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Switchable Dielectric Permittivity with Temperature and Dc-bias
in a Semifluorinated Azobenzene Derivative

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Supporting Information

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- Isomerization and ratio of isomers
- UV-Vis absorption spectra for compounds 4 and 5
- ^1^H-NMR characterization for compounds 4 and 5
- POM – Effect of surfaces
- Dielectric strength for the different processes of compound 4
A. Isomerization and ratio of isomers 4:4' and 5:5'  
The UV-Vis absorption spectra of compounds 4 and 5 in THF (at c = 3.2E-5 g/mL) before and after irradiation at 365 nm for 2 minutes are shown in Figure S1, Supporting Information. Because of the rather broad features $^1$H-NMR (500 MHz, THF) was employed instead to determine the ratio of cis/trans-isomers. At room temperature, a ratio of 97:3 for 4:4' (Figure S2a) and a ratio of 91:9 for 5:5' (Figure S2b) was found. Annealing at 40°C for 1 hour gave 100% of the trans-isomer (4, 5) for both compounds. Irradiating with light over 2 minutes yields a ratio of 81:19 for 4:4' and a ratio of 73:27 for 5:5'.

Scheme I: Isomerism of the trans-isomer of 4 and 5 to the corresponding cis-isomer 4' and 5' after irradiating at 365 nm.
B. UV-Vis absorption

![UV-Vis absorption spectra](image)

**Figure S1**: UV-Vis absorption spectra of 4 (black) and 5 (red) in THF at $c = 3.2E-5$ g/mL before (—) and after (- - -) irradiation at 365 nm for 2 minutes.
C. $^1$H-NMR characterization for compounds 4 and 5

![H-NMR spectra for compounds 4 and 5](image)

**Figure S2a**: $^1$H-NMR (700 MHz in THF-d8) of compound (4). Only trans-isomer after annealing at 40 °C in solution; 2) trans- and cis-isomer (ratio 97:3) at room temperature; 1) trans- and cis-isomer (ratio 81:19) after irradiation at 365 nm in solution. The isomer ratio was determined via integration of the corresponding signals (t vs. c).
Figure S2b: $^1$H-NMR (700 MHz in THF-d8) of compound 5. Only trans-isomer after annealing at 40 °C in solution; 2) trans- and cis-isomer (ratio 91:9) at room temperature; 1) trans- and cis-isomer (ratio 73:27) after irradiation at 365 nm in solution. The isomer ratio was determined via integration of the corresponding signals (t vs. c).
D. POM – Effect of surfaces

![POM images of compound 5 (left) and 4 (right) obtained on cooling at the indicated temperatures under different conditions: (top): drop prepared on microscope slides (Linkam cover slips W22G), (middle): samples are sandwiched between microscope slides (Linkam, W22G) the thickness maintained by Teflon spacers (25 μm) and (bottom): samples between ITO glasses with Teflon spacers (25 μm). A smectic phase (SmA) is formed at temperatures below the nematic phase when samples are sandwiched between ITO or microscope slides.](image-url)

**Figure S3.**
Figure S4. POM images of compound 4 obtained at T= C (nematic phase) by applying dc-bias as indicated. A preference for homeotropic alignment can be seen with increasing bias.
E. Dielectric strength for the different processes of compound 4

![Graph](image)

**Figure S5.** Product of the dielectric strength with temperature for the different processes of compound 4. Dashed and dash-dotted lines separate the nematic from the isotropic and crystalline phases.