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Electrochemically Controlled Energy Release from a Norbornadiene-Based Solar Thermal Fuel: Increasing the Reversibility to 99.8% using HOPG as the Electrode Material

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1. Band Assignment

The bands of the experimental spectra of 2-cyano-3-(3,4-dimethoxyphenyl)norbornadiene (NBD’) and 2-cyano-3-(3,4-dimethoxyphenyl)quadricyclane (QC’) were assigned to the vibrational modes as described in Table S1:

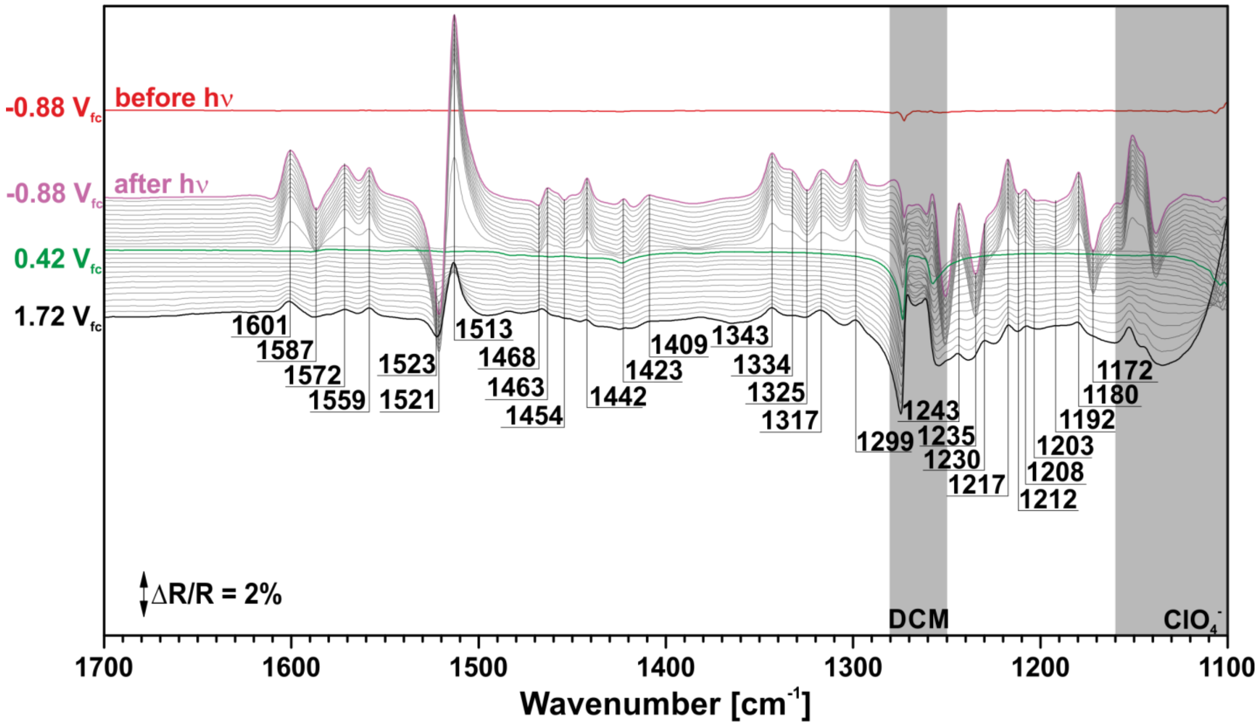

Figure S1: Photochemical conversion and electrochemical reconversion in the NBD’-QC’ system on HOPG. Fingerprint region of the potential dependent PEC-IRRAS spectra shown in Figure 1b. The reference spectrum was taken at -0.88 V_{fc} prior irradiation.

Table S1: Assignment of the experimentally observed bands shown in Figure S1 to the vibrational modes of NBD’ and QC’ based on DFT calculations reported in [1]

ν_{exp} [cm^{-1}]	Species	Vibrational modes referred to [1]
1172	QC’	$\nu(CC)_{QC}$, $\nu(COC)$, $\nu(CH_3)$
1180	NBD’	$\nu(CC)_{NBD}$
1192	QC’	$\nu(CC)_{QC}$
1212	QC’	$\nu(CC)_{QC}$, $\nu(COC)$
1217	NBD’	$\nu(COC)$, $\nu(CC)_{NBD}$

1230	NBD’	$\nu(COC)$
1235	QC’	$\nu(CC)_{QC,}$ $\nu(COC)$
1299	NBD’	$\nu(CC)_{NBD}$
1317	NBD’	$\nu(C_{NBD}C_{ring})$
1325	QC’	$\nu(CC)_{QC,}$ $\nu(CC)_{ring}$
1343	NBD’	$\nu(CC)_{ring}$
1409	NBD’	$\nu(CC)_{ring}$
1423	NBD’	$\nu(CC)_{ring}$
1442	NBD‘	$\nu(CC)_{ring}$
1454	QC’	$\nu_{sym}(CH_3)$
1463	NBD’	$\nu(CH_3)$, $\nu(CO)$, $\nu(CC)_{ring}$
1468	QC’	$\nu_{sym}(CH_3)$
1513	NBD’	$\nu(CC)_{ring}$, $\nu(CO)$, $\nu(C{=}C)_{NBD}$
1521	QC’	$\nu(CC)_{ring}$
1559	NBD’	$\nu(CC)_{ring,}$ $\nu(C{=}C)_{NBD}$
1572	NBD’	$\nu(CC)_{ring,}$ $\nu(C{=}C)_{NBD}$
1587	QC’	$\nu(CC)_{ring}$
1601	NBD’	$\nu(CC)_{ring,}$ $\nu(C{=}C)_{NBD}$

2. Differential Pulse Voltammetry

Figure SI2 shows the differential pulse voltammogram of NBD’ and a mixture of NBD’ and QC’ in MeCN. The measurements were performed with a step size of 5 mV, a pulse size of 20 mV, a sample period of 0.5 s and a pulse time of 0.25 s. In the DPV, the peak 0.95 V_{fc} is assigned to the electrooxidation and decomposition of NBD’. Above 1.0 V_{fc} further oxidation peaks appear which are ascribed to unspecific side reaction. In line with former studies made using Pt electrodes, no oxidation peak is observed for the oxidation of QC’ to NBD’. For details we refer to our previous work.[1]

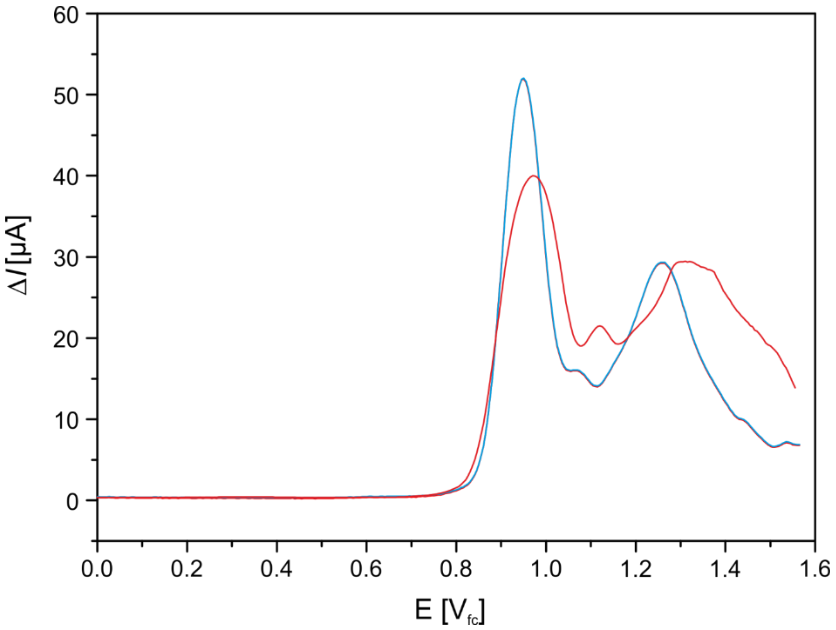

Figure S2: DVP of 10 mM NBD' (blue) and a 1:1 mixture of NBD'/QC' (red) with a glassy carbon in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte.

3. Quantitative analysis of the IR spectra

The NBD' and QC' concentrations were determined using the single channel spectra before and after irradiation, as shown in Figure S2. From the spectra, the absorbance A was calculated by

$$A = -\log_{10}T \qquad (1)$$

with the transmission T.

The change in the absorbance was used to determine the relative change in the concentration, with respect to Beer-Lamberts law

$$\Delta A_{NBD} = \varepsilon \cdot d \cdot \Delta c_{NBD} \sim \Delta c_{NBD} \qquad (2)$$

with the extinction coefficient ε and the layer thickness d. The concentration of NBD' before irradiation is known. As shown in Figure 1, all QC' formed can be reconverted to NBD', which is indicated by the absence of either NBD' or QC' bands at a potential of $0.42V_{fc}$. We conclude that the selectivity for the conversion and the reconversion is close to unity. Therefore, the QC' concentration after irradiation was normalized with respect to the NBD' consumption.

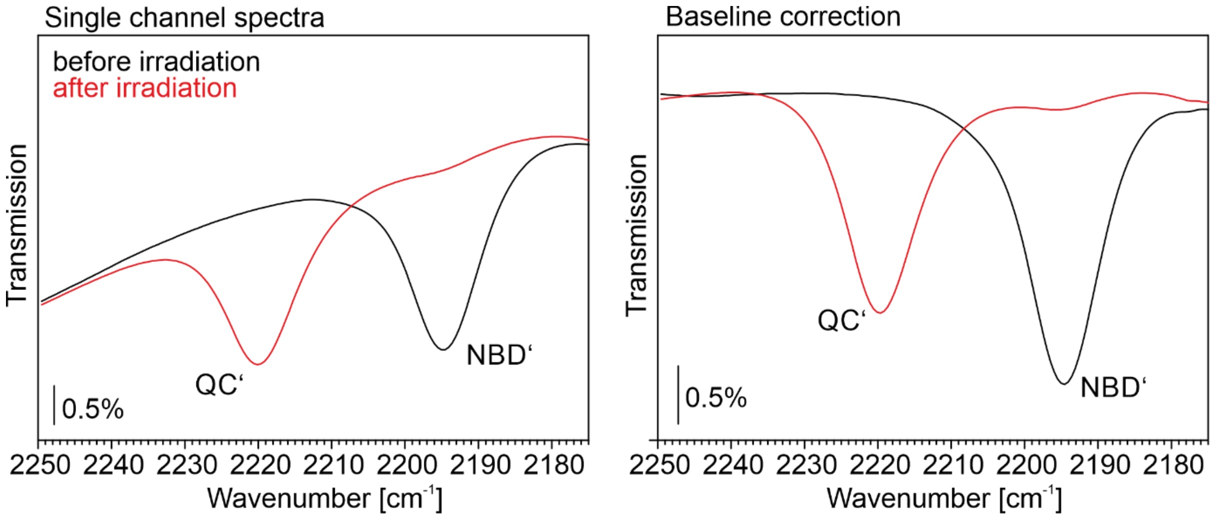

Figure S3: Single channel spectra before and after the photochemical conversion of NBD' to QC' at -0.88 V_{fc} on HOPG. (a) Single channel spectra as measured and (b) after baseline correction.

In the reversibility measurement (Figure 3), the first spectrum after the photochemical conversion was used for quantification. All further concentrations in this experiment are referred to the initial concentration of NBD' and QC' after the first photochemical conversion. The overall storage capacity was calculated as the difference of the QC' concentrations after the photochemical conversion and after the electrochemical reconversion. We calculated the reversibility from the point where the storage capacity decreased to 50% of its initial value.[1] In the reversibility measurements, we observe a decay of the storage capacity to 50% after 400 cycles. From these value, we calculate a reversibility of >99.8%.

4. Calculation of the Photo- and Electrochemical Selectivity on HOPG

Using the above mentioned procedure, we calculated the concentrations of NBD' and QC' as a function of irradiation time. Based on that, the kinetics were fitted using an exponential fit of the NBD'/QC' concentration

$$\Delta c_{NBD'/QC'} = \Delta c^{0}_{NBD'/QC'} e^{-\frac{t}{\tau}} + c$$

From the concentration changes of NBD' and QC', the selectivity is calculated as:

$$S_{photo} = \frac{\Delta c_{QC'}}{-\Delta c_{NBD'}} \quad \text{or} \qquad S_{electro} = \frac{\Delta c_{NBD'}}{-\Delta c_{QC'}}$$

The results as a function of irradiation time are given below:

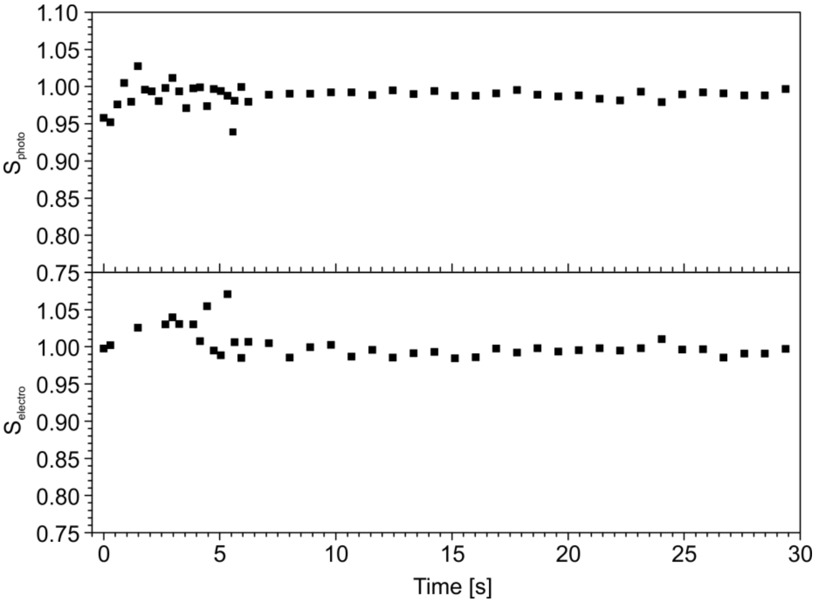

Figure S4: Selectivity as function of time during the time-resolved photochemical conversion and electrochemical reconversion on HOPG.

5. Time-resolved Electrochemically Triggered Reconversion

In order to exclude the effect of the Ohmic (iR) drop in the time-resolved measurements of the electrochemically triggered reconversion, we repeated the measurements with an increased thickness of the thin layer by using a 25 μm spacer. Note that in PEC-IRRAS experiments the layer thicknesses are typically in the low μm range.[2] Figure S5 shows a plot of corresponding currents and the band intensities of v(CN) modes during the time-resolved experiment for 3 repetitive cycles. The band intensities develop analogically to the measurements without spacer (see Figure 3e) and the current shows a nearly ideal exponential decay. From that observations we conclude that the development of the band intensity does not result from the iR drop.

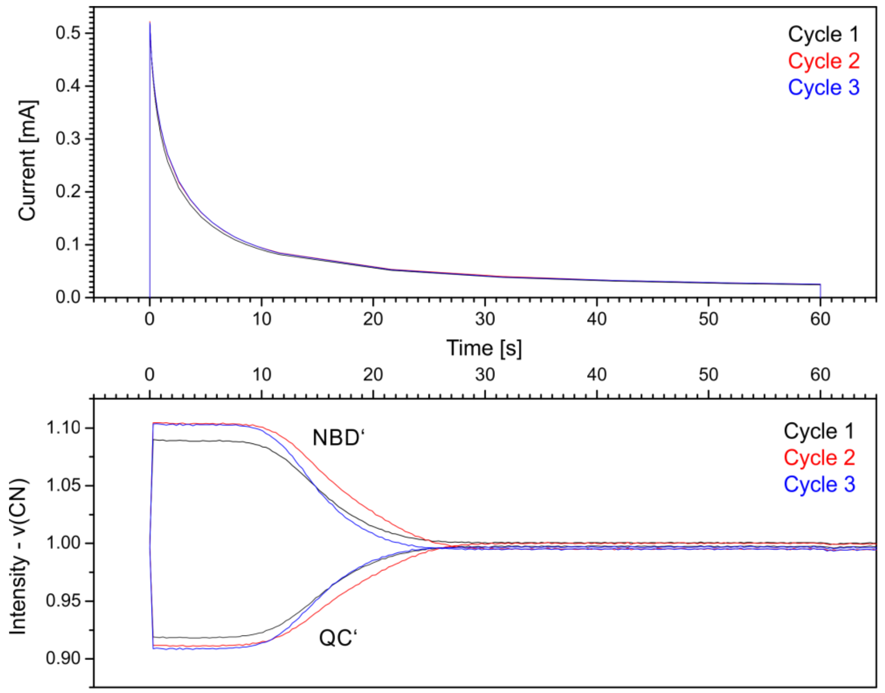

Figure S5: Comparison of the currents and the ν(CN) band intensities of NBD' and QC' during the repeating electrochemically triggered reconversion at 0.42 V_{fc} using a spacer of 25 μm.

6. Single Channel Spectra during the Cycling Experiment on HOPG

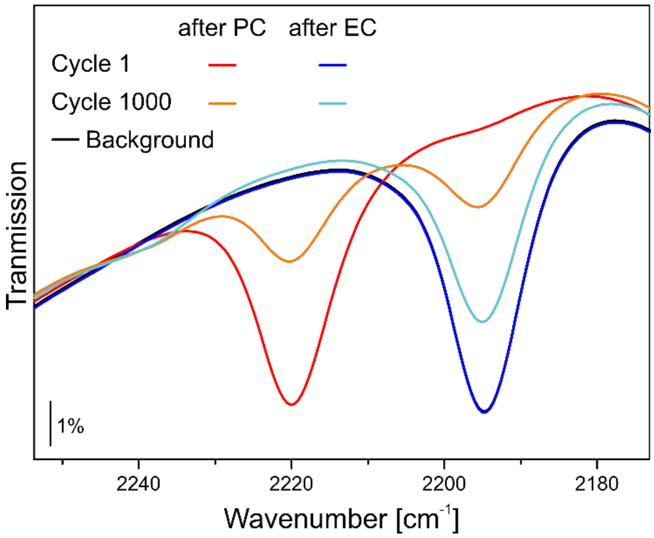

Figure S6: Comparison of the single channel spectra after photochemical conversion (PC) and electrochemical conversion (EC) of the first and last cycle during the reversibility testing of 1000 in-situ energy storage and release cycles on HOPG.

Figure S6 shows the single channel spectra of the first and 1000th cycle after the photo- and electrochemical conversion. While during the first cycle only features of NBD' (2195 cm^{-1}) and QC' (2220 cm^{-1}) are observed an additional band at 2237 cm^{-1} appears in the spectra of the 1000th cycle.

7. Electrochemical stability of NBD'

We address the origin of this additional species by following experiment. We recorded spectra of a 10 mM NBD' solution in DCM after switching the potential between -0.88 V_{fc} and 0.42 V_{fc} in repeated cycles. In analogy to the reversibility test in Figure 3, spectra were recorded with an acquisition time of one minute at -0.88 V_{fc} followed by a potential jump to 0.42 V_{fc} for 30 s. This procedure was repeated for 200 times. Selected spectra are presented in Figure S7. The spectra with irradiation show a negative band at 2237 cm^{-1} and a positive band at 2195 cm^{-1}, which we attribute to the formation of a decomposition product and the consumption of NBD', respectively. In contrast, the spectra in the experiment without irradiation hardly change (we assign the small negative band at 2195 cm^{-1} to minor changes of the thin layer). From these observations, we conclude that the decomposition takes place, either during photochemical conversion or during electrochemically triggered conversion with QC as reactant.

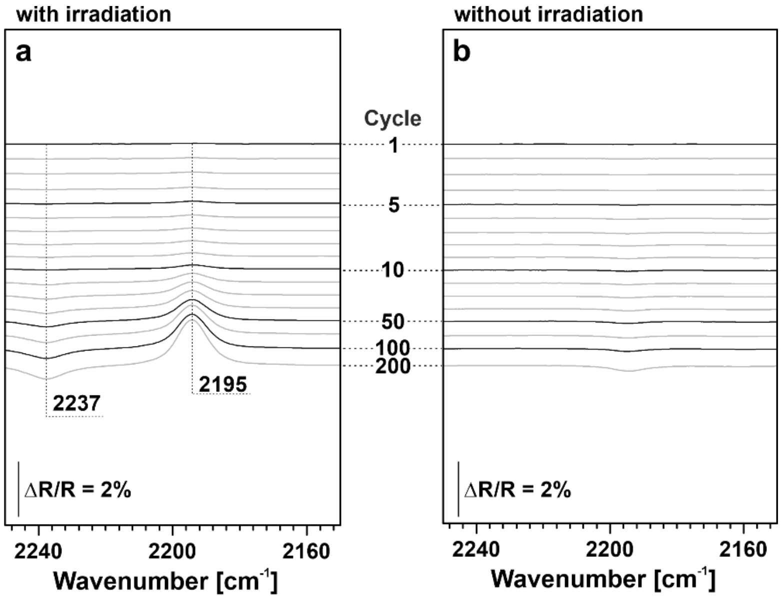

Figure S7: Comparison of selected difference spectra of NBD' after potential switching from -0.88 to 0.42 V_{fc} and back (a) during the reversibility test including an irradiation step and (b) without additional irradiation step. All spectra were recorded at -0.88 V_{fc}.

References:

1. F. Waidhas, M. Jevric, L. Fromm, M. Bertram, A. Görling, K. Moth-Poulsen, O. Brummel and J. Libuda, *Nano Energy*, 2019, **63**, 103872.
2. 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.