Norbornadiene-Quadricyclane Photoswitches with Enhanced Solar Spectrum Match

Adil S. Aslam, Lidiya M. Muhammad, Andreas Erbs Hillers-Bendtsen, Kurt V. Mikkelsen, and Kasper Moth-Poulsen*
Supplementary Information

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**General remarks**

All commercial chemicals were used as received. Toluene was dried on an MBraun MB SPS-800 solvent purification system. Column chromatography was performed on a Biotage Isolera One instrument using pre-packed silica columns (10 g, 25g, or 50g Biotage® SNAP Cartridge). Cyclopentadiene was distilled by cracking dicyclopentadiene over iron filings and stored at -80 °C. Purification of products was carried out by flash chromatography on silica gel (40–63 μm, 60 A). Thin layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Varian 400 MHz instrument, or $^1$H NMR (600 MHz) and $^{13}$C NMR (150 MHz) spectra were recorded on a Bruker 600 MHz instrument, using the residual solvent as the internal standard (CDCl$_3$, $^1$H = 7.26 ppm and $^{13}$C = 77.16 ppm, or CD$_2$CN, $^1$H = 1.94 ppm). All NMR experiments were acquired at 298 K unless specified. All chemical shifts are quoted on the δ scale (ppm), and all coupling constants (J) are expressed in Hz. All solution-based spectroscopic measurements were performed in a 1 cm path length cuvette on either a Cary 60 Bio or a Cary 100 UV–vis spectrophotometer, scanning the wavelength from 700 to 300 nm coupled with Peltier temperature control.
Experimental

Synthetic Scheme

A) 

NBD 4

\[ \text{PdCl}_2(\text{PPh}_3)_2, \text{Cul, TEA, THF, rt, 16 h, 24%} \]

NBD 3

\[ \text{PdCl}_2(\text{PPh}_3)_2, \text{Cul, TEA, THF, rt, 16 h, 33%} \]

NBD 1

Toluene, 100°C, 20 h, 24%

Toluene, 100°C, 20 h, 32%

B) 

NBD 2

\[ \text{P} \text{(OEt)}_3 \]

NBD 6

110°C, 5h, 25%

NBD 5

110°C, 5h, 29%

C) 

NBD 2

\[ \text{PdCl}_2(\text{PPh}_3)_2, \text{Cul, TEA, THF, 70°C, 12 h, 80%} \]

NBD 7

\[ \text{MnO}_2, \text{DCM} \]

7 X = CH₂OH, 110°C, 16 h, 83%

8 X = CHO, rt, 12 h, 50%
Figure S1. Synthetic route details for NBD 1-6.

Figure S2. Structures of NBDs and corresponding QCs

Synthesis

ethyl 3-(benzo[c][1,2,5]thiadiazol-4-yl)bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate NBD 1
ethyl 3-[(benzo[c][1,2,5]thiadiazol-4-yl)ethynyl]bicyclo[2.2.2]hepta-2,5-diene-2-carboxylate **NBD 2**

To a round bottom flask, heated at 70°C for 20 min, the reaction mixture was cooled to rt and the solvent was evaporated. The crude product was purified over automated flash chromatography by gradient elution to obtain **NBD 2** (37% yield). Rf = 0.2 (EtOAc/Hexane 10:1); 1H NMR (400 MHz, CDCl3): δ = 7.94 (dd, J = 8.7, 1.2 Hz, 1H), 7.64 (dd, J = 7.0, 1.2 Hz, 1H), 7.57 (dd, J = 8.7, 7.0 Hz, 1H), 7.11 – 7.02 (m, 2H), 4.03 (qd, J = 7.1, 0.8 Hz, 2H), 2.44 (dt, J = 6.6, 1.7 Hz, 1H), 2.17 (dt, J = 6.7, 1.6 Hz, 1H), 1.03 (t, J = 7.1 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ = 165.29, 163.16, 154.96, 153.02, 143.74, 143.22, 142.36, 129.60, 128.97, 128.56, 121.23, 71.54, 60.12, 58.46, 52.50, 13.94; HRMS (ESI+) m/z: [M+H]+ calcd. for C29H22N2O2S: 329.0854; found: 329.0851.

diethyl 3,3’-[(benzo[c][1,2,5]thiadiazole-4-yl)diyl]bis[bicyclo[2.2.2]hepta-2,5-diene-2-carboxylate] **NBD 3**

To a round bottom flask, heated at 70°C for 20 min, the reaction mixture was cooled to rt and the solvent was evaporated. The crude product was purified over automated flash chromatography by gradient elution to obtain **NBD 3** (30 mg, 24%). Rf = 0.3 (EtOAc/Hexane 10:1); 1H NMR (400 MHz, CDCl3): δ = 7.68 (s, 1H), 7.64 (s, 1H), 7.09 – 7.02 (m, 4H), 4.12 (dqq, J = 5.4, 2.6, 1.2 Hz, 5H), 4.09 – 4.02 (m, 4H), 2.42 (ddt, J = 8.3, 6.6, 1.7 Hz, 2H), 2.18 – 2.14 (m, 2H), 1.90 (td, J = 7.1, 3.7 Hz, 7H); 13C NMR (101 MHz, CDCl3): δ = 164.11, 154.62, 154.20, 151.17, 146.86, 142.73, 141.46, 133.07, 129.21, 122.41, 117.03, 101.21, 94.79, 72.14, 60.66, 58.38, 51.53, 14.42; HRMS (ESI+) m/z: [M+H]+ calcd. for C32H26N2O2S: 461.1535; found: 461.1523.
To a round bottom flask, compound 9 (100 mg, 0.37 mmol, 1 eq.), 1,3-dithiole-2-thione (75 mg, 0.56 mmol, 1.5 eq.), and P(OEt)3 (3 mL) were added. The mixture was heated at 110°C for 5h. P(OEt)3 was evaporated, and the crude product was purified over column chromatography to obtain NBD 5 (37mg, 29%) as a dark red solid. Rf = 0.4 (EtOAc/Hexane 15%); 1H NMR (400 MHz, CDCl3) δ= 7.81 (dd, J= 8.8, 1.0 Hz, 1H), 7.54 (dd, J= 8.8, 7.0 Hz, 1H), 7.28 (dd, J= 7.0, 1.0 Hz, 1H), 7.12 (dd, J= 5.0, 1.8 Hz, 1H), 6.86 (dd, J= 5.3, 2.9, 0.8 Hz, 1H), 6.50 (t, J= 0.9 Hz, 1H), 6.22 (dd, J= 2.6, 1.0 Hz, 1H), 4.42 (t, J= 2.3 Hz, 1H), 4.20 (dd, J= 3.7, 1.1 Hz, 1H), 2.30 (dd, J= 6.5, 1.7 Hz, 1H), 2.17 (dt, J= 6.4, 1.7 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ= 155.72, 153.65, 150.19, 144.66, 143.98, 142.26, 136.97, 131.46, 129.69, 126.79, 119.10, 118.43, 117.80, 108.87, 69.50, 55.35, 51.78; HRMS (ESI+) m/z: [M+H]+ calcd. for C17H18N2S3: 340.021; found: 340.023.

4-{{(1S,4R)-3-{{(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)methyl}bicyclo[2.2.1]hepta-2,5-dien-2-yl}benzo[c][1,2,5]thiadiazole NBD 6

To a round bottom flask, compound 9 (158 mg, 0.62 mmol, 1 eq.), 4,5-bis(methylthio)-1,3-dithiole-2-thione (281.6 mg, 1.24 mmol, 2 eq.) and P(OEt)3 (3 mL) were added. The mixture was heated at 110°C under an Ar atmosphere for 5h. P(OEt)3 was evaporated, and the crude product was purified over column chromatography to obtain NBD 6 (67.5 mg, 29%) as a dark red solid. Rf = 0.4 (EtOAc/Hexane 5%); 1H NMR (400 MHz, CDCl3) δ= 7.85 (dd, J= 8.8, 1.0 Hz, 1H), 7.54 (dd, J= 8.8, 7.0 Hz, 1H), 7.28 (dd, J= 7.0, 1.0 Hz, 1H), 7.12 (dd, J= 5.0, 1.8 Hz, 1H), 6.86 (dd, J= 5.3, 2.9, 0.8 Hz, 1H), 6.50 (t, J= 0.9 Hz, 1H), 6.22 (dd, J= 2.6, 1.0 Hz, 1H), 4.42 (t, J= 2.3 Hz, 1H), 4.20 (dd, J= 3.7, 1.1 Hz, 1H), 2.30 (dd, J= 6.5, 1.7 Hz, 1H), 2.17 (dt, J= 6.4, 1.7 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ= 155.72, 153.65, 150.19, 144.66, 143.98, 142.26, 136.97, 131.46, 129.69, 126.79, 119.10, 118.43, 117.80, 108.87, 69.50, 55.35, 51.78, 19.15, 18.94; HRMS (ESI+) m/z: [M+H]+ calcd. for C34H28N2S2: 432.9995; found: 432.9995.

3-{benzo[c][1,2,5]thiadiazol-4-yl}prop-2-yn-1-ol 7

To a round bottom flask 4-bromobenzo[c][1,2,5]thiadiazole (750 mg, 3.48 mmol, 1 eq.), Pd(PPh3)4Cl2 (122.4 mg, 0.17 mmol, 0.05 eq.) and Cul (33.2 mg, 0.17 mmol, 0.05 eq.) were added followed by anhydrous THF (16 mL). The reaction mixture was purged with N2 for 10 mins followed by Et3N (10 mL) and prop-2-yn-1-ol (586.04 mg, 10.46 mmol, 3 eq) addition. It was heated at 70°C for 16 h and the progress was monitored by TLC. The mixture was cooled to rt then poured into H2O (100 mL) and extracted with EtOAc (3 x 25 mL). The mixture was purified over column chromatography to obtain 7 (500 mg, 75.4%) as a solid. Rf = 0.3 (EtOAc/Hexane, 10%); 1H NMR (400 MHz, CDCl3) δ= 7.99 (dd, J= 8.8, 1.1 Hz, 1H), 7.72 (dd, J= 7.0, 1.1 Hz, 1H), 7.55 (dd, J= 8.8, 7.0 Hz, 1H), 4.66 (s, 2H), 2.58 (s, 1H). 13C NMR (101 MHz, CDCl3) δ= 154.96, 154.91, 133.48, 129.62, 122.58, 116.77, 94.41, 81.63, 52.14; HRMS (ESI+) m/z: [M+H]+ calcd. for C21H16N2OS: 191.0279; found: 191.0274.

3-{benzo[c][1,2,5]thiadiazol-4-yl}propionaldehyde 8

In a round bottom flask MnO2 (3.4 g, 39.4 mmol, 15 eq.) was added to a solution of compound 7 (500 mg, 2.63 mmol, 1 eq.) in CH2Cl2 (20 mL) under Ar. Progress was monitored by TLC. The mixture was stirred for 12 h and the crude product was passed through the cellite to remove insoluble material. It was then concentrated, loaded onto a silica gel, and purified over flash chromatography to obtain 8 (250mg, 50%) as a solid. Rf = 0.3 (EtOAc/Hexane, 10%); m.p. 119°C; 1H NMR (400 MHz, CDCl3) δ= 9.56 (d, J = 0.6 Hz, 1H), 8.16 (dt, J = 8.8, 0.9 Hz, 1H), 7.95 (dt, J = 7.0, 0.8 Hz, 1H), 7.64 (dd, J = 8.9, 6.9, 0.7 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ= 176.43, 154.34, 154.16, 136.11, 128.93, 125.00, 113.41, 92.62, 89.16; HRMS (ESI+) m/z: [M+H]+ calcd. for C9H7N2O: 189.0123; found: 189.0128.

(1R,4S)-3-{benzo[c][1,2,5]thiadiazol-4-yl}bicyclo[2.2.1]hepta-2,5-dien-2-carbaldehyde 9

To a microwave vial compound 8 (150 mg, 0.79 eq.), freshly cracked cyclopentadiene (210.6 mg, 3.19 mmol, 4 eq.), and toluene (2 mL) were added. It was sealed and heated at 110°C for 12 h. The mixture was cooled to room temperature and concentrated. The crude product was loaded onto silica gel and purified using automated column chromatography to obtain 9 (170 mg, 83%) as a light-yellow solid. Rf = 0.4 (EtOAc/Hexane 15%); m.p. 85°C; 1H NMR (400 MHz, CDCl3) δ= 9.84 (s, 1H), 8.03 (dd, J= 8.8, 1.1 Hz, 1H), 7.62 (dd, J= 8.8, 6.9 Hz, 1H), 7.51 (dd, J= 6.9, 1.1 Hz, 1H), 7.13 – 6.91 (m, 2H), 4.35 – 4.12 (m, 2H), 2.31 (ddt, J= 51.5, 6.9, 1.6 Hz, 2H); 13C NMR (101 MHz, CDCl3) δ= 186.94, 171.27, 155.18, 152.91, 152.51, 143.33, 142.25, 129.05, 128.85, 128.14, 122.53, 70.89, 57.82, 48.45; HRMS (ESI+) m/z: [M+H]+ calcd. for C14H11N2OS: 255.055; found: 255.059.
$^1$H & $^{13}$C NMR spectra

**Figure S3.** $^1$H NMR of NBD 1 recorded in CDCl$_3$.

**Figure S4.** $^{13}$C NMR of NBD 1 recorded in CDCl$_3$. 
Figure S5. $^1$H NMR of NBD 2 recorded in CDCl$_3$.

Figure S6. $^{13}$C NMR of NBD 2 recorded in CDCl$_3$. 
Figure S7. $^1$H NMR of NBD 3 recorded in CDCl$_3$.

Figure S8. $^{13}$C NMR of NBD 3 recorded in CDCl$_3$. 
Figure S9. $^1$H NMR of NBD 4 recorded in CDCl$_3$. 

**Figure S9.** $^1$H NMR of NBD 4 recorded in CDCl$_3$. 

- **F (s)** 7.76 ppm
- **E (tdd)** 6.91 ppm
- **D (td)** 4.08 ppm
- **C (dd)** 3.94 ppm
- **B (dt)** 2.33 ppm
- **A (dt)** 2.19 ppm
- **G (t)** 1.35 ppm
- **H (m)** 4.30 ppm
**Figure S10.** $^{13}$C NMR of NBD 4 recorded in CDCl$_3$.

**Figure S11.** $^1$H NMR of NBD 5 recorded in CDCl$_3$. 
Figure S12. $^{13}$C NMR of NBD 5 recorded in CDCl$_3$.

Figure S13. $^1$H NMR of NBD 6 recorded in CDCl$_3$. 
Figure S14. $^{13}$C NMR of NBD 6 recorded in CDCl$_3$.

Figure S15. $^1$H NMR of 7 recorded in CDCl$_3$. 
Figure S16. $^{13}$C NMR of 7 recorded in CDCl$_3$.

Figure S17. $^1$H NMR of 8 recorded in CDCl$_3$. 
Figure S18. $^{13}$C NMR of 8 recorded in CDCl$_3$.

Figure S19. $^1$H NMR of 9 recorded in CDCl$_3$. 
Figure S20. $^{13}$C NMR of 9 recorded in CDCl$_3$.

$^1$H NMR irradiation studies
Figure S21. $^1$H NMR of NBD 1 before photoirradiation (top), NBD 1 after photoirradiation at 405 nm for 2h (bottom) was recorded in CDCl$_3$, the asterisk represents new QC signals. Inset: zoomed in section corresponds to aliphatic CH signals for QC.

Figure S22. $^1$H NMR of NBD 2 before photoirradiation (top), NBD 2 after photoirradiation at 405 nm for 2h (bottom) was recorded in CDCl$_3$. 
**Figure S23.** $^1$H NMR of NBD 3 before photoirradiation (top), NBD 3 after photoirradiation at 340 nm for 2h (bottom) was recorded in CDCl$_3$, asterisk represents new QC signals.

**Figure S24.** $^1$H NMR of NBD 4 before photoirradiation (top), NBD 4 after photoirradiation at 340 nm for 2h (bottom) was recorded in CD$_2$CN.

**UV/Vis Studies**
To study the photoisomerization process (NBD to QC), photophysical properties were studied. It was irradiated with a 310, 340, 405, and 455 nm LED light at various intervals. After an initial decrease in absorbance and a minor blue shift, no further change was observed.
**Figure S25.** Photoirradiation of NBD1 at 310 nm recorded in toluene.

![NBD1 structure](structure_image)

**Figure S26.** Photoirradiation of NBD2 at 405 nm was recorded in toluene.
Figure S27. Photoirradiation of NBD3 at 340 and 415 nm was recorded in toluene.
Figure S28. Photoirradiation of NBD4 at 340 nm was recorded in toluene.

**kinetic study of back conversion**

The norbornadienes were dissolved in toluene and irradiated with a metal-halide-UV lamp (310, 340, 405, 455 nm) until PSS was observed to obtain the corresponding quadricyclanes. Thereafter, the increase of the norbornadiene concentration over time was measured by recording the increase in absorption at 360 nm with a Cary 50 Bio UV/Vis-spectrophotometer for 10-15. The measurements were performed at different temperatures (323 K, 333 K, 343 K, 353 K) for the back conversion. An exponential fit of the Eyring equation was applied to the obtained data to determine the rate constants at the different temperatures for all compounds. The enthalpy and entropy of activation were derived from the linear form of the Eyring equation.
Figure S29. Kinetic study of the back conversion for 10 to 1 and linear Eyring plot.
Figure S30. Kinetic study of the back conversion for 11 to 2 and linear Eyring plot.
Figure S31. Kinetic study of the back conversion for 11 to 2 and linear Eyring plot.

Quantum yield measurement

Different light sources were used to irradiate the different norbornadiene compounds. The photon flux of each light source was determined using potassium ferrioxalate actinometry before the actual measurement. NBD 1 was exposed to a fiber-coupled LED (M310L3 (310nm)), and NBD 2, NBD 3, NBD 4, and NBD 6 were irradiated with a fiber-coupled LED (M405LP1 (405nm)). To determine the quantum yield, a solution of the norbornadienes in toluene was irradiated, and the decrease in absorption was monitored using a Cary 60-UV-Visible spectrophotometer. Optically thick solutions (absorption over 2 at 310 nm for NBD 1 and 405 nm for NBD 2, NBD 3, NBD 4, and NBD 6) were prepared to ensure all
the photons were absorbed. These solutions were prepared and kept in the dark to prevent photoconversion before measurement. A linear relationship was established between the decrease in absorption and irradiation time, and the quantum yield was determined from the slope.

**Figure S32.** Absorption at 510 nm versus the irradiation time for Photonflux determination before measurement for 310 LED.

**Figure S33.** Absorption at 387 nm versus the irradiation time for the two quantum yield measurements of NBD1. Experimental data is presented as symbols, and the line represents the linear fit.

**Figure S34.** Absorption at 510 nm versus the irradiation time for Photonflux determination before measurement for 405 LED.
Figure S35. Absorption at 424 nm, 440 nm, and 543 nm versus the irradiation time for the two quantum yield measurements of **NBD2**, **NBD3**, and **NBD6**, respectively. Experimental data is presented as symbols; the line represents the linear fit.

**Computational Details**

We determine the theoretical upper limit of solar conversion efficiency of each compound as done in previous studies\(^1\)

\[
\eta_{eff} = \Delta E_s \frac{\int_{\Delta E_{cut}}^{\infty} \frac{P_{sun}(\omega)}{h\omega} - A(\omega)S(\omega)d\omega}{\int_0^{\infty} P_{sun}(\omega)d\omega}
\]
According to the procedure outlined in previous studies. In the equation for $\eta_{\text{eff}}$, $\Delta E_S$ is the storage energy, $\Delta E_{\text{cut}} = \Delta E_S + \Delta E_{\text{TBR}}$ is the cutoff energy where $\Delta E_{\text{TBR}}$ is the thermal back reaction barrier, $P_{\text{sun}}(\omega)$ gives the solar irradiation at frequency $\omega$ as given by the AM1.5G solar spectrum, $A(\omega)$ is the attenuation of sunlight determined according to the Beer-Lambert’s law, and lastly $S(\omega)$ is the fraction of sunlight absorbed by the reaction molecule assuming 50% conversion.

### Table S1. Computed onset photophysical properties of NBD 1-6

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<th>System</th>
<th>$\lambda_{\text{onset}}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\epsilon_{\text{max}}$</th>
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<tr>
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<td>394.85 nm</td>
<td>336.00 nm</td>
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<td>QC 1</td>
<td>352.23 nm</td>
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### Table S2. Theoretical upper limit of solar conversion efficiency

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<td>NBD 6</td>
<td>0.72 %</td>
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![Diagram](image)
Figure S36. Computed spectra of NBD 1 (brown/r) and corresponding QC 10 (blue/p).

![NBD 1 diagram](image1)

Figure S37. Computed spectra of NBD 2 (brown/r) and corresponding QC 11 (blue/p).

![NBD 2 diagram](image2)
Figure S38. Computed spectra of NBD 3 (brown/r) and corresponding QC 12 (blue/p).

Figure S39. Computed spectra of NBD 4 (brown/r) and corresponding QC 13 (blue/p).
Figure S40. Computed spectra of NBD 5 (brown/r) and corresponding QC 14 (blue/p).

Figure S41. Computed spectra of NBD 6 (brown/r) and corresponding QC 15 (blue/p).

Computed LUMO and HOMO levels of NBDs

Table S3. Computed LUMO and HOMO Level of NBD 1-6
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