Fluorescence switching with subphthalocyanine-dihydroazulene dyads

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Electronic supporting information

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Figure S2. $^{13}$C-NMR (126 MHz) spectrum of 3 recorded in CDCl$_3$.

Figure S3. $^1$H-NMR (500 MHz) spectrum of 6 recorded in CDCl$_3$.

Figure S4. $^{13}$C-NMR (126 MHz) spectrum of 6 recorded in CDCl$_3$. 
## Selected Crystallographic Data

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<td>b/Å</td>
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<td>Goodness-of-fit on F^2</td>
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<td>Final R indexes [all data]</td>
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<td>Largest diff. peak/hole / e Å^{-3}</td>
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**UV-Vis Absorption Spectra**

**Figure S5.** UV-Vis absorption spectrum of 3 recorded in toluene.

**Figure S6.** UV-Vis absorption spectrum of 6 recorded in toluene.
Fluorescence Quantum Yields

Fluorescence quantum yields (QYs) were measured by multipoint determination using a Cary 300 UV-Vis spectrophotometer for absorption measurements and a Fluotime 300 (PicoQuant) instrument for fluorescence measurements. Cresyl violet perchlorate in absolute ethanol was used as reference dye.¹

The quantum yields ($\Phi_F$) were determined using the relative method according to the following formula.²

$$\Phi_F = \Phi_{F,\text{ref}} \cdot \frac{\alpha \cdot n^2}{\alpha_{\text{ref}} \cdot n_{\text{ref}}^2}$$

The subscript $\text{ref}$ designates the reference dye (cresyl violet perchlorate or CVP, $\Phi_{F,\text{ref}} = 0.56$ in ethanol), $n$ the refractive index of the solvent and $\alpha$ the slope obtained from a linear-fit to a set of data points ($I_{\text{int}}$ vs. $f_a$). Here $I_{\text{int}}$ refers to the integrated emission intensity and $f_a$ to the fraction of absorbed light ($f_a = 1-10^{-A}$, $A$ being the absorbance measured at the wavelength of excitation, 507 nm). For all QY determinations five or more data points were collected with a measured absorbance below 0.1 for the longest wavelength absorption.
Figure S7. Fraction of absorbed light for CVP (reference dye, left) in EtOH and compound 3 (right) in toluene at different concentrations.

Figure S8. Emission spectra (excitation at 507 nm) of CVP (reference dye, left) in EtOH and 3 (right) in toluene at different concentrations.

Figure S9. Linear-fit of data points (I_{int} vs f_a) for CVP (left) and 3 (right).
Switching Studies

Figure S10. Left: Change in absorption spectra upon converting 3-DHA to 3-VHF in toluene by irradiation at 420 nm. Right: Change in absorption spectra upon thermal conversion of 3-VHF to 3-DHA in toluene at 25 °C.

Figure S11. Left: Change in absorption spectra upon converting 6-DHA to 6-VHF in toluene by irradiation at 420 nm. Right: Change in absorption spectra upon thermal conversion of 6-VHF to 6-DHA in toluene at 25 °C. The conversions do not occur with isosbestic points due to degradation.

A sample of a pure photochromic SubPc-DHA was dissolved in toluene. This stock solution was kept in the dark at all times. A sample of the stock solution was placed in the cuvette, and a spectrum was acquired (25 °C). The sample was then irradiated at 420 nm for a short while (seconds to minutes for 3 and minutes to hours for 6), then a spectrum was acquired (UV-Vis or fluorescence). This procedure was repeated until no change in the spectrum could be seen, going from SubPc-DHA to SubPc-VHF (for 6 this was repeated until what seemed to be degradation of
the system instead of conversion from 6-DHA to 6-VHF). When fully converted, the SubPc-VHF to SubPc-DHA back-reaction was monitored at 25 °C by acquiring a UV-Vis absorption spectrum over more than one half-live. The conversion of 3-DHA to 3-VHF occurred with isosbestic points in the absorption spectra and also from 3-VHF to 3-DHA (see Figure 4 in article). The decay of absorption at 460 nm of the SubPc-VHF-species was plotted against time. The exponential decay of the SubPc-VHF absorbance was subjected to curve fitting (first-order kinetics), from which the rate constant \( k_{25^\circ C} \) (SubPc-VHF to SubPc-DHA) was determined (Figures S12 and S13).

**Figure S12.** Decay in absorbance of 3-VHF at 460 nm in time at 25 °C in toluene.

**Figure S13.** Decay in absorbance of 6-VHF (plus degradation products) at 460 nm in time at 25 °C in toluene.
References