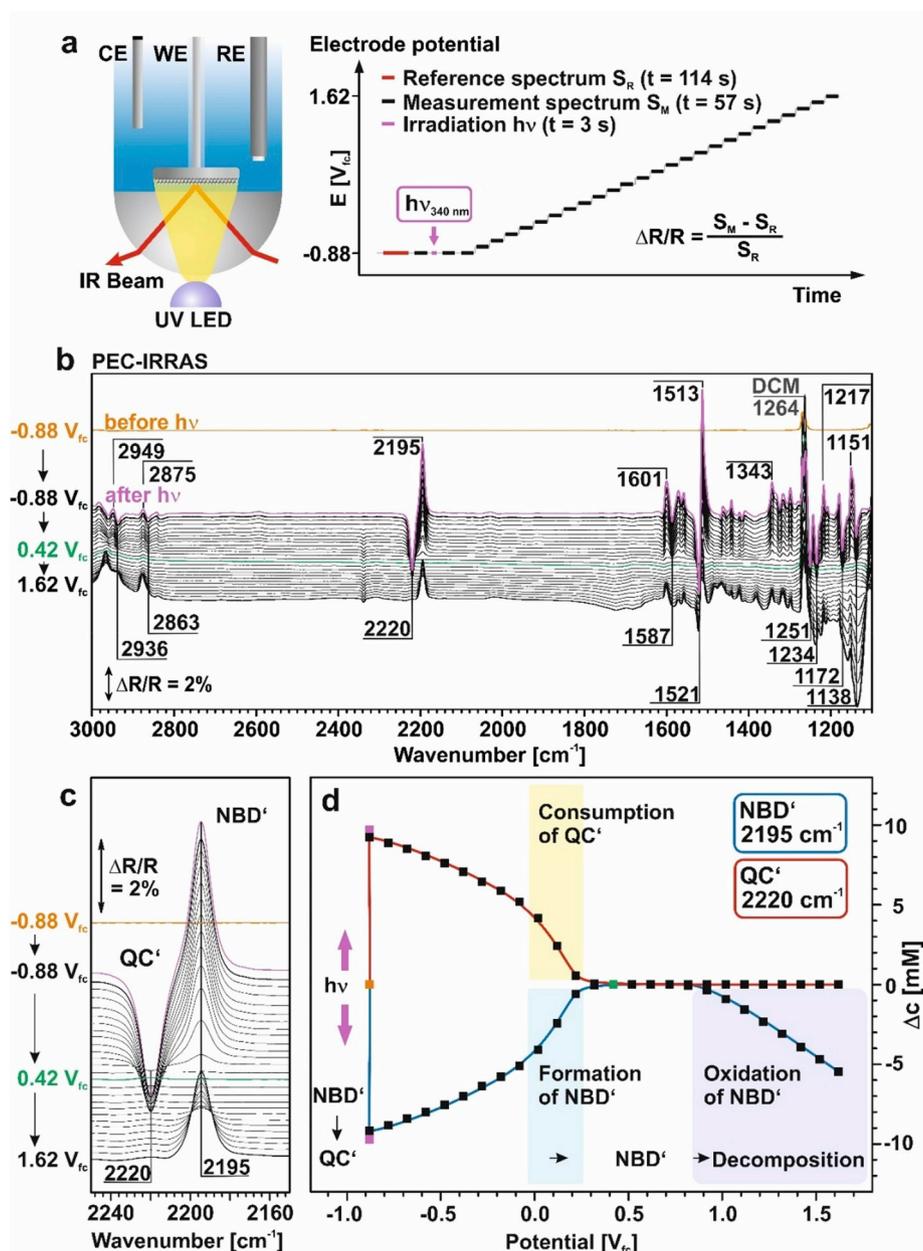


Fig. 2. Photochemical conversion and electrochemical reversion in the NBD'-QC'system; (a) schematic representation of the PEC-IRRAS setup and experimental procedure; (b) IR spectra as a function of the electrode potential during reversion from QC' to NBD'; (c) $\nu(\text{CN})$ region as a function of the electrode potential; (d) concentration of NBD' and QC' as a function of the potential as derived from the band intensities in the $\nu(\text{CN})$ region. The reference spectrum was taken at -0.88 V_{fc}.

formation of QC'). The results of a quantitative analysis are shown in Fig. 3c. We observe only a minor decrease of the concentration of QC' from 94 to 82 mol·l⁻¹ after the 1000 irradiation cycles. This shows that the storage system is stable even upon prolonged irradiation.

In Fig. 3d, the corresponding IR spectra are shown after the electrochemically triggered reversion. As a reference, we used the spectrum recorded after the irradiation step (S_{R-E}), i.e. when QC was formed. We observe a positive band at 2220 cm⁻¹ indicating the consumption of QC' and a negative band at 2195 cm⁻¹ indicating the formation of NBD'. However, the band intensities decrease over the course of the 1000 storage cycles. Quantitative analysis shows more than 90% reversion in the initial cycle, while the reversion decreases to approximately 50% after 70 storage and release cycles. From these values, we estimate a reversibility of more than 99% per cycle, assuming that the conversion in the reversion decays exponentially. Note that within approximately 2 s QC' reverts to NBD' on a freshly prepared Pt(111) electrode (see Supporting Information Chapter 3, Fig.

S4). We attribute the decreasing efficiency of the reversion reaction to fouling of the Pt(111) electrode [28,48]. This hypothesis is in line with an XPS analysis showing the formation of a hydrocarbon film on the surface after repeated switching (see Supporting Information Chapter 7). Apart from the slow degradation of the electrode, no other side reactions could be observed.

4. Conclusions

In summary, we showed that solar energy storage and electrochemically triggered energy release can be achieved with a high reversibility in tailor-made solar fuels based on the valence couple norbornadiene-quadracyclane. We investigated the photoconversion of 2-cyano-3-(3,4-dimethoxyphenyl)-NBD (NBD') to 2-cyano-3-(3,4-dimethoxyphenyl)-QC (QC') and the electrochemically triggered reversion in a photospectroelectrochemical in-situ IR experiment at a Pt(111) electrode. At a potential of -0.88 V_{fc}, the energy-rich QC' is

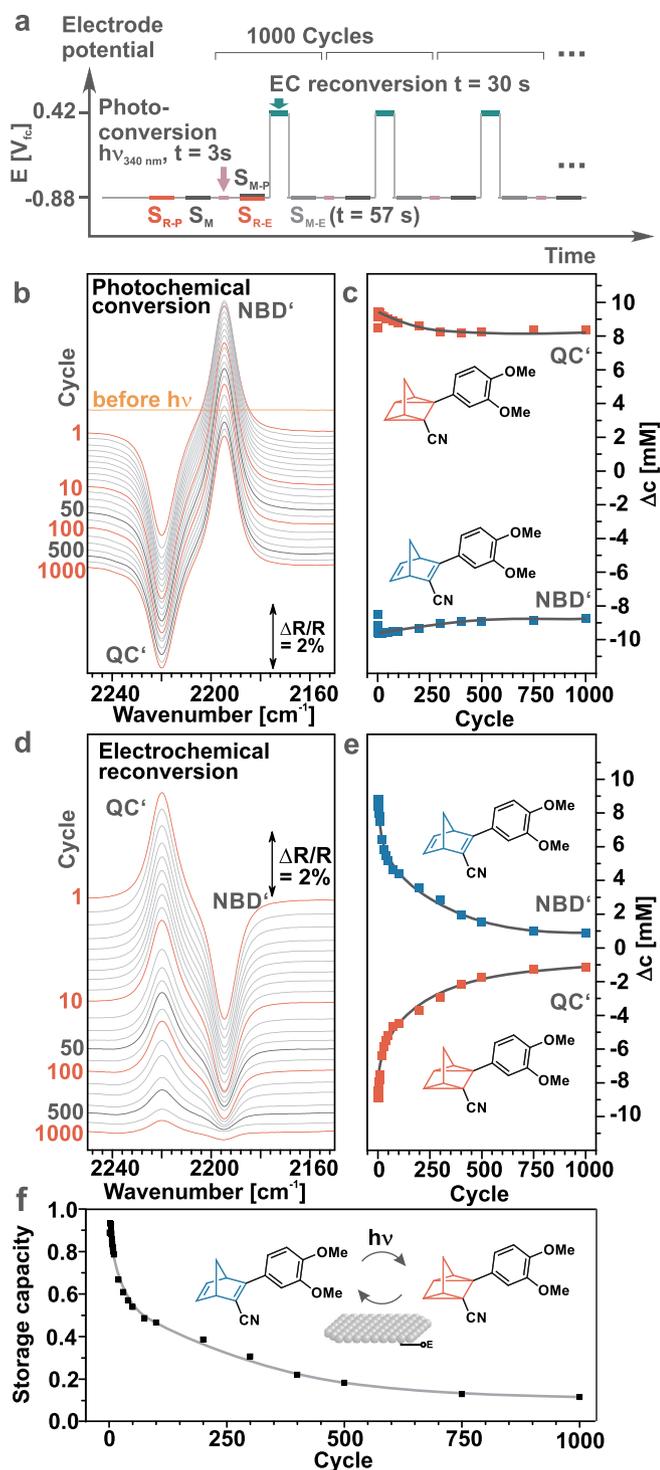


Fig. 3. Stability test of the electrochemically triggered NBD'-QC' energy storage system; (a) experimental procedure covering 1000 conversion cycles monitored by PEC-IRRAS; S_{R-P} and S_{M-P} reference and measurement spectra of photochemical conversion, S_{R-E} and S_{M-E} reference and measurement spectra of electrochemical conversion; (b, c) IR spectra and concentrations after photochemical conversion; (d, e) IR spectra and concentrations after electrochemically triggered reversion; (f) storage capacity versus the number of storage cycles. All spectra were taken at $-0.88 V_{fc}$.

stable at the Pt electrode on the timescale of the experiment. At potentials between $0.02 V_{fc}$ and $0.92 V_{fc}$, fast energy release is triggered by reversion to NBD'. At higher potentials, NBD' is unstable and undergoes electrooxidation. We tested the reversibility of the solar

energy storage system over 1000 storage and release cycles and observed a reversibility of more than 99% per cycle. At this point, electrode fouling is the factor that limits the reversibility. We expect that further improvements will be feasible by engineering the electrode structure and material as well as the structure of the NBD/QC derivatives.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.nanoen.2019.103872>.

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