Tunable Photoswitching in Norbornadiene (NBD)/Quadricyclane (QC) – Fullerene Hybrids

Patrick Lorenz, Florian Wullschläger, Antonia Rüter, Bernd Meyer, and Andreas Hirsch*
Contents
Syntheses ......................................................................................................................... 2
Compound 4 ..................................................................................................................... 3
NBD acid 5 ....................................................................................................................... 4
Compound 6 ..................................................................................................................... 4
Compound 7 ..................................................................................................................... 4
NBD 8 ................................................................................................................................. 5
NBD 9 ................................................................................................................................. 5
QC 8 ..................................................................................................................................... 6
QC 9 ..................................................................................................................................... 6
Photoisomerization of NBD-C_{60} 1-3 to QC-C_{60} 1-3 with 310 nm UV-LED ............ 7
Photoisomerization of QC-C_{60} 1-3 to NBD-C_{60} 1-3 with 400 nm UV-LED .......... 15
Irradiation of NBD-C_{60} 1-3 with the 400 nm UV-LED ..................................................... 22
Effect of the different isomers ......................................................................................... 28
Spectra ............................................................................................................................... 31
Additional histograms ....................................................................................................... 44
Frontier molecular orbitals ............................................................................................. 46
   QC-C_{60} 1 ....................................................................................................................... 47
   QC-C_{60} 2 ....................................................................................................................... 51
   QC-C_{60} 3 ....................................................................................................................... 54
References ......................................................................................................................... 61
Syntheses

Scheme S1: Synthesis of \textit{NBD-C}_{60} 1-3. The synthesis of \textit{NBD-C}_{60} 1 is reported in our earlier publication.\textsuperscript{[1]}
Scheme S2: Synthesis of NBD 9 as well as the photoisomerization of NBD 8 and NBD 9 to QC 8 and QC 9, respectively. The synthesis as well as the spectroscopic data of NBD 8 has already been reported in our earlier publications.[2]

**Compound 4**

The synthesis of compound 4 was adapted from the literature.[3] C$_{60}$ (150 mg, 1.00 eq., 2.08 x 10$^{-4}$ mol) was dissolved in toluene (75 mL) under inert atmosphere. Afterwards, 4-hydroxybenzaldehyde (286 mg, 11.3 eq., 2.34 x 10$^{-3}$ mol) and sarcosine (94.0 mg, 5.07 eq., 1.06 x 10$^{-3}$ mol) were added and the solution was heated to reflux for 19 hours. After cooling, the reaction mixture was concentrated and purified by column chromatography (SiO$_2$, toluene/ethyl acetate, 95/5, v:v). After the solvent was removed, the product was dried in vacuo. Compound 4 was obtained as a dark brown solid.

**Yield** 73 mg, 8.39 x 10$^{-5}$ mol, 40%

**M.p.** /, thermal decomposition (TLC analysis of the left-over material after heating compound 4 to 360 °C indicated decomposition).

**MS** (MALDI-TOF, DCTB) [M–H]$^-$ m/z = 868.1070.
NBD acid 5

NBD acid 5 was prepared according to the procedure reported in our earlier publication. All spectroscopic data were in agreement with those previously published.

M.p. 133.1-135.4 °C.

Compound 6

4-Ethynylbenzaldehyde (210 mg, 1.00 eq., 1.61 \times 10^{-3} \text{ mol}), 4-iodophenethyl alcohol (440 mg, 1.10 eq., 1.77 \times 10^{-3} \text{ mol}) and Cul (12.3 mg, 0.0400 eq., 6.44 \times 10^{-5} \text{ mol}) were dissolved in degassed THF (20 mL) under inert atmosphere. Successively, TEA (334 μL, 1.50 eq., 2.42 \times 10^{-3} \text{ mol}) and Pd(PPh_3)_2Cl_2 (23.0 mg, 0.0200 eq., 3.22 \times 10^{-5} \text{ mol}) were added and the reaction was stirred at room temperature for 21 h. After this time CH_2Cl_2 (50 mL) was added and the organic phase was washed with water (3 \times 50 mL). After removal of the solvent the crude product was purified by multiple column chromatography (first column: SiO_2, hexanes/ethyl acetate, 7/3, v:v; second column: SiO_2, CH_2Cl_2/ethyl acetate, 8/2, v:v).

Yield 176 mg, 7.04 \times 10^{-4} \text{ mol, 44%}.

M.p. 231.2-235.1 °C.

^1H NMR (400 MHz, CD_2Cl_2) δ = 10.00 (s, 1H), 7.88-7.85 (m, 2H), 7.70-7.67 (m, 2H), 7.52-7.50 (m, 2H), 7.28-7.26 (m, 2H), 3.87-3.83 (m, 2H), 2.88 (t, J = 6.5 Hz, 2H), 1.51 (bs, 1H) ppm.

^13C NMR (101 MHz, CDCl_3) δ = 191.7, 140.1, 135.6, 132.3, 132.2, 130.0, 129.8, 129.5, 120.9, 93.7, 88.6, 63.6, 39.4 ppm.

HRMS (APPI, CH_2Cl_2) [M]^+ m/z = 250.0988 (calcd.), 250.0984 (found).

Compound 7

C_{60} (380 mg, 1.50 eq., 5.27 \times 10^{-4} \text{ mol}) was dissolved in toluene (200 mL) under inert atmosphere. Afterwards, compound 6 (88.0 mg, 1.00 eq., 3.52 \times 10^{-4} \text{ mol}) and sarcosine (313 mg, 10.0 eq., 3.51 \times 10^{-3} \text{ mol}) were added and the solution was heated to reflux overnight. After cooling, the reaction mixture was concentrated and purified by column chromatography (SiO_2, toluene/ethyl acetate, 8/2, v:v). The solvent was
removed, and the product obtained as a brown powder after precipitation from CS$_2$
with *n*-pentane.

**Yield** 205 mg, $2.05 \times 10^{-4}$ mol, 58%.

**$^1$H NMR** (600 MHz, CD$_2$Cl$_2$) $\delta = 7.84$ (bs, 2H), 7.62-7.61 (m, 2H), 7.48-7.43 (m, 2H), 7.22-7.19 (m, 2H), 5.08 (bs, 2H), 4.34 (bs, 1H), 3.87 (bs, 2H), 2.89-2.87 (m, 5H), 1.37 (bs, 1H) ppm.

**$^{13}$C NMR** (151 MHz, CDCl$_3$) $\delta =$ 147.5, 146.6, 146.5, 146.4, 146.3, 146.1, 146.0, 145.9, 145.8, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.1, 144.9, 144.7, 144.5, 144.4, 143.3, 143.2, 142.9, 142.8, 142.7, 142.4, 142.3, 142.2, 142.1, 141.8, 141.7, 140.4, 140.3, 140.1, 139.8, 139.3, 136.0, 135.8, 132.2, 132.0, 130.0, 129.6, 129.3, 121.3, 90.3, 89.0, 83.5, 71.9, 68.9, 63.6, 40.2, 39.3 ppm.

**HRMS** (MALDI-TOF, DCTB) [M]$^-$ m/z = 997.1467 (calcd.), 997.1461 (found).

**NBD 8**
The synthesis of **NBD 8** as well as its spectroscopic data has already been reported in our previous publications.$^{[1,2]}$

**M.p.** <35 °C (31.0-33.0 °C).

**NBD 9**
NBD acid 5 (133 mg, 1.00 eq., $6.27 \times 10^{-4}$ mol), 4-isopropylphenol (171 mg, 2.00 eq., $1.26 \times 10^{-3}$ mol) and DCC (130 mg, 1.00 eq., $6.27 \times 10^{-4}$ mol) were dissolved in CH$_2$Cl$_2$ (25 mL) under inert atmosphere. DMAP (7.7 mg, 0.10 eq., $6.3 \times 10^{-5}$ mol) was added and the reaction was stirred at room temperature for two days. After that time the solvent was removed and the crude product was purified by flash column chromatography (SiO$_2$, hexanes/ethyl acetate, 9/1 $\to$ 8/2, v:v).

**Yield** 144 mg, $4.36 \times 10^{-4}$ mol, 70%.

**M.p.** 74.1-76.8 °C.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta =$ 7.62-7.60 (m, 2H), 7.38-7.29 (m, 3H), 7.21-7.17 (m, 2H), 7.08-7.06 (m, 1H), 7.00-6.97 (m, 3H), 4.24-4.21 (m, 1H), 3.95-3.93 (m, 1H), 2.89
(hept, $J = 7.0$ Hz, 1H), 2.37-2.35 (m, 1H), 2.16-2.13 (m, 1H), 1.22 (d, $J = 6.9$ Hz, 6H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 169.4$, 164.1, 148.8, 146.2, 144.0, 140.9, 138.5, 135.6, 129.0, 128.1, 127.9, 127.3, 121.5, 70.7, 59.0, 53.3, 33.8, 24.2 ppm.

HRMS (ESI, acetonitrile) [M+H]$^+$ m/z = 331.1693 (calcd.), 331.1699 (found).

QC 8
The synthesis of QC 8 as well as its spectroscopic data has already been reported in our previous publications.$^{[1,2]}$

M.p. 90.6-93.0 °C (derived from the DSC measurement in our earlier publication.$^{[2b]}$).

QC 9
For the preparation of QC 9, an NMR tube was charged with NBD 9 (15.0 mg) dissolved in CDCl$_3$ (1.00 mL) and irradiated with a 310 nm UV-LED in a custom-made set-up. The reaction progress was monitored by $^1$H NMR spectroscopy, after 4 h of irradiation the conversion of NBD 9 to QC 9 was complete. After removal of the solvent QC 9 remains as a highly viscous oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.35-7.32$ (m, 2H), 7.28-7.24 (m, 2H), 7.19-7.12 (m, 3H), 6.89-6.85 (m, 2H), 2.91-2.82 (m, 1H), 2.80-2.78 (m, 1H), 2.69-2.67 (m, 1H), 2.51-2.47 (m, 1H), 2.34-2.32 (m, 1H), 2.24-2.21 (m, 1H), 1.80-1.79 (m, 1H), 1.20 (d, $J = 6.9$ Hz, 6H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 170.6$, 148.6, 146.0, 136.8, 128.8, 127.9, 127.2, 126.3, 121.3, 38.3, 33.7, 33.1, 32.5, 32.0, 31.8, 30.7, 24.2, 21.3 ppm.
Photoisomerization of \textbf{NBD-C}_{60} 1-3 to \textbf{QC-C}_{60} 1-3\textbf{ with 310 nm UV-LED

To study the photoisomerization of \textbf{NBD-C}_{60} 1-3 to \textbf{QC-C}_{60} 1-3} 1.0 mL of a 1.5 mmol/L solution of the respective NBD – fullerene hybrid was prepared in thoroughly (freeze-pump-thaw) degassed CDCl$_3$. The so prepared solution was transferred to an NMR tube under argon atmosphere in the glovebox. The NMR tube was sealed, removed from the glovebox, and irradiated with a 310 nm UV-LED in a custom-made set-up. Every 30 min the irradiation was paused and an $^1$H NMR was measured. For all three molecules (\textbf{NBD-C}_{60} 1-3) a vanishing of the olefinic proton signals of the NBD moiety was observed. This was accompanied by the rise of new signals in the aliphatic region, corresponding to the formed QC moiety. From the integral ratio of the NBD/QC signals, the amount of formed QC was estimated (Table S1-S3). At approximately 97 \% conversion to the corresponding QC derivative, the remaining NBD signals were below the NMR detection limit and full conversion was assumed. No side-products were detected in any of the conducted experiments. In order to ensure reliable data, each derivative was tested in two independent experiments.
**NBD-C\textsubscript{60} 1 to QC-C\textsubscript{60} 1**

\[ \text{Scheme S3: Photoisomerization of NBD-C}\textsubscript{60} 1 \text{ to QC-C}\textsubscript{60} 1. } \]

\[ \text{Table S1: Results of the photoisomerization of NBD-C}\textsubscript{60} 1 \text{ to QC-C}\textsubscript{60} 1. } \]

| Irradiation time [min] | 1\textsuperscript{st} experiment | 2\textsuperscript{nd} experiment | Average QC [%] | standard deviation |
|------------------------|-------------------------------|---------------------------------|----------------|-------------------|
| 0                      | 0                             | 0                               | 0              | 0                 |
| 30                     | 39                            | 38                              | 38,5           | 0,5               |
| 60                     | 59                            | 61                              | 60             | 1                 |
| 90                     | 76                            | 75                              | 75,5           | 0,5               |
| 120                    | 83                            | 83                              | 83             | 0                 |
| 150                    | 88                            | 88                              | 88             | 0                 |
| 180                    | 91                            | 91                              | 91             | 0                 |
| 210                    | 92                            | 93                              | 92,5           | 0,5               |
| 240                    | 94                            | 94                              | 94             | 0                 |
| 270                    | 95                            | 95                              | 95             | 0                 |
| 300                    | 97                            | 97                              | 97             | 0                 |

In the following, the \(^1\text{H} \text{NMR spectra obtained during the irradiation of NBD-C}\textsubscript{60} 1 \text{ with the 310 nm UV-LED are depicted. Two different regions are highlighted by the colored boxes. The blue box indicates the region where the signals corresponding to the olefinic protons of the NBD moiety can be found. With increasing irradiation time, the at first pronounced signal diminishes until it can no longer be observed. The red box indicates the region where the signals corresponding to the six aliphatic protons of the QC framework are to be expected. At the start of the irradiation (blue spectrum at the bottom) only the signal corresponding to the bridgehead protons of the NBD moiety can be observed in this region. With increasing irradiation time these signals diminish, and six new signals arise which can be assigned to the aliphatic protons of the formed QC. This nicely demonstrates the photoisomerization of NBD-C\textsubscript{60} 1 \text{ to QC-C}\textsubscript{60} 1 \text{ upon irradiation with the 310 nm UV-LED.}
Figure S1: $^1$H NMR spectra of the photoisomerization of NBD-$C_{60}$ 1 (blue spectrum at the bottom) to QC-$C_{60}$ 1 (red spectrum at the top); first experiment.

Figure S2: $^1$H NMR spectra of the photoisomerization of NBD-$C_{60}$ 1 (blue spectrum at the bottom) to QC-$C_{60}$ 1 (red spectrum at the top); second experiment.
NBD-C$_{60}$ 2 to QC-C$_{60}$ 2

Scheme S4: Photoisomerization of NBD-C$_{60}$ 2 to QC-C$_{60}$ 2.

Table S2: Results of the photoisomerization of NBD-C$_{60}$ 2 to QC-C$_{60}$ 2.

| Irradiation time [min] | 1st experiment | 2nd experiment | Average QC [%] | Standard deviation |
|------------------------|----------------|----------------|----------------|--------------------|
| 0                      | 0              | 0              | 0              | 0                  |
| 30                     | 42             | 43             | 42,5           | 0,5                |
| 60                     | 65             | 67             | 66             | 1                  |
| 90                     | 79             | 80             | 79,5           | 0,5                |
| 120                    | 88             | 87             | 87,5           | 0,5                |
| 150                    | 93             | 92             | 92,5           | 0,5                |
| 180                    | 94             | 94             | 94             | 0                  |
| 210                    | 96             | 96             | 96             | 0                  |
| 240                    | 97             | 97             | 97             | 0                  |
| 270                    | /              | 97             | 97             | 0                  |
| 300                    | /              | 97             | 97             | 0                  |

In the following, the $^1$H NMR spectra obtained during the irradiation of NBD-C$_{60}$ 2 with the 310 nm UV-LED are depicted. Two different regions are highlighted by the colored boxes. The blue box indicates the region where the signals corresponding to the olefinic protons of the NBD moiety can be found. With increasing irradiation time, the at first pronounced signal diminishes until it can no longer be observed. The red box indicates the region where the signals corresponding to the six aliphatic protons of the QC framework are to be expected. At the start of the irradiation (blue spectrum at the bottom) the signal corresponding to the bridgehead protons of the NBD moiety and the signal of the N-CH$_3$ group can be observed in this region. With increasing irradiation time these signals diminish, and six new signals arise which can be assigned to the aliphatic protons of the formed QC, the signal corresponding to the N-CH$_3$ group is
slightly shifted upfield. This nicely demonstrates the photoisomerization of $\text{NBD-C}_6\text{O}_2$ to $\text{QC-C}_6\text{O}_2$ upon irradiation with the 310 nm UV-LED.

Figure S3: $^1$H NMR spectra of the photoisomerization of $\text{NBD-C}_6\text{O}_2$ (blue spectrum at the bottom) to $\text{QC-C}_6\text{O}_2$ (red spectrum at the top); first experiment.
Figure S4: $^1$H NMR spectra of the photoisomerization of $\text{NBD-C}_{60}$ 2 (blue spectrum at the bottom) to $\text{QC-C}_{60}$ 2 (red spectrum at the top); second experiment.
Scheme S5: Photoisomerization of NBD-C₆₀ 3 to QC-C₆₀ 3.

Table S3: Results of the photoisomerization of NBD-C₆₀ 3 to QC-C₆₀ 3.

| Irradiation time [min] | 1st experiment | 2nd experiment | Average QC [%] | standard deviation |
|------------------------|----------------|----------------|----------------|--------------------|
| 0                      | 0              | 0              | 0              | 0                  |
| 30                     | 33             | 30             | 31,5           | 1,5                |
| 60                     | 55             | 53             | 54             | 1                  |
| 90                     | 71             | 68             | 69,5           | 1,5                |
| 120                    | 79             | 78             | 78,5           | 0,5                |
| 150                    | 85             | 85             | 85             | 0                  |
| 180                    | 90             | 88             | 89             | 1                  |
| 210                    | 93             | 92             | 92,5           | 0,5                |
| 240                    | 97             | 95             | 96             | 1                  |
| 270                    | 97             | 97             | 97             | 0                  |
| 300                    | 97             | 97             | 97             | 0                  |

In the following, the ¹H NMR spectra obtained during the irradiation of NBD-C₆₀ 3 with the 310 nm UV-LED are depicted. Two different regions are highlighted by the colored boxes. The blue box indicates the region where the signals corresponding to the olefinic protons of the NBD moiety can be found. With increasing irradiation time, the at first pronounced signal diminishes until it can no longer be observed. The red box indicates the region where the signals corresponding to the six aliphatic protons of the QC framework are to be expected. At the start of the irradiation (blue spectrum at the bottom) only the signal corresponding to the bridgehead protons of the NBD moiety can be observed in this region. With increasing irradiation time these signals diminish, and six new signals arise which can be assigned to the aliphatic protons of the formed QC. This nicely demonstrates the photoisomerization of NBD-C₆₀ 3 to QC-C₆₀ 3 upon irradiation with the 310 nm UV-LED.
Figure S5: $^1$H NMR spectra of the photoisomerization of NBD-$C_{60}$ 3 (blue spectrum at the bottom) to QC-$C_{60}$ 3 (red spectrum at the top); first experiment.

Figure S6: $^1$H NMR spectra of the photoisomerization of NBD-$C_{60}$ 3 (blue spectrum at the bottom) to QC-$C_{60}$ 3 (red spectrum at the top); second experiment.
Photoisomerization of **QC-C₆₀ 1-3** to **NBD-C₆₀ 1-3** with 400 nm UV-LED

After the successful conversion of **NBD-C₆₀ 1-3** to **QC-C₆₀ 1-3** (see previous chapter) the backreaction should be studied. For this purpose, the NMR tubes with the QC derivatives (**QC-C₆₀ 1-3**; \( V = 1.0 \) mL; \( c = 1.5 \text{ mmol/L} \)) from the previous experiments, were irradiated with a 400 nm UV-LED in a custom-made set-up. The reaction progress was monitored over a timespan of five hours.

**QC-C₆₀ 1 to NBD-C₆₀ 1**

![Chemical Structures](image)

*Scheme S6: Photoisomerization of QC-C₆₀ 1 towards NBD-C₆₀ 1.*

**Table S4: Results of the photoisomerization of QC-C₆₀ 1 towards NBD-C₆₀ 1.**

| Irradiation time [min] | 1st experiment | 2nd experiment | Average QC [%] | standard deviation |
|------------------------|----------------|----------------|----------------|-------------------|
| 0                      | 100            | 100            | 100            | 0                 |
| 30                     | 87             | 85             | 86             | 1                 |
| 60                     | 79             | 78             | 78,5           | 0,5               |
| 90                     | 70             | 68             | 69             | 1                 |
| 120                    | 66             | 63             | 64,5           | 1,5               |
| 150                    | 59             | 57             | 58             | 1                 |
| 180                    | 53             | 53             | 53             | 0                 |
| 210                    | 47             | 46             | 46,5           | 0,5               |
| 240                    | 41             | 42             | 41,5           | 0,5               |
| 270                    | 36             | 36             | 36             | 0                 |
| 300                    | 33             | 33             | 33             | 0                 |

In the following, the \(^1\text{H}\) NMR spectra obtained during the irradiation of **QC-C₆₀ 1** with the 400 nm UV-LED are depicted. Two different regions are highlighted by the colored boxes. The blue box indicates the region where the signals corresponding to the olefinic protons of the NBD moiety are expected, upon irradiation the corresponding signals arise. The red box indicates the region where the signals corresponding to the six aliphatic protons of the QC framework can be found. At the start of the irradiation (red spectrum at the bottom) six pronounced signals can be observed in this region.
With increasing irradiation time these signals diminish, however, even after an irradiation time of 300 min they can still be detected. This nicely demonstrates the partial photoisomerization of QC-C₆₀ 1 to NBD-C₆₀ 1 upon irradiation with the 400 nm UV-LED.

**Figure S7**: ¹H NMR spectra of the photoisomerization of QC-C₆₀ 1 (red spectrum at the bottom) towards NBD-C₆₀ 1. After 5 h of irradiation the NBD/QC ratio was 67/33; first experiment.
Figure S8: $^1$H NMR spectra of the photoisomerization of QC-C$_{60}$ 1 (red spectrum at the bottom) towards NBD-C$_{60}$ 1. After 5 h of irradiation the NBD/QC ratio was 67/33; second experiment.
**QC-\textsubscript{C\textsubscript{60}} 2 to NBD-\textsubscript{C\textsubscript{60}} 2**

![Scheme S7: Photoisomerization of QC-\textsubscript{C\textsubscript{60}} 2 towards NBD-\textsubscript{C\textsubscript{60}} 2.](image)

**Table S5: Results of the photoisomerization of QC-\textsubscript{C\textsubscript{60}} 2 towards NBD-\textsubscript{C\textsubscript{60}} 2.**

| Irradiation time [min] | 1\textsuperscript{st} experiment | 2\textsuperscript{nd} experiment | Average QC [%] | standard deviation |
|------------------------|----------------------------------|----------------------------------|---------------|-------------------|
| 0                      | 100                              | 100                              | 100           | 0                 |
| 30                     | 94                               | 95                               | 94,5          | 0,5               |
| 60                     | 93                               | 93                               | 93            | 0                 |
| 90                     | /                                | 92                               | /             | /                 |
| 120                    | 89                               | 90                               | 89,5          | 0,5               |
| 150                    | /                                | 88                               | /             | /                 |
| 180                    | 86                               | 87                               | 86,5          | 0,5               |
| 210                    | /                                | 84                               | /             | /                 |
| 240                    | 83                               | 83                               | 83            | 0                 |
| 270                    | /                                | 81                               | /             | /                 |
| 300                    | 78                               | 80                               | 79            | 1                 |

In the following, the \textsuperscript{1}H NMR spectra obtained during the irradiation of QC-\textsubscript{C\textsubscript{60}} 2 with the 400 nm UV-LED are depicted. Two different regions are highlighted by the colored boxes. The blue box indicates the region where the signals corresponding to the olefinic protons of the NBD moiety are expected, upon prolonged irradiation the corresponding signals arise slowly. The red box indicates the region where the signals corresponding to the six aliphatic protons of the QC framework and the signal corresponding to the N-CH\textsubscript{3} group can be found. At the start of the irradiation (red spectrum at the bottom) pronounced signals are observed. With increasing irradiation time these signals diminish, however, even after an irradiation time of 300 min they can still be detected. This nicely demonstrates the partial photoisomerization of QC-\textsubscript{C\textsubscript{60}} 2 to NBD-\textsubscript{C\textsubscript{60}} 2 upon irradiation with the 400 nm UV-LED.
Figure S9: $^1$H NMR spectra of the photoisomerization of QC-$C_{60}$ 2 (red spectrum at the bottom) towards NBD-$C_{60}$ 2. After 5 h of irradiation the NBD/QC ratio was 22/78; first experiment.

Figure S10: $^1$H NMR spectra of the photoisomerization of QC-$C_{60}$ 2 (red spectrum at the bottom) towards NBD-$C_{60}$ 2. After 5 h of irradiation the NBD/QC ratio was 20/80; second experiment.
Table S6: Results of the photoisomerization of QC-C\textsubscript{60} 3 towards NBD-C\textsubscript{60} 3.

| Irradiation time [min] | 1\textsuperscript{st} experiment | 2\textsuperscript{nd} experiment | Average QC [%] | standard deviation |
|------------------------|------------------------------------|-----------------------------------|----------------|--------------------|
| 0                      | 100                                | 100                               | 100            | 0                  |
| 30                     | 97                                 | 97                                | 97             | 0                  |
| 60                     | 96                                 | 95                                | 95,5           | 0,5                |
| 90                     | /                                  | 93                                | /              | /                  |
| 120                    | 97                                 | 93                                | 95             | 2                  |
| 150                    | /                                  | 93                                | /              | /                  |
| 180                    | 93                                 | 92                                | 92,5           | 0,5                |
| 210                    | /                                  | 91                                | /              | /                  |
| 240                    | 93                                 | 86                                | 89,5           | 3,5                |
| 270                    | /                                  | 85                                | /              | /                  |
| 300                    | 91                                 | 84                                | 87,5           | 3,5                |

In the following, the \textsuperscript{1}H NMR spectra obtained during the irradiation of QC-C\textsubscript{60} 3 with the 400 nm UV-LED are depicted. Two different regions are highlighted by the colored boxes. The blue box indicates the region where the signals corresponding to the olefinic protons of the NBD moiety are expected, upon prolonged irradiation the corresponding signals arise slowly. The red box indicates the region where the signals corresponding to the six aliphatic protons of the QC framework can be found. At the start of the irradiation (red spectrum at the bottom) six pronounced signals can be observed in this region. With increasing irradiation time these signals diminish slightly, however, even after an irradiation time of 300 min they can still be detected. This nicely demonstrates the partial and very slow photoisomerization of QC-C\textsubscript{60} 3 to NBD-C\textsubscript{60} 3 upon irradiation with the 400 nm UV-LED.
Figure S11: $^1$H NMR spectra of the photoisomerization of QC-C$_{60}$ 3 (red spectrum at the bottom) towards NBD-C$_{60}$ 3. After 5 h of irradiation the NBD/QC ratio was 9/91; first experiment.

Figure S12: $^1$H NMR spectra of the photoisomerization of QC-C$_{60}$ 3 (red spectrum at the bottom) towards NBD-C$_{60}$ 3. After 5 h of irradiation the NBD/QC ratio was 16/84; second experiment.
Irradiation of NBD-C_{60} 1-3 with the 400 nm UV-LED

As a control experiment NBD-C_{60} 1-3 were irradiated with the 400 nm UV-LED under the same experimental conditions as were used in the two previous experiments. Therefore, 1.0 mL of a 1.5 mmol/L solution of the respective NBD – fullerene hybrids (NBD-C_{60} 1-3) was prepared in thoroughly (freeze-pump-thaw) degassed CDCl₃. The so prepared solution was transferred to an NMR tube under argon atmosphere in the glovebox. The NMR tube was sealed, removed from the glovebox, and irradiated with the 400 nm UV-LED in a custom-made set-up. The reaction progress was monitored by $^1$H NMR spectroscopy.

NBD-C_{60} 1 irradiated with the 400 nm UV-LED

Scheme S9: Irradiation of NBD-C_{60} 1 with the 400 nm UV-LED, no reaction was observed over a timespan of five hours.

Figure S13: $^1$H NMR spectra of the irradiation of NBD-C_{60} 1 (blue spectrum at the bottom) using the 400 nm UV-LED. No reaction was observed over a timespan of five hours.
NBD-C$_{60}$ 3 irradiated with the 400 nm UV-LED

Scheme S10: Irradiation of NBD-C$_{60}$ 3 with the 400 nm UV-LED, no formation of QC-C$_{60}$ 3 was observed over a timespan of five hours.

Figure S14: $^1$H NMR spectra of the irradiation of NBD-C$_{60}$ 3 (blue spectrum at the bottom) using the 400 nm UV-LED. No formation of QC-C$_{60}$ 3 was observed over a timespan of five hours, however, minor signs of degradation were observed.
Scheme S11: Photoisomerization of \textit{NBD-C}_60 \textit{2} towards \textit{QC-C}_60 \textit{2} by irradiation with the 400 nm UV-LED

Table S7: Results of the photoisomerization of \textit{NBD-C}_60 \textit{2} towards \textit{QC-C}_60 \textit{2} using the 400 nm UV-LED.

| Irradiation time [min] | QC [%] |
|------------------------|--------|
| 0                      | 0      |
| 60                     | 3      |
| 120                    | 9      |
| 180                    | 10     |
| 240                    | 14     |
| 300                    | 15     |
| 600                    | 23     |
Figure S15: $^1$H NMR spectra of the photoisomerization of NBD-C$_{60}$ 2 (blue spectrum at the bottom) towards QC-C$_{60}$ 2 using the 400 nm UV-LED. After 5 h of irradiation the NBD/QC ratio was 85/15, and after 10 h the NBD/QC ratio was 77/23.

As evident from Table S7 as well as Figure S15 slow isomerization of NBD-C$_{60}$ 2 towards QC-C$_{60}$ 2 can be observed during irradiation with the 400 nm UV-LED. In contrast, no formation of QC-C$_{60}$ 1 and QC-C$_{60}$ 3 was observed in the respective experiments. This can be explained by taking a closer look at the NBD moieties incorporated in the NBD fullerene hybrids (Figure S16). As highlighted by the different color coding two different push-pull substituted NBD moieties are incorporated in the NBD fullerene hybrids NBD-C$_{60}$ 1-3. Whereas NBD-C$_{60}$ 1 and NBD-C$_{60}$ 3 feature the same system, namely an NBD carrying a phenyl ring as an EDG and an ethyl ester as the EWG (see Figure S17, top-left). In contrast, the push-pull NBD incorporated in NBD-C$_{60}$ 2 has a para-substituted phenyl ester instead of the ethyl ester as the EWG (see Figure S17, bottom-left).

Figure S16: NBD fullerene hybrids NBD-C$_{60}$ 1 (left), NBD-C$_{60}$ 2 (middle), and NBD-C$_{60}$ 3 (right); the incorporated push-pull substituted NBD moieties are encircled.
To verify our hypothesis that the different behavior of NBD-C\textsubscript{60} 1/3 compared to NBD-C\textsubscript{60} 2 during irradiation with the 400 nm UV-LED can be attributed to the different NBD moieties, we synthesized the two ‘isolated’ push-pull substituted NBDs and used them as a reference. Figure S17 depicts the structure as well as the UV/vis absorption spectra of these two model systems.

![Structure of NBD 8 and NBD 9](image)

\[ \lambda_{\text{onset}} = 359 \text{ nm} \]

\[ \lambda_{\text{onset}} = 370 \text{ nm} \]

**Figure S17: Structure of the two ‘isolated’ push-pull substituted NBDs NBD 8 and NBD 9 as well as their UV/vis absorption spectra.**

As evident, the small variation of the EWG has a significant influence on the UV/vis absorption, a red-shift of the absorption onset (\( \lambda_{\text{onset}} \)); defined as the wavelength where \( \log(\varepsilon) = 2 \)) from 359 nm (NBD 8) to 370 nm (NBD 9) is observed. This results in NBD 9 being isomerized by the 400 nm UV-LED as is shown in Table S8 and Figure S18.

![Photoisomerization Scheme](image)

**Scheme S12: Photoisomerization of NBD 9 to QC 9 by irradiation with the 400 nm UV-LED.**
To ensure good comparability to the previous experiments, an NMR tube was charged with 1.0 mL of a 1.5 mmol/L solution of **NBD 9** in CDCl₃ and irradiated with the 400 nm UV-LED in a custom-made set-up. The reaction was followed by $^1$H NMR spectroscopy.

**Table S8**: Results of the photoisomerization of **NBD 9** towards **QC 9** using the 400 nm UV-LED.

| Irradiation time [min] | QC [%] |
|------------------------|--------|
| 0                      | 0      |
| 30                     | 11     |
| 60                     | 17     |
| 90                     | 25     |
| 120                    | 32     |
| 150                    | 36     |
| 180                    | 41     |
| 210                    | 47     |
| 240                    | 50     |
| 270                    | 54     |
| 300                    | 56     |

Figure S18: $^1$H NMR spectra of the photoisomerization of **NBD 9** (blue spectrum at the bottom) towards **QC 9** using the 400 nm UV-LED. After 5 h of irradiation the NBD/QC ratio was 44/56.
Effect of the different isomers

Since racemic NBD-acid 5 was used for the syntheses of NBD-C\textsubscript{60} 1-3 the resulting NBD – fullerene hybrids as well as their corresponding QC derivatives were obtained as a mixture of different enantiomers (in the case of NBD-C\textsubscript{60} 1/QC-C\textsubscript{60} 1) or enantiomers/diastereomers (in the case of NBD-C\textsubscript{60} 2/QC-C\textsubscript{60} 2 and NBD-C\textsubscript{60} 3/QC-C\textsubscript{60} 3) – vide infra.

NBD/QC-C\textsubscript{60} 1

Scheme S13: NBD-C\textsubscript{60} 1 and therefore also QC-C\textsubscript{60} 1 consists of a racemic mixture of these two enantiomers.
Scheme S14: \textit{NBD-C}_60 2 and therefore also \textit{QC-C}_60 2 consists of a mixture of these four isomers.
Scheme S15: NBD-C$_{60}$ 3 and therefore also QC-C$_{60}$ 3 consists of a mixture of these four isomers.
Spectra

Compound 6

Figure S19: $^1$H NMR spectrum of compound 6 (400 MHz, CD$_2$Cl$_2$, rt). Residues of ethyl acetate are marked with a star.
Figure S20: $^{13}$C NMR spectrum of compound 6 (101 MHz, CDCl$_3$, rt).
Figure S21: $^1$H NMR spectrum of compound 7 (600 MHz, CDCl₃, rt). Residues of n-pentane are marked with a star.

Figure S22: $^{13}$C NMR spectrum of compound 7 (151 MHz, CDCl₃, rt). Residues of n-pentane and one unassignable signal are marked with a star.
Figure S23: $^1$H NMR spectrum of NBD 9 (400 MHz, CDCl$_3$, rt). Residues of CH$_2$Cl$_2$ are marked with a star.

Figure S24: $^{13}$C NMR spectrum of NBD 9 (101 MHz, CDCl$_3$, rt).
Figure S25: UV/vis absorption spectrum of **NBD 9** measured in ACN.
Figure S26: $^1$H NMR spectrum of **NBD-C$_{60}$ 2** (600 MHz, CDCl$_3$/CS$_2$, rt). Residues of n-pentane and grease are marked with a star. The signal splitting observed for the CH$_3$ group results from the different diastereomers.

Figure S27: DEPTQ-135 NMR spectrum of **NBD-C$_{60}$ 2** (151 MHz, CDCl$_3$/CS$_2$, rt). Residues of n-pentane are marked with a star. Signals phase up (CH, CH$_3$), signals phase down (CH$_2$, C).
Figure S28: UV/vis absorption spectrum of NBD-C$_{60}$ 2 measured in CH$_2$Cl$_2$. 
Figure S29: $^1$H NMR spectrum of NBD-$C_{60}$ 3 (600 MHz, CDCl$_3$, rt). Due to the greater distance between the stereocenters no signal splitting is observed.

Figure S30: DEPTQ-135 NMR spectrum of NBD-$C_{60}$ 3 (151 MHz, CDCl$_3$, rt). Signals phase up (CH, CH$_3$), signals phase down (CH$_2$, C).
Figure S31: UV/vis absorption spectrum of \textbf{NBD-C}_60 \textbf{3} measured in CH$_2$Cl$_2$.

\textbf{QC 9}

Figure S32: $^1$H NMR spectrum of \textbf{QC 9} (400 MHz, CDCl$_3$, rt).
Figure S33: $^{13}$C NMR spectrum of QC9 (101 MHz, CDCl$_3$, rt).

QC-C$_{60}$ 1

Figure S34: $^1$H NMR spectrum of QC-C$_{60}$ 1 (400 MHz, CDCl$_3$, rt). Residues of n-pentane are marked with a star.
Figure S35: $^1$H NMR spectrum of QC-C$_{60}$ 2 (600 MHz, CDCl$_3$, rt). Residues of n-pentane and grease are marked with a star. The signal splitting observed for the CH$_3$ group results from the different diastereomers, however it is not as pronounced as in the spectrum of NBD-C$_{60}$ 2.
Figure S36: DEPTQ-135 NMR spectrum of QC-C_{60} 2 (151 MHz, CDCl₃, rt). Signals phase up (CH, CH₃), signals phase down (CH₂, C). Due to the presence of the different diastereomers a splitting of some aliphatic signals can be observed. Small residues of grease are marked with a star.
Figure S37: $^1$H NMR spectrum of QC-C$_{60}$ 3 (600 MHz, CDCl$_3$, rt).

Figure S38: DEPTQ-135 NMR spectrum of QC-C$_{60}$ 3 (151 MHz, CDCl$_3$, rt). Signals phase up (CH, CH$_3$), signals phase down (CH$_2$, C).
Additional histograms

Figure S39. Histogram of the distance between the centers of mass of the NBD moiety and the fullerene for the three NBD–fullerene hybrids NBD-C_{60} 1-3, derived from the MD simulations. $R_{vdW}$ is calculated as the sum of the van der Waals radius of a C_{60} fullerene$^{4}$, the average distance of the carbon atoms of the NBD moiety from the NBD center of mass, and the van der Waals radius of a carbon atom$^{5}$. 

Figure S40. Histogram of the distance between the centers of mass of the QC moiety and the fullerene for the four QC-C$_{60}$ 3 enantiomers shown in Scheme S15, derived from MD simulations. $R_{vdW}$ is calculated as the sum of the van der Waals radius of a C$_{60}$ fullerene$^4$, the average distance of the carbon atoms of the QC moiety from the QC center of mass, and the van der Waals radius of a carbon atom$^5$. 
Frontier molecular orbitals

Molecular orbitals were calculated at the B3LYP/def2-TZVP level of theory and are visualized with an isovalue of 0.0128 au. Calculations were performed for all three QC-$C_{60}$ molecules in their relaxed geometry as well as for snapshots from the MD simulations, which are representative for frequently observed distances between the centers of mass of QC and $C_{60}$ (see Figure 2 in the manuscript).

For all structures, we observe that two more orbitals are close to the LUMO (within about 0.5 eV) and the HOMO is part of a dense set of states. To illustrate this, we show for all structures an energy level diagram and a set of 10 orbitals ranging from HOMO-6 to LUMO+2. With this set of states, we cover an energy range of about 0.5 eV below the HOMO to about 0.5 eV above the LUMO level.

The LUMO to LUMO+2 orbitals are always exclusively located at the $C_{60}$, which demonstrates the strong electron accepting property of the fullerene. For the HOMO to HOMO-6 levels, the picture is different. Many of these orbitals also show a strong localization on the fullerene. However, there are always two to three orbitals within the range of a few tenths of an eV of the HOMO with exclusive localization on the QC and the bridge of the molecule. The energetically order of these orbitals strongly fluctuates between the snapshot configurations from the MD simulations, which is not surprising since they represent thermally excited, non-equilibrium geometries. Nevertheless, even if the orbital localized at the QC unit is no longer the HOMO as in Figure 5 of the manuscript, its orbital energy remains close to the HOMO and is readily available for initializing the back-reaction from QC to NBD.
Figure S41. Energy level diagram of the molecular orbitals of QC-C_{60} 1 for the relaxed and two representative structures shown in Figure 2 of the manuscript. The red line indicates the mid-point between HOMO and LUMO.
Figure S42. Frontier molecular orbitals of the relaxed structure of QC-C₆₀ 1.
Figure S43. Frontier molecular orbitals of the QC-C$_{60}$ 1 structure with a distance of 7.4 Å between the QC moiety and the fullerene.
Figure S44. Frontier molecular orbitals of the QC-C$_{60}$ 1 structure with a distance of 9.3 Å between the QC moiety and the fullerene.
Figure S45. Energy level diagram of the molecular orbitals of QC-C$_{60}$ 2 for the relaxed and the representative structure shown in Figure 2 of the manuscript. The red line indicates the mid-point between HOMO and LUMO.
Figure S46. Frontier molecular orbitals of the relaxed QC-C₆₀ 2 structure.
Figure S47. Frontier molecular orbitals of the QC-C60 2 structure with a distance of 11.2 Å between the QC moiety and the fullerene.
Figure S48. Energy level diagram of the molecular orbitals of QC-C$_{60}$ 3 for the relaxed and five representative structures shown in Figure 2 of the manuscript. The red line indicates the mid-point between HOMO and LUMO.
Figure S49. Frontier molecular orbitals of the relaxed QC-C$_{60}$ 3 structure.
Figure S50. Frontier molecular orbitals of the QC-C₆₀ 3 structure with a distance of 8.5 Å between the QC moiety and the fullerene.
Figure S51. Frontier molecular orbitals of the QC-$C_{60}$ 3 structure with a distance of 11.5 Å between the QC moiety and the fullerene.
Figure S52. Frontier molecular orbitals of the QC-C\textsubscript{60} 3 structure with a distance of 14.6 Å between the QC moiety and the fullerene.
Figure S53. Frontier molecular orbitals of the QC-C₆₀ 3 structure with a distance of 17.1 Å between the QC moiety and the fullerene.
Figure S54. Frontier molecular orbitals of the QC-C₆₀ 3 structure with a distance of 20.6 Å between the QC moiety and the fullerene.
References

[1] P. Lorenz, A. Hirsch, Chem. Eur. J. 2020, 26, 5220–5230.

[2] a) P. Lorenz, T. Luchs, A. Hirsch, Chem. Eur. J. 2021, 27, 4993–5002; b) T. Luchs, P. Lorenz, A. Hirsch, ChemPhotoChem 2020, 4, 52–58;

[3] T. Cao, K. Chen, Q. Chen, Y. Zhou, N. Chen, Y. Li, ACS Appl. Mater. Interfaces 2019, 11, 33825–33834.

[4] M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, Science of fullerenes and carbon nanotubes; Acad. Press, San Diego, 1996.

[5] A. Bondi, J. Phys. Chem. 1964, 68, 441–451.