Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Fluorescence switching with subphthalocyanine-dihydroazulene dyads

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Electronic supporting information

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NMR Spectra

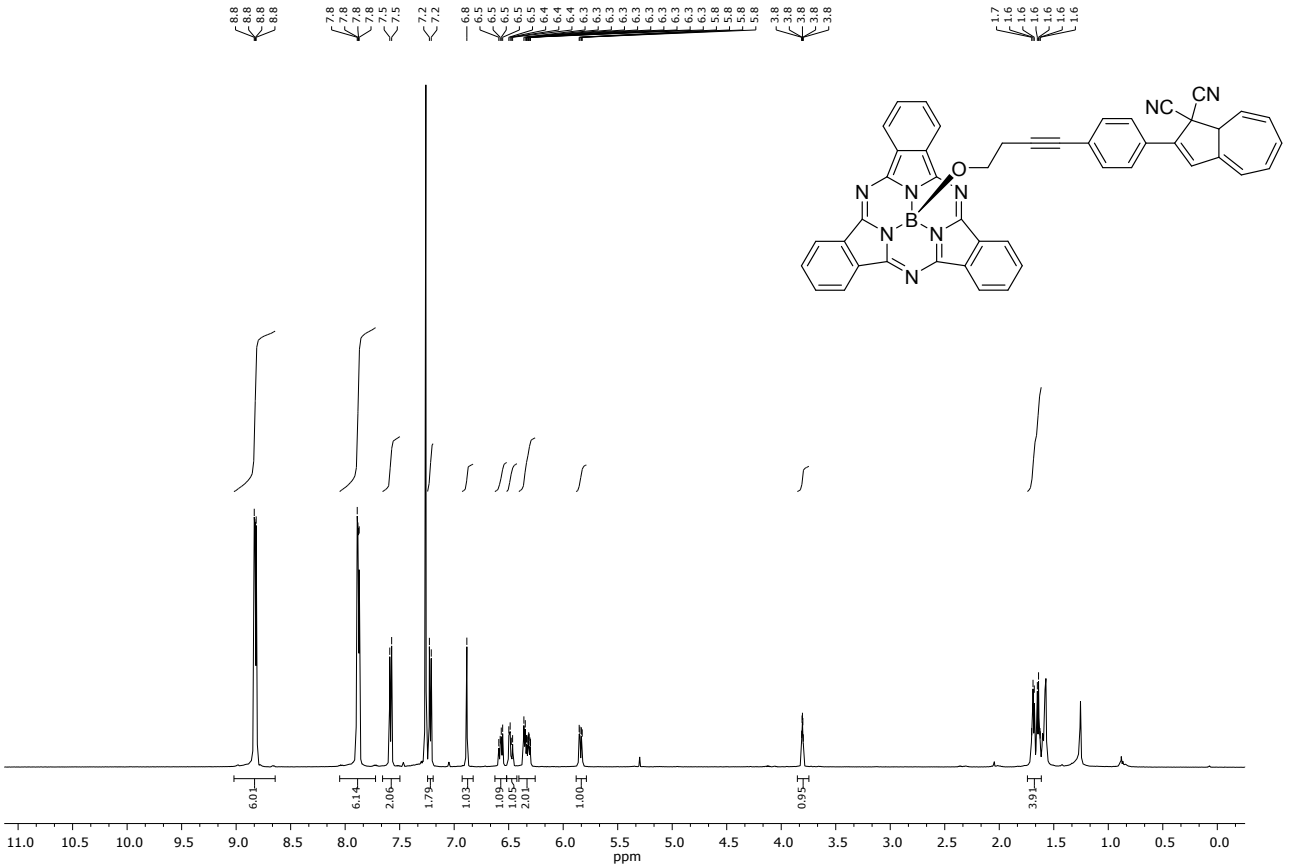


Figure S1. ^{1}H-NMR (500 MHz) spectrum of **3** recorded in $CDCl_3$.

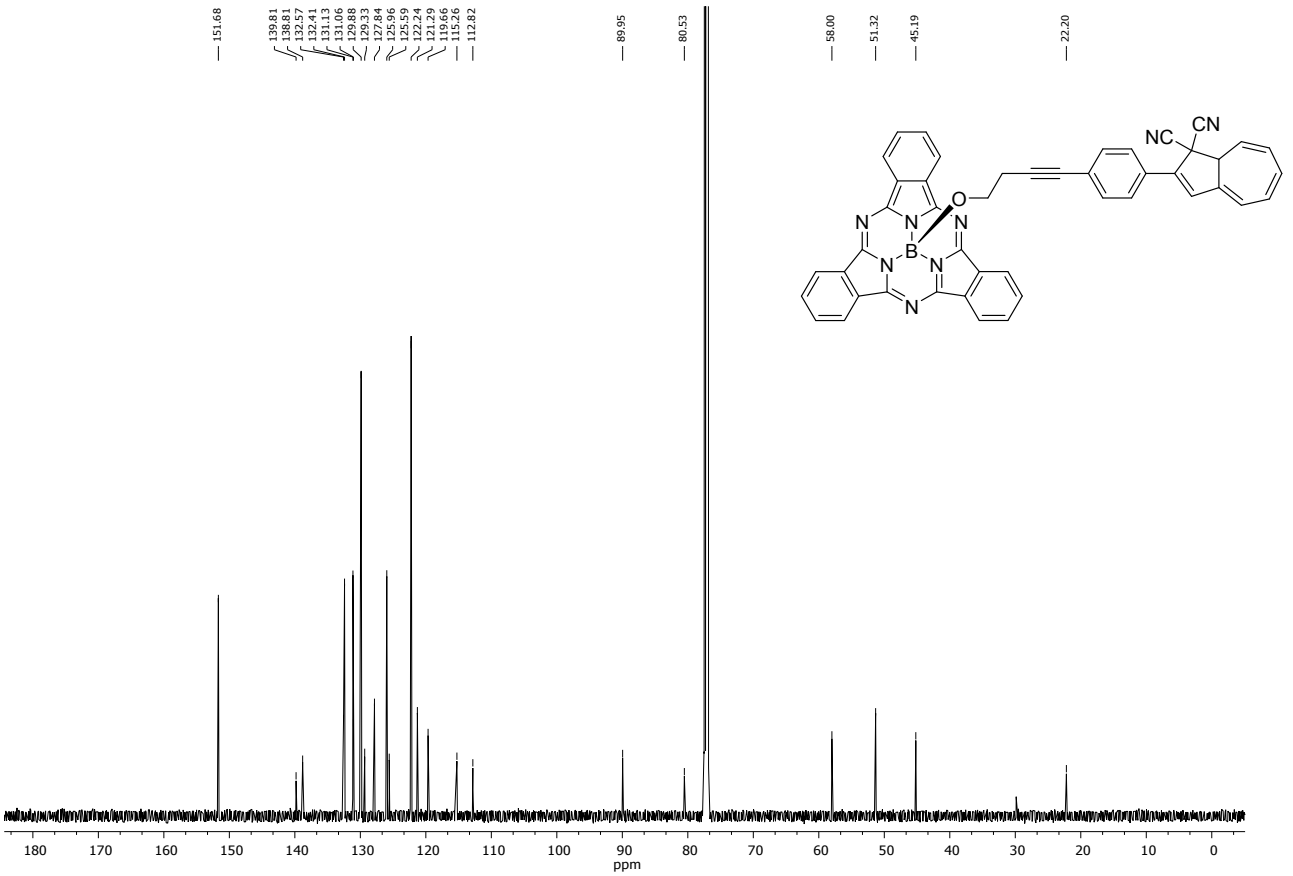


Figure S2. ^{13}C-NMR (126 MHz) spectrum of **3** recorded in $CDCl_3$.

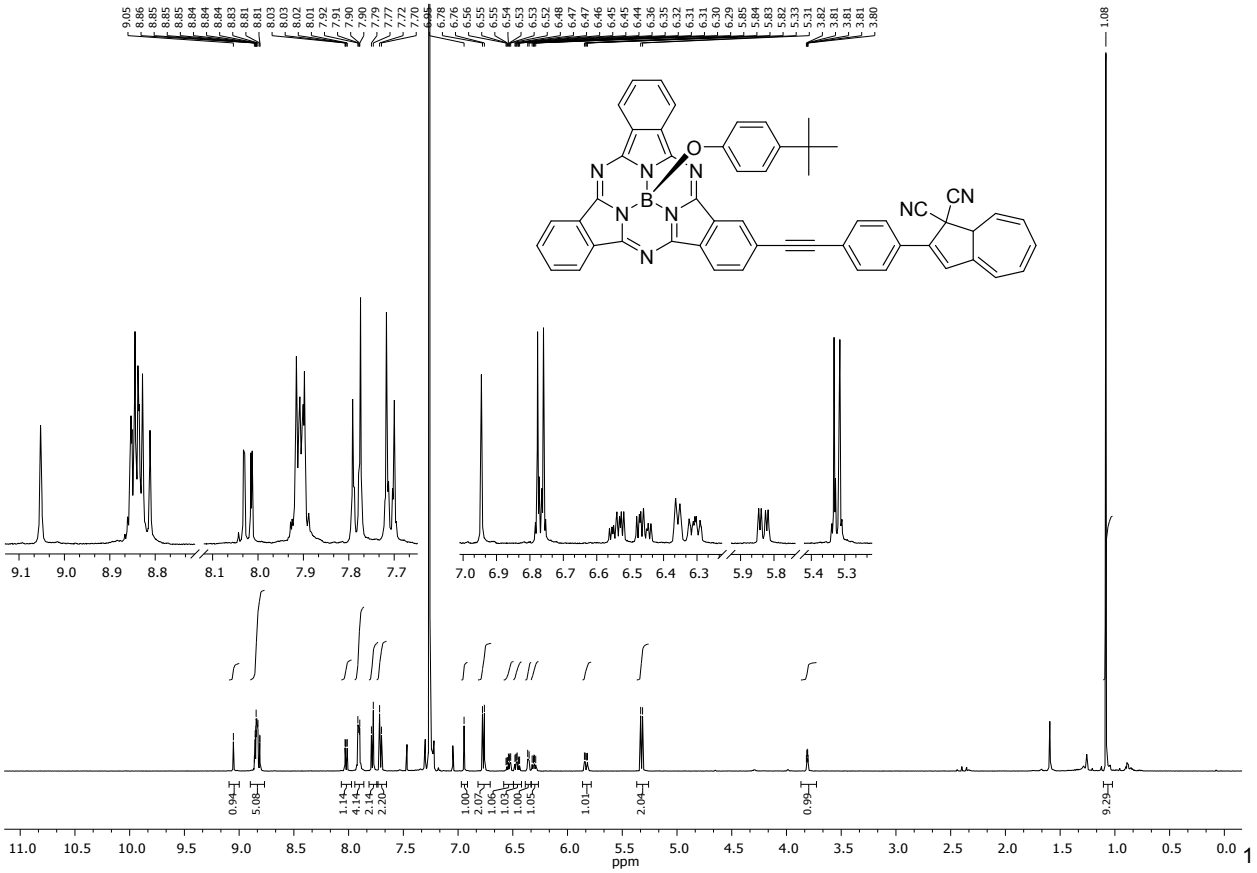


Figure S3. ^{1}H-NMR (500 MHz) spectrum of **6** recorded in $CDCl_3$.

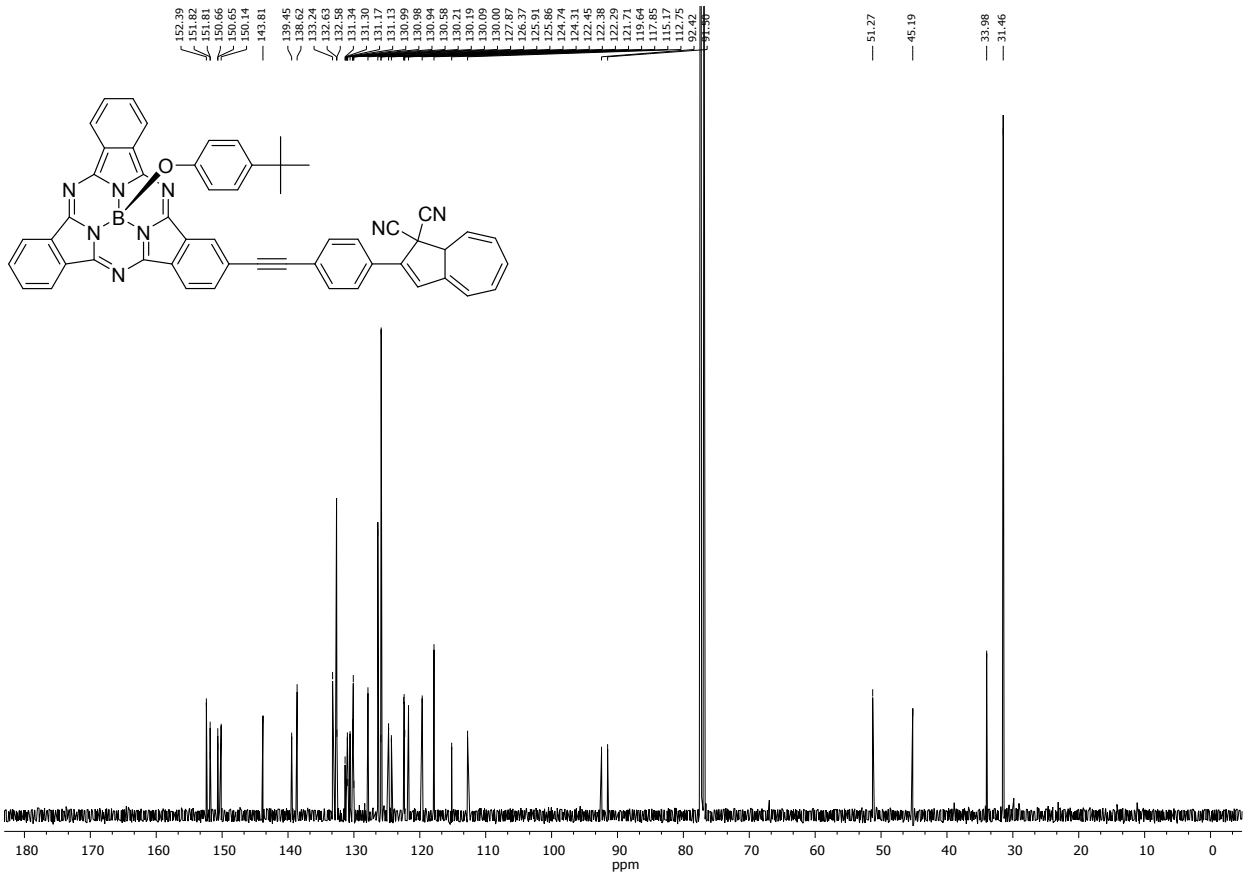
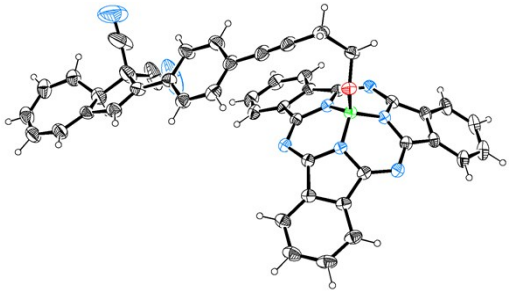


Figure S4. ^{13}C-NMR (126 MHz) spectrum of **6** recorded in $CDCl_3$.

Selected Crystallographic Data



CCDC	1861766
Empirical formula	$C_{46}H_{27}BN_8O$
Formula weight	718.57
Temperature/K	122(2)
Space group	P-1
a/Å	10.374(14)
b/Å	12.619(14)
c/Å	15.496(17)
α/°	71.92(6)
β/°	80.91(5)
γ/°	71.19(4)
Volume/Å^3	1822(4)
Z	2
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	0.081
F(000)	744.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.62 to 50.7
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15, -18 ≤ l ≤ 18
Reflections collected	47387
Independent reflections	6522 [R_{int} = 0.0359]
Data/restraints/parameters	6522/0/505
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0760, wR_2 = 0.2092
Final R indexes [all data]	R_1 = 0.0943, wR_2 = 0.2286
Largest diff. peak/hole / e Å^{-3}	1.26/-0.45

UV-Vis Absorption Spectra

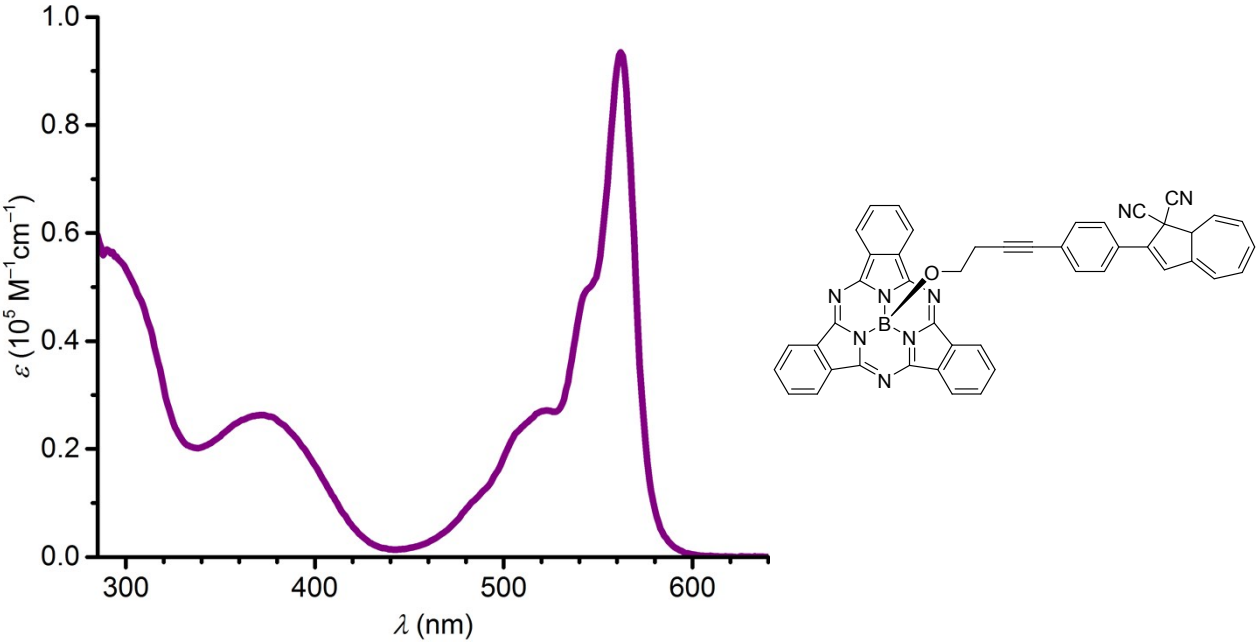


Figure S5. UV-Vis absorption spectrum of **3** recorded in toluene.

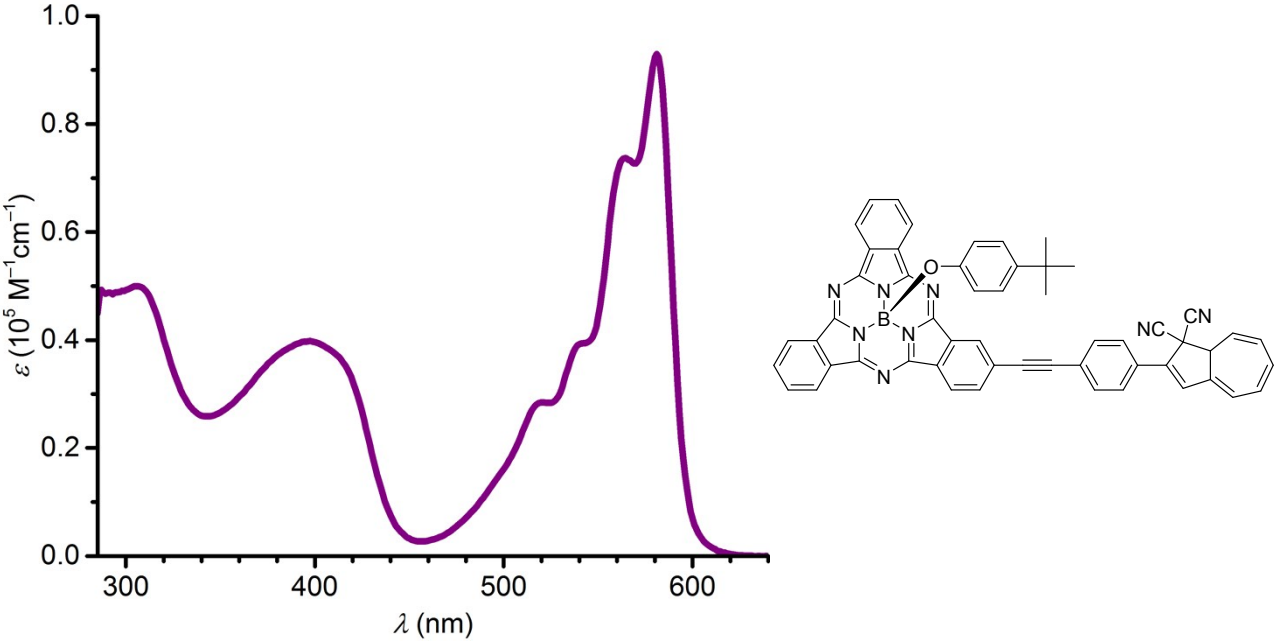


Figure S6. UV-Vis absorption spectrum of **6** recorded in toluene.

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 (Φ_F) were determined using the relative method according to the following formula.[2]

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

The subscript *ref* designates the reference dye (cresyl violet perchlorate or CVP, $\Phi_{F,ref}$ = 0.56 in ethanol), n the refractive index of the solvent and α the slope obtained from a linear-fit to a set of data points (I_{int} vs. f_a). Here I_{int} refers to the integrated emission intensity and f_a to the fraction of absorbed light ($f_a = 1\text{-}10^{-A}$, 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.

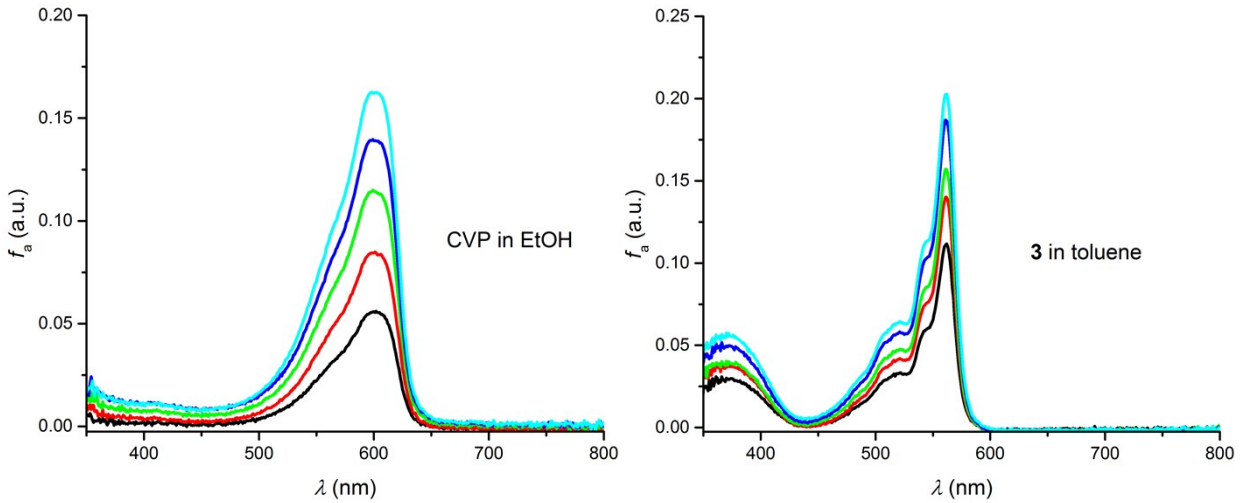


Figure S7. Fraction of absorbed light for **CVP** (reference dye, left) in EtOH and compound **3** (right) in toluene at different concentrations.

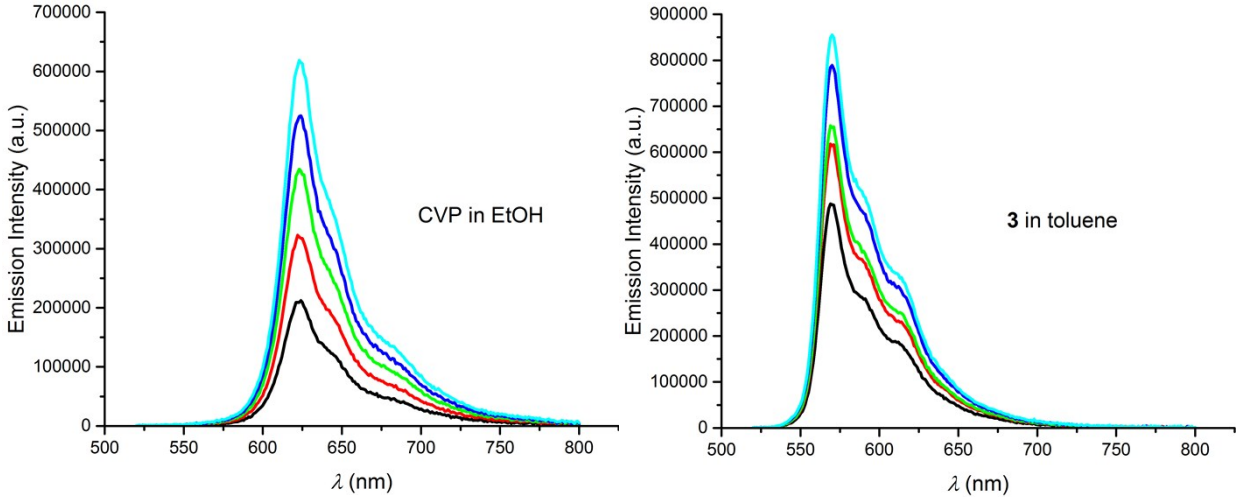


Figure S8. Emission spectra (excitation at 507 nm) of **CVP** (reference dye, left) in EtOH and **3** (right) in toluene at different concentrations.

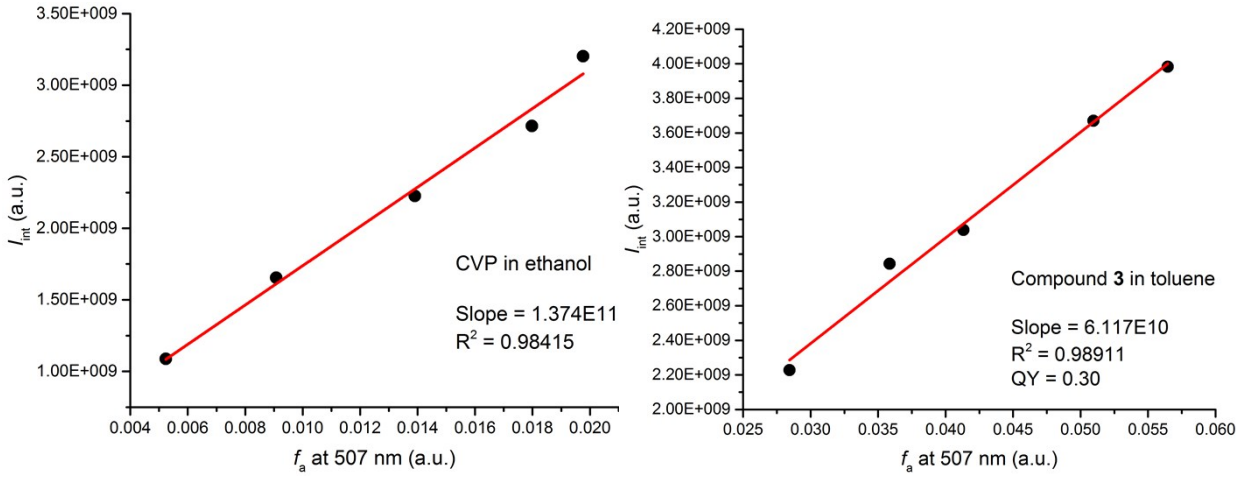


Figure S9. Linear-fit of data points (I_{int} vs f_a) for **CVP** (left) and **3** (right).

Switching Studies

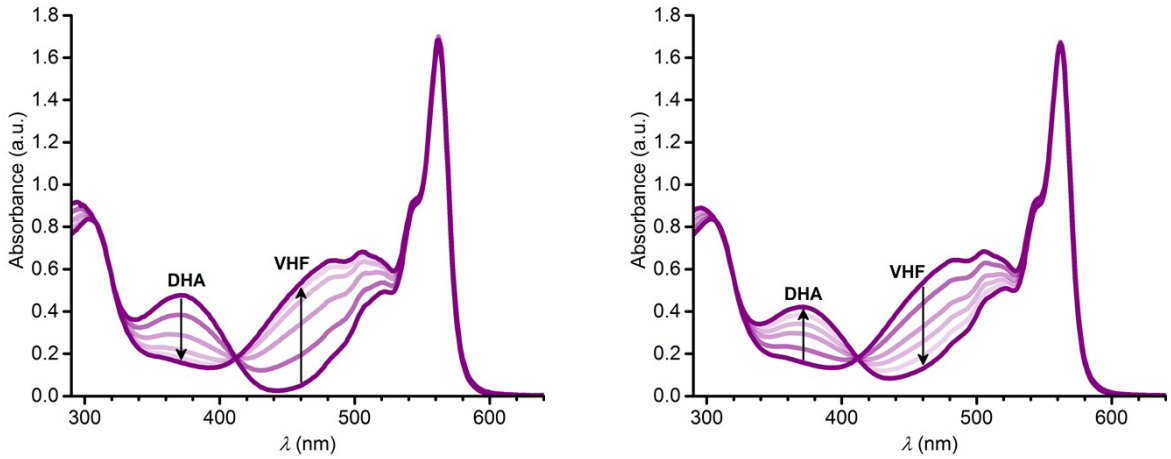


Figure S10. Left: Change in absorption spectra upon converting **3-DHA** to **3-VHF** in toluene by irradiation at 420 nm. Right: Change in absorption spectra upon thermal conversion of **3-VHF** to **3-DHA** in toluene at 25 °C.

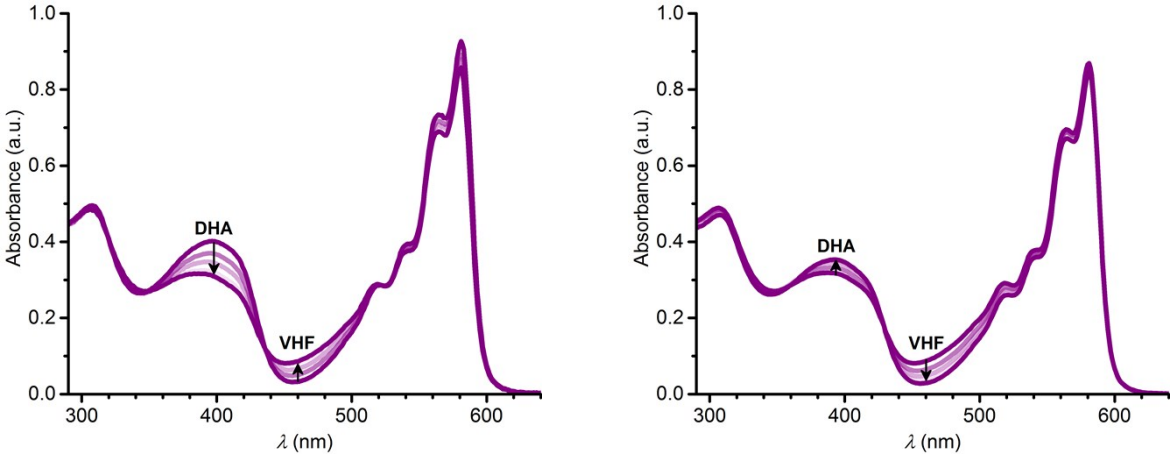
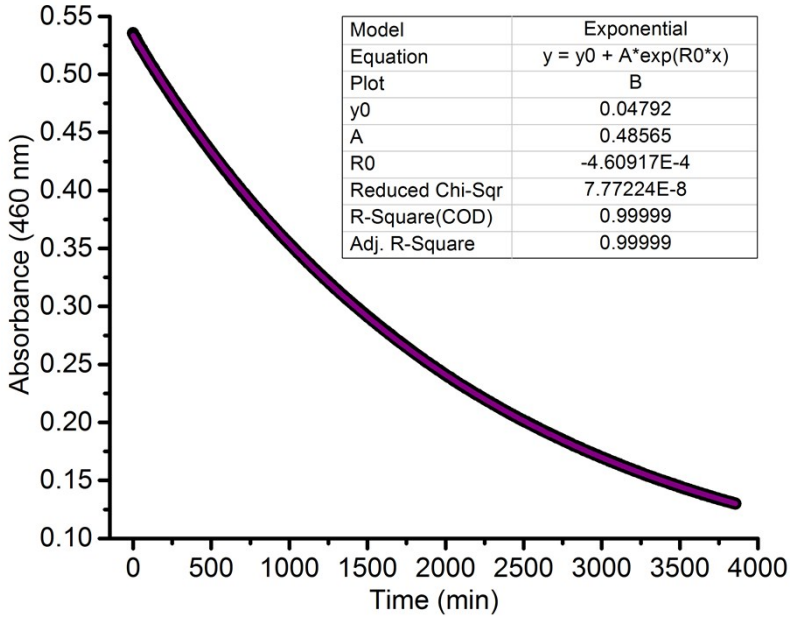


Figure S11. Left: Change in absorption spectra upon converting **6-DHA** to **6-VHF** in toluene by irradiation at 420 nm. Right: Change in absorption spectra upon thermal conversion of **6-VHF** to **6-DHA** in toluene at 25 °C. The conversions do not occur with isosbestic points due to degradation.

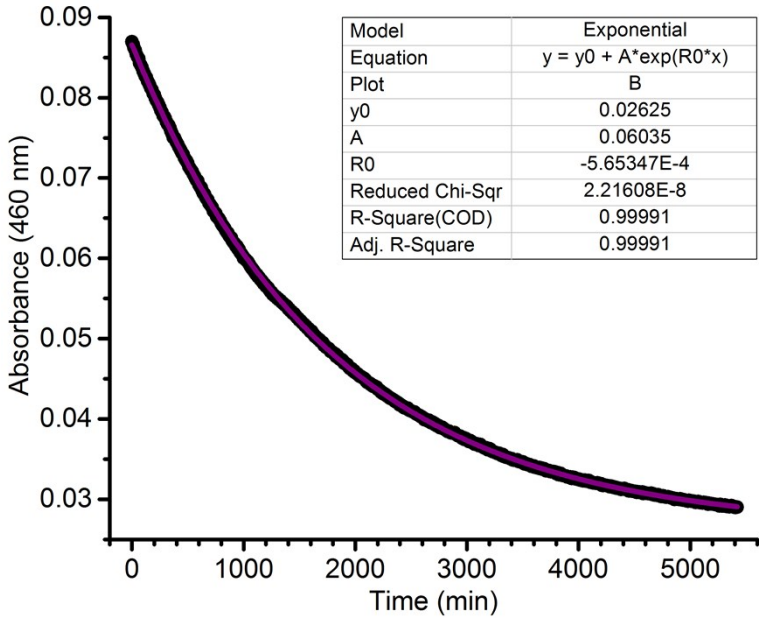
A sample of a pure photochromic SubPc-DHA was dissolved in toluene. This stock solution was kept in the dark at all times. A sample of the stock solution was placed in the cuvette, and a spectrum was acquired (25 ºC). The sample was then irradiated at 420 nm for a short while (seconds to minutes for **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 $k_{25}{}^{o}{}_{C}$ (SubPc-VHF to SubPc-DHA) was determined (Figures S12 and S13).



Model	Exponential
Equation	y = y0 + A*exp(R0*x)
Plot	B
y0	0.04792
A	0.48565
R0	-4.60917E-4
Reduced Chi-Sqr	7.77224E-8
R-Square(COD)	0.99999
Adj. R-Square	0.99999

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



Model	Exponential
Equation	y = y0 + A*exp(R0*x)
Plot	B
y0	0.02625
A	0.06035
R0	-5.65347E-4
Reduced Chi-Sqr	2.21608E-8
R-Square(COD)	0.99991
Adj. R-Square	0.99991

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

References

1. R. Sems and K. H. Drexhage, *J. Lumin.,* 1981, **24-25**, 709-712.
2. C. Würt, M. Grabolle, J. Pauli, M. Spieles and U. Resch-Genger, *Nat. Protoc.*, 2013, **8**, 1535-1550.