

Supporting Information

A simplicity-guided cocktail approach toward multicolor fluorescent systems

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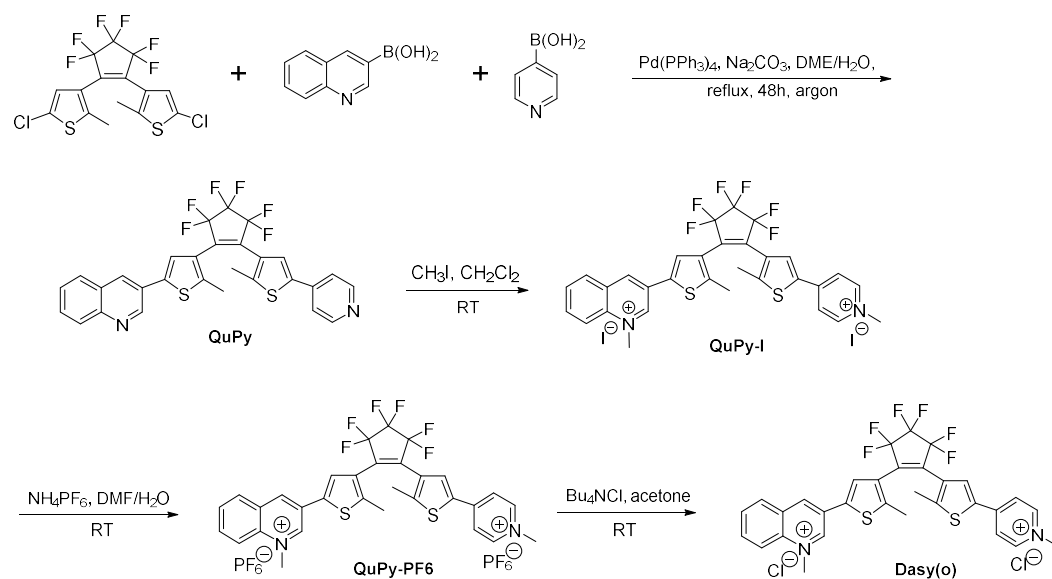
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Synthesis

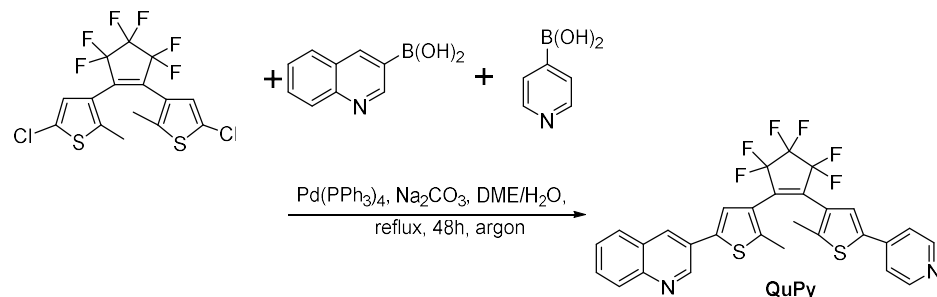
General methods and materials for synthesis

All chemicals for the synthesis were used as received without further purification, unless stated otherwise. CH_2Cl_2 was distilled over CaH_2 . ^1H NMR (400 MHz) and ^{13}C NMR (101 or 125 MHz) spectra were recorded on Varian Unity 400 or 500 spectrometers at 25 °C. In the ^1H and ^{13}C NMR spectra, chemical shifts (δ/ppm) are referenced to the residual solvent peak: CDCl_3 , 7.26 ppm (^1H NMR) and 77.20 ppm (^{13}C NMR); $\text{MeOH-}d_4$, 3.10 ppm (^1H NMR) and 49.00 ppm (^{13}C NMR); $\text{DMSO-}d_6$, 2.50 ppm (^1H NMR) and 39.00 ppm (^{13}C NMR). Thin-layer chromatography to monitor the reactions was performed on silica gel plates (Merck Kieselgel 60, F_{254}).



Scheme S1. Synthesis of 1-[2'-methyl-5'-(N-methylpyrid-4''-yl)-thien-3'-yl]-2-[2'-methyl-5'-(N-methylquinolin-3''-yl)thien-3'-yl]perfluorocyclopentene dichloride (**Dasy(o)**)

Synthesis of 1-[2'-methyl-5'-(pyrid-4''-yl)-thien-3'-yl]-2-[2'-methyl-5'-(quinolin-3''-yl)thien-3'-yl]-perfluorocyclopentene (**QuPy**)

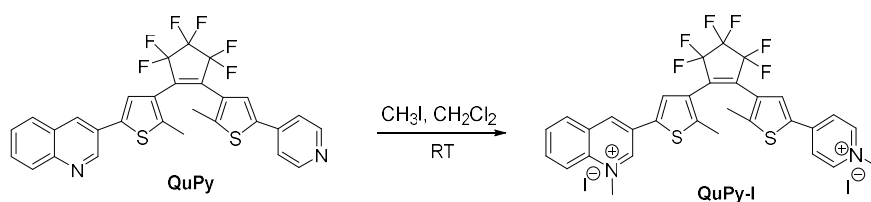


A published method¹ was modified to synthesize 1-[2'-methyl-5'-(pyrid-4''-yl)-thien-3'-yl]-2-[2'-methyl-5'-(quinolin-3''-yl)thien-3'-yl]-perfluorocyclopentene (**QuPy**). 1,2-Bis(5-chloro-2-methyl-3-thienyl)cyclopentene² (876 mg, 2.0 mmol), quinolin-3-ylboronic acid (346 mg, 2.0 mmol), 4-pyridinylboronic acid (246 mg, 2.0 mmol), Na₂CO₃ (0.88 g, 2 mmol) and Pd(PPh₃)₄ (232 mg, 0.20 mmol) were placed in a flask under Ar. Dimethoxyethane (DME, 40 ml, degassed) and water (10 ml, degassed) were subsequently added and the reaction mixture was refluxed (90 °C) for 48 h under argon. After cooling to room temperature, the reaction was quenched with water (40 ml) and Et₂O (80 ml). The organic layer was separated, and the water phase was extracted with Et₂O (100 ml x 2). The combined organic phases were dried (Na₂SO₄), filtered, and the solvent was evaporated in vacuo. The crude product was purified by repeating column chromatography (SiO₂, MeOH/CH₂Cl₂ = 2:98) to afford **QuPy** (342 mg, 30% yield).

¹H NMR (400 MHz, CDCl₃) δ 9.11 (d, *J* = 2.4 Hz, 1H, Ar-H), 8.62 (br. s, 2H, Py-H), 8.22 (dd, *J* = 2.4 and 0.8 Hz, 1H, Ar-H), 8.10 (dd, *J* = 8.4 and 1.0 Hz, 1H, Ar-H), 7.84 (ddd, *J* = 8.2, 1.4 and 0.7 Hz, 1H, Ar-H), 7.72 (ddd, *J* = 8.4, 6.9 and 1.5 Hz, 1H, Ar-H), 7.58 (ddd, *J* = 8.2, 6.9 and 1.2 Hz, 1H, Ar-H), 7.49 (d, *J* = 1.3 Hz, 1H, thiophene-H), 7.44 (d, *J* = 1.1 Hz, 1H, thiophene-H), 7.44 - 7.39 (m, 2H, Py-H), 2.044 (s, 3H, CH₃). 2.039 (s, 3H, CH₃).

¹³C NMR (101 MHz, CDCl₃) δ 150.7 (2C, CH), 148.2 (CH), 147.7 (C_{quat}), 143.9 (C_{quat}), 142.7 (C_{quat}), 140.3 (C_{quat}), 139.4 (C_{quat}), 139.2 (C_{quat}), 131.6 (CH), 129.9 (CH), 129.6 (CH), 128.0 (CH), 127.9 (C_{quat}), 127.7 (CH), 126.5 (C_{quat}), 126.4 (C_{quat}), 126.3 (C_{quat}), 125.0 (CH), 123.8 (CH), 119.8 (2C, CH), 15.0 (CH₃), 14.9 (CH₃).

*Synthesis of 1-[2'-methyl-5'-(N-methylpyrid-4''-yl)-thien-3'-yl]-2-[2'-methyl-5'-(N-methylquinolin-3''-yl)thien-3'-yl]perfluorocyclopentene diiodide (**QuPy-I**)*



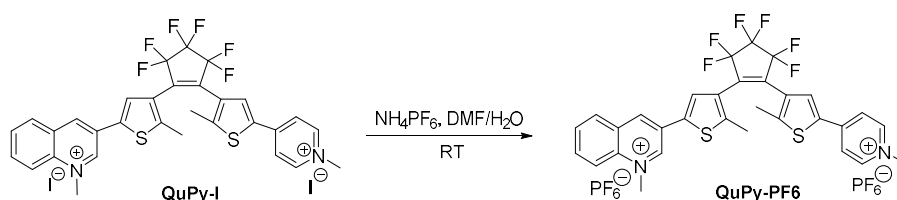
To a stirred solution of 1-[2'-methyl-5'-(pyrid-4''-yl)-thien-3'-yl]-2-[2'-methyl-5'-(quinolin-3''-yl)thien-3'-yl]-perfluorocyclopentene (**QuPy**) (280 mg, 0.49 mmol) in distilled dichloromethane (5 ml) was slowly added methyl iodide (2 ml). The reaction was stirred at room temperature under argon. After 48 h, the resulting suspension was filtered, the solid washed repeatedly with dichloromethane, and then dried in vacuo to afford pure (¹H NMR) **QuPy-I** (286 mg, 33% yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.04 (d, *J* = 1.6 Hz, 1H, Ar-H), 9.46 (d, *J* = 2.0 Hz, 1H, Ar-H), 8.96 - 8.89 (m, 2H, Py-H), 8.51 (dd, *J* = 8.9, 0.9 Hz, 1H, Ar-H), 8.48 (dd, *J* = 8.4, 1.4 Hz, 1H, Ar-H), 8.43 - 8.36 (m, 2H, Py-H), 8.37 (s, 1H, thiophene-H), 8.25 (ddd, *J* = 8.8, 7.0

and 1.5 Hz, 1H, Ar-H), 8.12 - 8.02 (m, 2H, Ar-H and thiophene-H), 4.69 (s, 3H, N-CH₃), 4.29 (s, 3H, N-CH₃), 2.12 (s, 3H, CH₃), 2.07 (s, 3H, CH₃).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 148.4, 147.5, 145.8, 145.2, 144.5, 139.9, 136.5, 135.0, 134.7, 134.6, 130.4, 129.9, 129.8, 128.6, 126.1, 125.9, 125.7, 124.5, 121.6, 118.6, 46.5, 44.9, 14.2, 13.9.

Synthesis of 1-[2'-methyl-5'-(N-methylpyrid-4''-yl)-thien-3'-yl]-2-[2'-methyl-5'-(N-methylquinolin-3''-yl)thien-3'-yl]perfluorocyclopentene bishexafluorophosphate (QuPy-PF6)

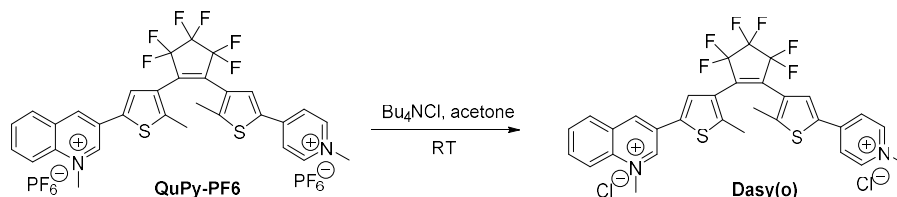


A solution of 1-[2'-methyl-5'-(N-methylpyrid-4''-yl)thien-3'-yl]-2-[2'-methyl-5'-(N-methylquinolin-3''-yl)thien-3'-yl]perfluorocyclopentene diiodide (**QuPy-I**) (257 mg, 0.3 mmol) in DMF (20 ml) was poured into a solution of NH₄PF₆ (3 g) in deionized water (30 ml). The reaction mixture was stirred at room temperature for 20 h. The precipitate was collected by filtration and washed with deionized water to afford pure (¹H NMR) bishexafluorophosphate **QuPy-PF6** (217 mg, 81% yield).

¹H NMR (400 MHz, MeOH-*d*₄) δ 9.81 (d, *J* = 2.0 Hz, 1H, Ar-H), 9.33 (d, *J* = 2.0 Hz, 1H Ar-H), 8.75 (m, 2H, Py-H), 8.49 (dd, *J* = 8.8 and 0.8 Hz, 1H, Ar-H), 8.42 (dd, *J* = 8.4 and 1.2 Hz, 1H, Ar-H), 8.29 - 8.20 (m, 3H, Ar-H and Py-H), 8.15 (s, 1H, thiophene-H), 8.06 (ddd, *J* = 8.1, 7.0 and 0.9 Hz, 1H, Ar-H), 7.94 (s, 1H, thiophene-H), 4.75 (s, 3H, N-CH₃), 4.32 (s, 3H, N-CH₃), 2.21 (s, 3H, CH₃), 2.14 (s, 3H, CH₃).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 149.0, 148.1, 146.3, 145.7, 145.0, 140.5, 137.0, 135.6, 135.3, 135.2, 130.8, 130.5, 130.4, 129.1, 126.6, 126.29, 126.26, 125.1, 122.1, 119.1, 47.0, 45.4, 14.6, 14.4.

Synthesis of 1-[2'-methyl-5'-(N-methylpyrid-4''-yl)-thien-3'-yl]-2-[2'-methyl-5'-(N-methylquinolin-3''-yl)thien-3'-yl]perfluorocyclopentene dichloride (Dasy(o))

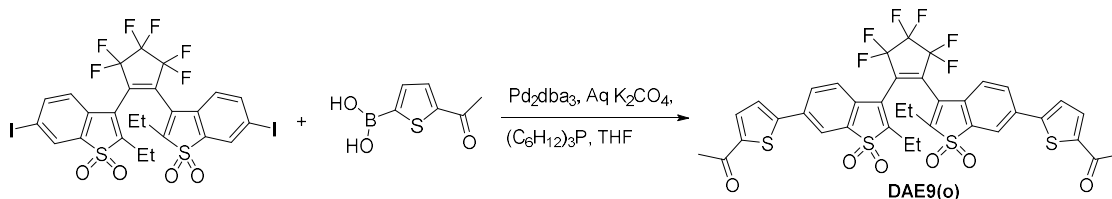


A solution of Bu₄NCl (1 g, 3.6 mmol) in acetone (40 ml) was added to 1-[2'-methyl-5'-(N-methylpyrid-4''-yl)-thien-3'-yl]-2-[2'-methyl-5'-(N-methylquinolin-3''-yl)thien-3'-yl]perfluorocyclopentene bishexafluorophosphate (**QuPy-PF6**) (217 mg, 0.3 mmol) in acetone (40 ml). The reaction mixture was stirred at room temperature for 20 h. The precipitate was collected by filtration and washed with deionized water to afford pure (¹H NMR) dichloride **Dasy(o)** (180 mg, 81% yield).

yl]perfluorocyclopentene bis(hexafluorophosphate) (**QuPy-PF6**) (104 mg, 0.12 mmol) in acetone (20 ml). The solution was stirred at room temperature for 20 h. The mixture was centrifuged and the solid was collected and washed with acetone to give pure (¹H NMR) **QuPy-Cl** (48 mg, 60% yield).

¹H NMR (400 MHz, MeOH-*d*₄) δ 9.88 (d, *J* = 2.0 Hz, 1H, Ar-H), 9.36 (d, *J* = 2.0 Hz, 1H, Ar-H), 8.79 (m, 2H, Py-H), 8.49 (dd, *J* = 9.2 and 1.2 Hz, 1H, Ar-H), 8.43 (dd, *J* = 8.4 and 1.2 Hz, 1H, Ar-H), 8.30-8.23 (m, 3H, Py-H and Ar-H), 8.22 (s, 1H, thiophene-H), 8.06 (ddd, *J* = 8.4, 7.2 and 0.8 Hz, 1H, Ar-H), 7.99 (s, 1H, thiophene-H), 4.76 (s, 3H, N-CH₃), 4.33 (s, 3H, N-CH₃), 2.17 (s, 3H, CH₃), 2.11 (s, 3H, CH₃).

¹³C NMR (126 MHz, MeOH-*d*₄) δ 151.3, 149.2, 149.1, 146.9, 146.8, 142.5, 139.1, 137.0, 136.8, 136.5, 132.4, 131.9, 131.8, 131.2, 129.2, 128.6, 128.1, 127.4, 123.6, 119.8, 48.0, 46.3, 15.2, 14.8.



Scheme S2. Synthesis of 1,2-Bis(2-ethyl-6-(5-acetylthiophen-2-yl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**DAE9(o)**)

The synthesis of **DAE9(o)** followed a published procedure.³ The data of ¹H and ¹³C NMR (400 MHz, 1,4-dioxane-*d*₈) has been published³. The data of ¹H and ¹³C NMR (400 MHz, CDCl₃) is reported in this paper. In the following ¹H NMR data, ap and p indicate the proton signals assigned to antiparallel and parallel conformations of the open-ring isomers, respectively.

¹H NMR (400 MHz, CDCl₃) (ap/p = 57/43) δ 8.02 (dd, *J* = 1.6 Hz, 1.2H (ap), Ar-H), 7.94 (dd, *J* = 1.6 Hz, 0.8H (p), Ar-H), 7.85 (dd, *J* = 8.0, 1.6 Hz, 1.2H (ap), Ar-H), 7.71-7.66 (m, 2.0H (ap) and (p), thiophene-H and Ar-H), 7.65 (d, *J* = 4.0 Hz, 0.8 H (p), thiophene-H), 7.43 (d, *J* = 4.0 Hz, 1.2H (ap), thiophene-H), 7.36 (d, *J* = 4.0 Hz, 0.8 H (p), thiophene-H), 7.25 (d, *J* = 8.0 Hz, 1.2H (ap), Ar-H), 7.17 (d, *J* = 8.0 Hz, 0.8H (p), Ar-H), 2.50-2.74 (m, 8.8H (ap) and (p), Ar-H), 2.47-2.35 (m, 1.2H (ap), Ar-H), 1.42 (t, *J* = 7.6 Hz, 2.6H (p), CH₃), 1.10 (t, *J* = 7.6 Hz, 3.4H (ap), CH₃).

¹³C NMR (101 MHz, CDCl₃) δ 190.5, 149.4, 148.9, 148.4, 148.3, 145.5, 145.4, 137.0, 136.9, 136.6, 136.6, 133.51, 133.47, 131.3, 131.0, 129.2, 129.1, 126.2, 126.1, 123.6, 123.3, 123.2, 123.1, 120.0, 26.9, 26.8, 19.5, 19.4, 12.1, 11.8.

Chemical structure of compound 10: Cc1cc2c(cc1C(F)(F)F)c3ccccc3n2

¹H NMR spectrum (CDCl₃) of compound 10. The spectrum shows peaks in the aromatic region (7.2-9.1 ppm) and aliphatic region (1.250 ppm). The integration values are provided for each peak.

Chemical Shift (ppm)	Integration
9.109, 9.103	1.00
8.619	2.02
8.227, 8.225, 8.221, 8.219	1.04
8.117, 8.114, 8.095, 8.093	1.05
7.849, 7.830, 7.829, 7.827	1.06
7.723, 7.719, 7.702	1.14
7.583, 7.496, 7.493, 7.489	1.08
7.445, 7.442, 7.426, 7.414	1.84
2.044	2.039
1.250	5.60

The chemical structure of compound 10 is shown at the top left. It is a 1,1,1,2,2-pentafluoro-4,4'-bis(2-(pyridin-2-yl)thien-5-yl)-1,2-difluoroethane derivative. The structure consists of a central 1,1,1,2,2-pentafluoroethane core with two 2-(pyridin-2-yl)thien-5-yl groups attached to the 1 and 2 positions.

The ^{13}C NMR spectrum is displayed below the structure. The x-axis represents the chemical shift in ppm, ranging from 200 to 0. The spectrum shows several peaks corresponding to the different carbon environments in the molecule. The peaks are labeled with their chemical shift values in ppm:

- 150.718
- 148.177
- 147.676
- 143.852
- 142.718
- 140.343
- 139.414
- 139.162
- 131.552
- 129.940
- 129.564
- 128.025
- 127.714
- 126.549
- 126.443
- 126.280
- 124.953
- 123.845
- 119.752
- 77.200 (solvent)
- 14.992
- 14.874

S6

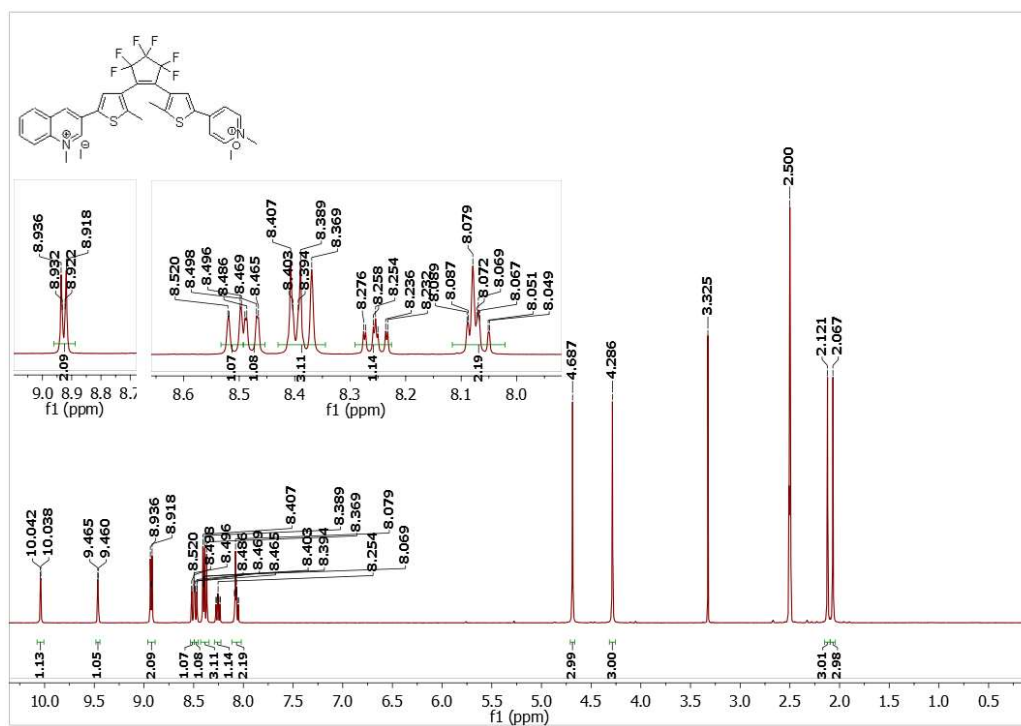


Figure S3. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of QuPy-I.

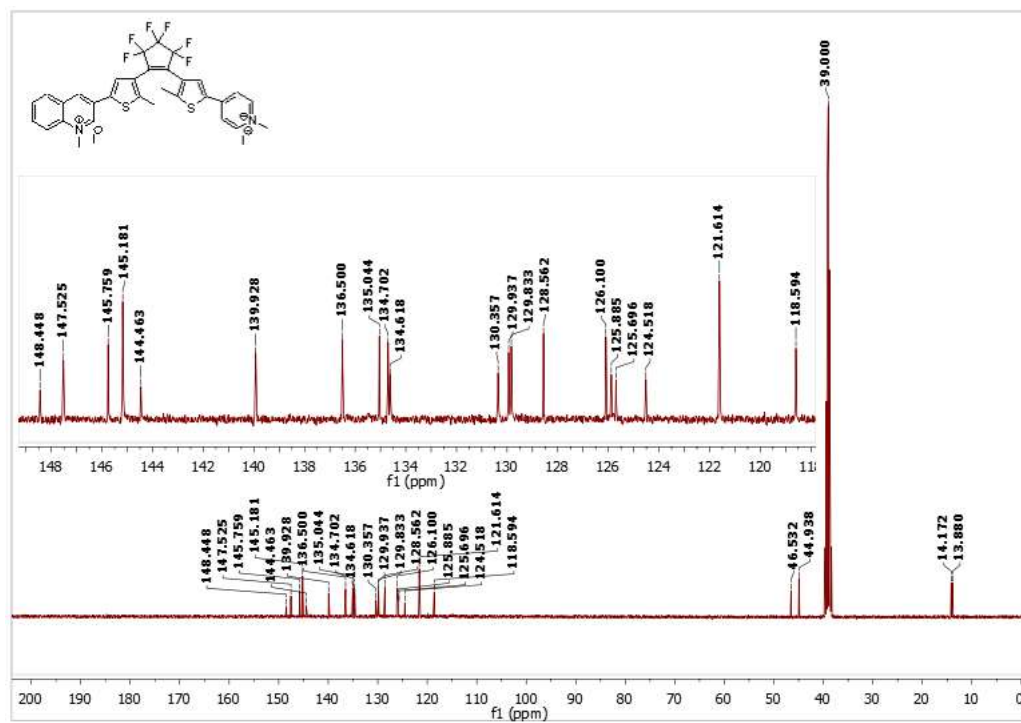


Figure S4. ¹³C NMR spectrum (101 MHz, DMSO-*d*₆) of QuPy-I.

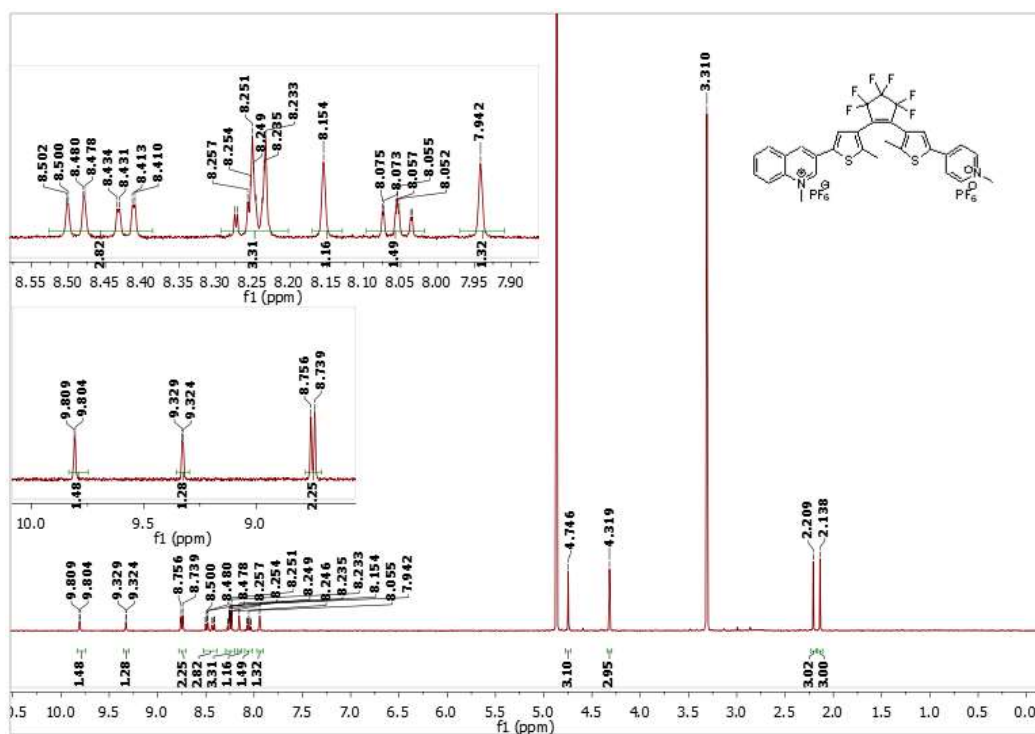


Figure S5. ¹H NMR spectrum (400 MHz, MeOH-*d*₄) of QuPy-PF₆.

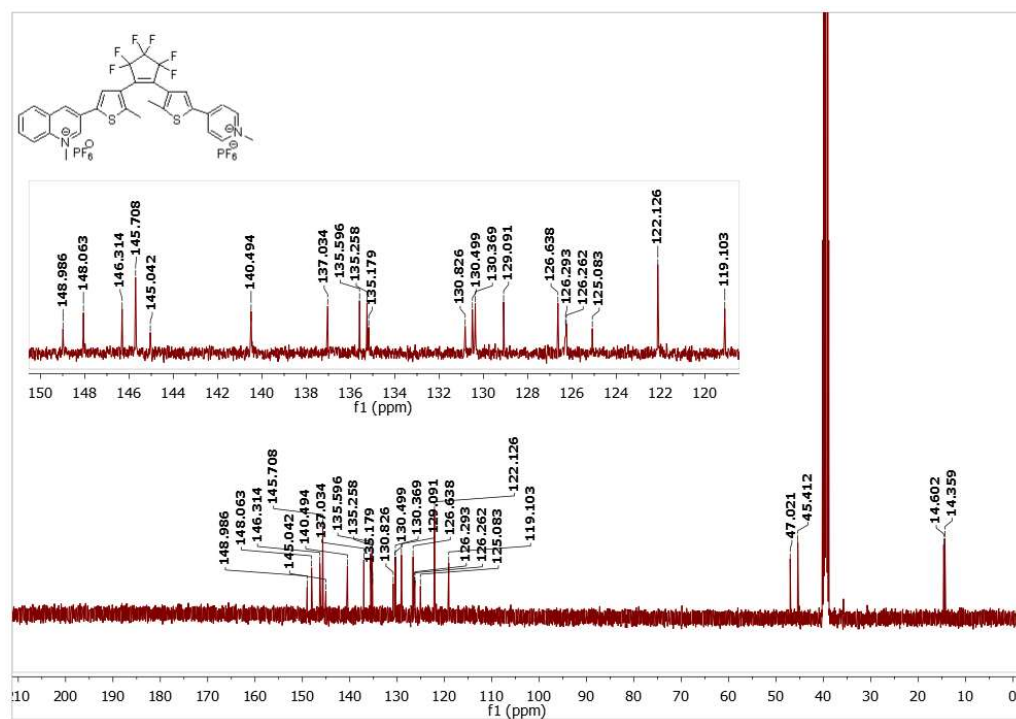


Figure S6. ¹³C NMR spectrum (101 MHz, DMSO-*d*₆) of QuPy-PF₆.

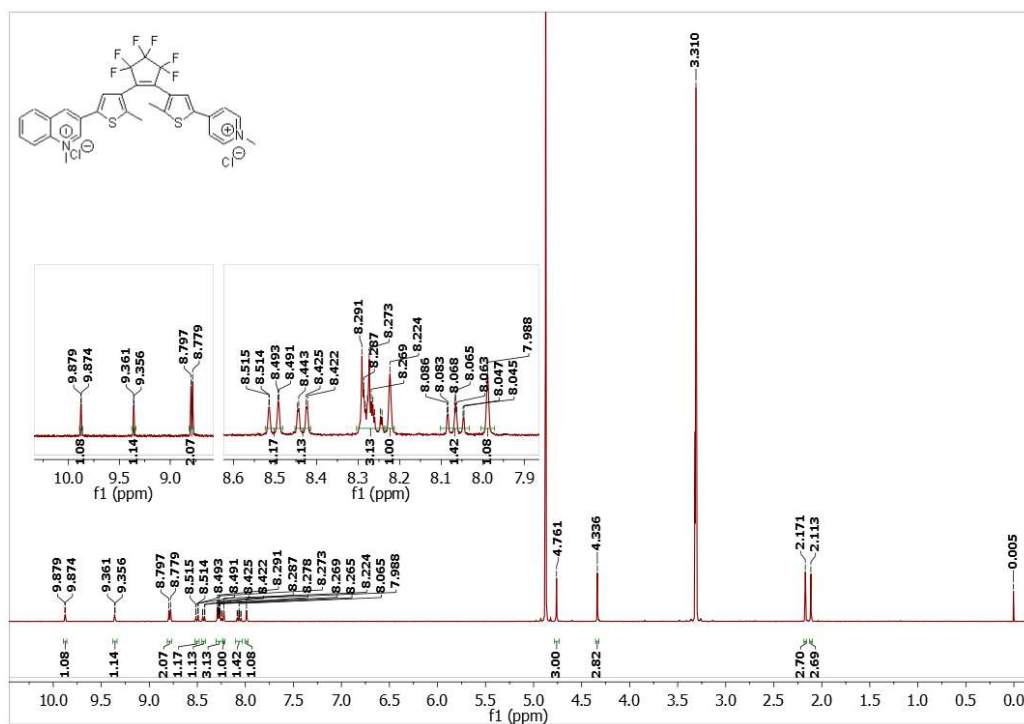


Figure S7. ¹H NMR spectrum (400 MHz, MeOH-*d*₄) of QuPy-Cl.

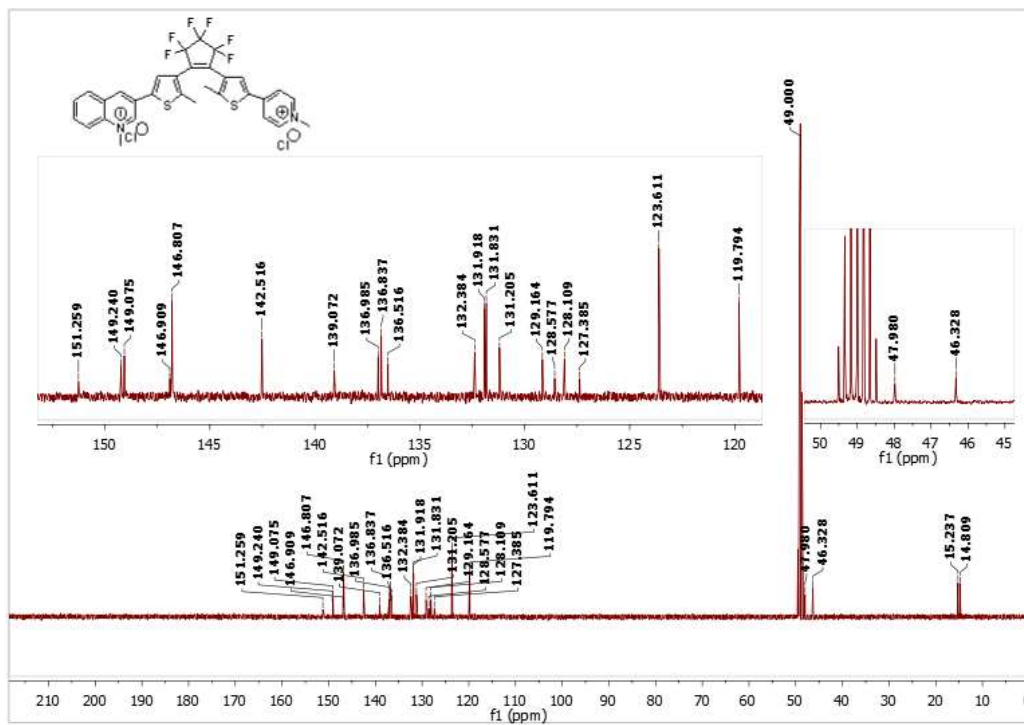


Figure S8. ¹³C NMR spectrum (125 MHz, MeOH-*d*₄) of QuPy-Cl.

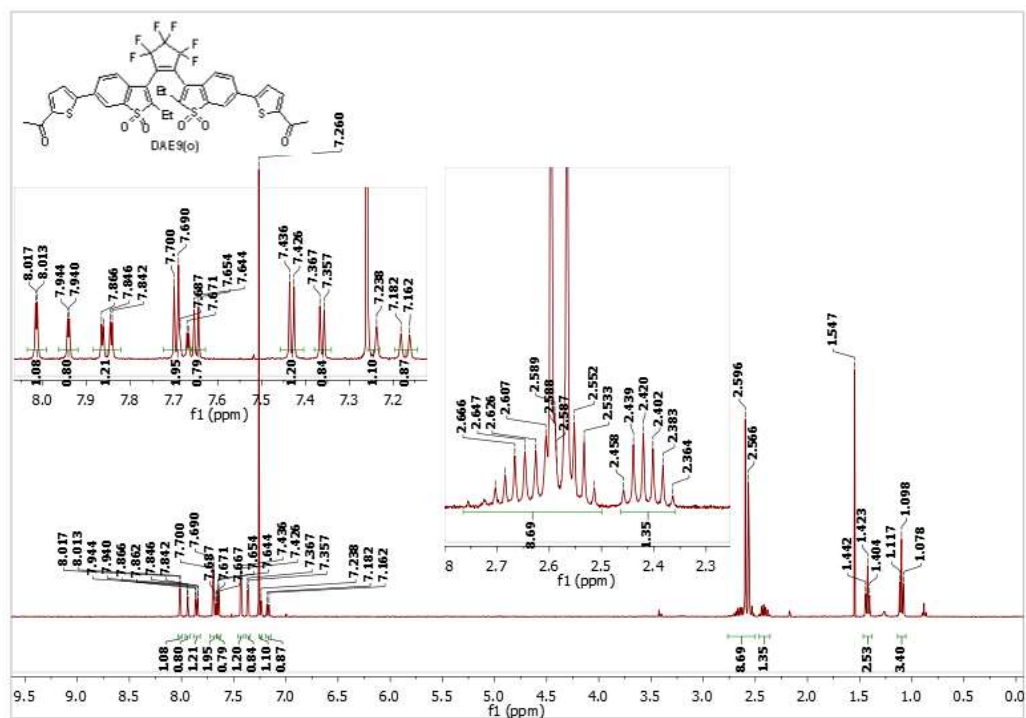


Figure S9. ¹H NMR spectrum (400 MHz, CDCl₃) of DAE9(o).

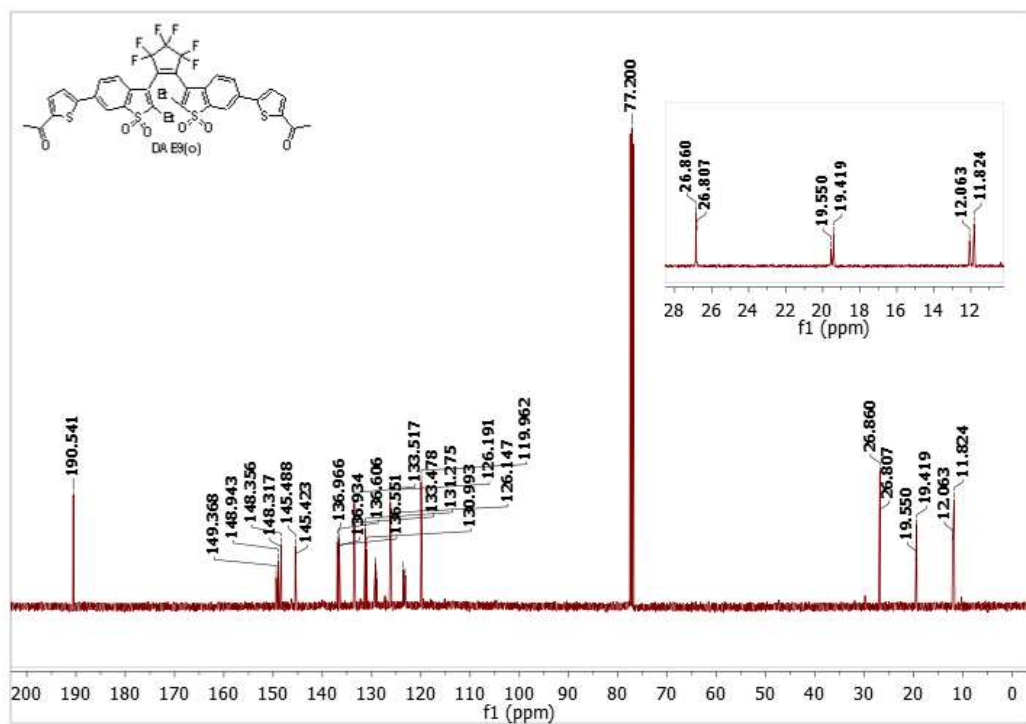


Figure S10. ¹³C NMR spectrum (101 MHz, CDCl₃) of DAE9(o).

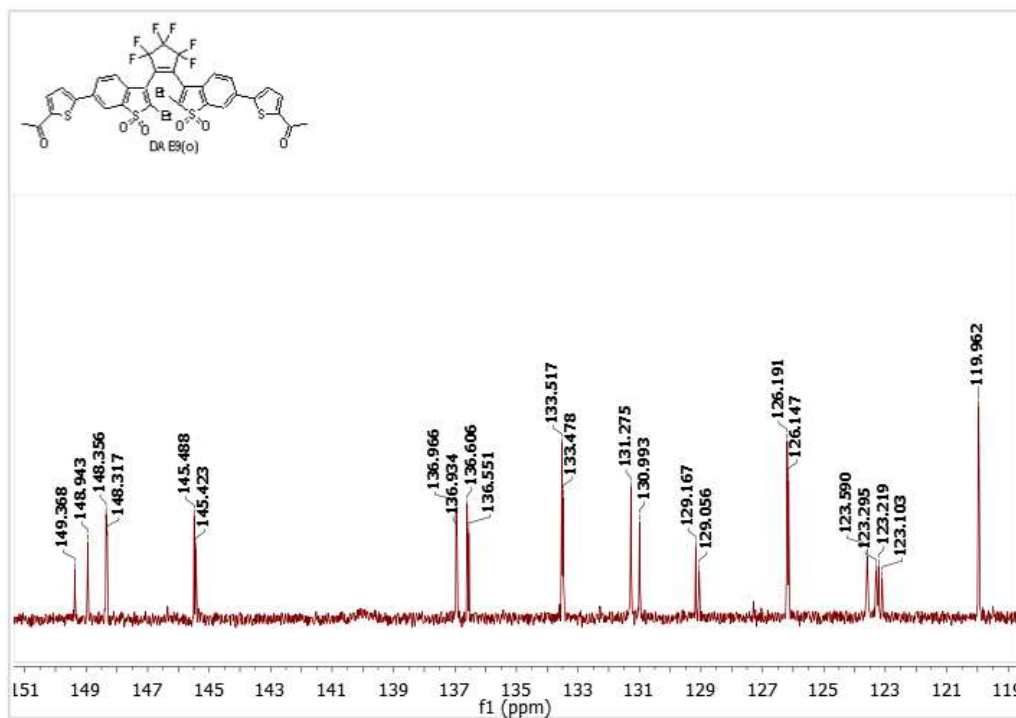


Figure S11. ^{13}C NMR spectrum (101 MHz, CDCl_3) of **DAE9(o)** (δ 120-150).

Experimental section (spectroscopy)

Ground state absorption spectra were recorded on a Cary 50 UV/vis spectrometer. Corrected fluorescence spectra were recorded on a SPEX Fluorolog-3 spectrofluorometer. Fluorescence lifetimes were measured using a time correlated single photon counting (TC-SPC) setup. The excitation light, $\lambda_{\text{exc}} = 377$ nm, was provided at a repetition rate of 20 kHz by a 377 nm diode laser (PicoQuant) and a MCP-PMT detector (5 000 counts in the top channel, 1024 channels). The emitted photons were collected at the magic angle (54.7°). The measured fluorescence decays were fitted using the program FluoFit Pro v.4 (PicoQuant GmbH, Germany) after deconvolution of the data with the instrument response function (IRF) with FWHM~90 ps.

The light for isomerization of the cocktail at 381 nm was provided by the 450W xenon lamp in the SPEX Fluorolog-3 spectrofluorometer after passage through the monochromator (4 nm spectral bandwidth).

The isomerization quantum yields for the ring-closing reactions were determined using UV light at 365 nm from a hand-held UV-lamp (UVGL-25, 1.5 mW/cm^2). The absorbance changes as a function of irradiation time were monitored and compared to those of the reference compound Furfylfulgide 2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride⁴ under identical irradiation power/geometries and corrected for the molar absorption coefficients at 365 nm. The isomerization quantum yield for **Dasy** may be inflicted with a larger uncertainty, as the absorption spectrum of **Dasy(o)** is dependent on the concentration and also displays changes with time. The latter observation signals either a change in the **Dasy(o)** conformation with time, alternatively the formation of dimers or higher order aggregates. Efforts to investigate this matter further were fruitless.

For fluorescence quantum yield determination, relative measurements using a SPEX Fluorolog-3 spectrofluorometer together with reference compounds were used (9,10-diphenylanthracene in cyclohexane, $\Phi_F=0.93$; perylene orange in CHCl_3 , $\Phi_F=0.99$).⁵

Finding the optimal experimental conditions

1) *Selecting the wavelength for isomerization to the colored forms.* It is desired that the photoswitches isomerize with comparable rates in order for a continuous color change to occur. This implies that $\epsilon(\text{open}) \times \Phi_{\text{iso}}$, i.e., the product of the molar absorption coefficient of the open isomer and the isomerization quantum yield (open→closed) should be matched for **Dasy** and **DAE9**. With Φ_{iso} for both compounds in hand (neglecting any wavelength dependence), the wavelength is chosen accordingly.

2) *Achieving a constant overall emission intensity throughout the isomerization (colorization) process.* At a given excitation light intensity, the overall emission intensity of the cocktail is proportional to

$$c(\text{Dasy(o)}) \times \epsilon(\text{Dasy(o)}) \times \Phi_{\text{em}}(\text{Dasy(o)}) + c(\text{DAE9(c)}) \times \epsilon(\text{DAE9(c)}) \times \Phi_{\text{em}}(\text{DAE9(c)}).$$

The first boundary condition is, of course, that the excitation light for emission readout must be chosen in a wavelength region where **Dasy(o)** and **DAE9(c)** have non-zero absorbance. Knowing $\Phi_{\text{em}}(\text{Dasy(o)})$ and $\Phi_{\text{em}}(\text{DAE9(c)})$, $c(\text{Dasy(o)}) \times \epsilon(\text{Dasy(o)})$ and $c(\text{DAE9(c)}) \times \epsilon(\text{DAE9(c)})$ should be chosen as to correct for the differences in the fluorescence quantum yields, Φ_{em} . This can be done by either choosing the excitation wavelength wisely to find the correct relations between $\epsilon(\text{Dasy(o)})$ and $\epsilon(\text{DAE9(c)})$ at a fixed concentration of the two photoswitches, alternatively changing the relative concentrations between them using a fixed excitation wavelength. Note, however, that in order to avoid FRET reactions interfering with the linear relation between fluorophore concentration and the corresponding emission intensity (neglecting any inner-filter effect), the concentration of the photoswitches must be such that the average nearest neighbor distance should be well below the critical Förster radius R_0 .

3) *Non-destructive readout.* The excitation light for emission readout should have minimal effect on the isomeric distribution of the photoswitches to achieve a good “color stability”. This implies that the excitation light for emission readout should be selected as to cause minimal isomerization, while still maintaining a sufficiently good signal-to-noise ratio of the emission spectra. Herein, the emission quantum yields of the photoswitches are fairly high, which allows us to excite for emission readout at a wavelength where the absorption of the photochromically most active forms are minimal, while still allowing for a constant overall emission intensity according to 2) above.

Supporting figures (spectroscopy)

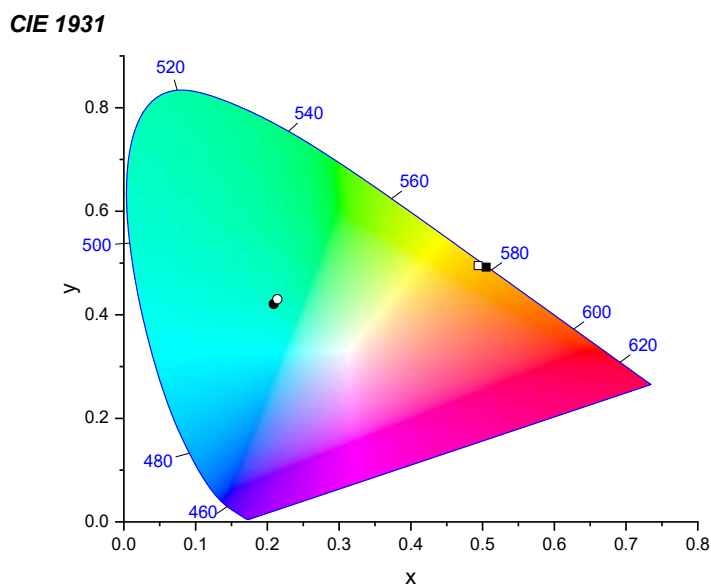


Figure S12. CIE coordinates for the emission from **Dasy(o)** alone (black circle) and **DAE9(c)** alone (black square) in acetonitrile. Also shown are the CIE coordinates for the emission from the **Dasy+DAE9** acetonitrile cocktail before (white circle) and after full exposure to 381 nm UV light. All spectra recorded upon excitation at 410 nm.

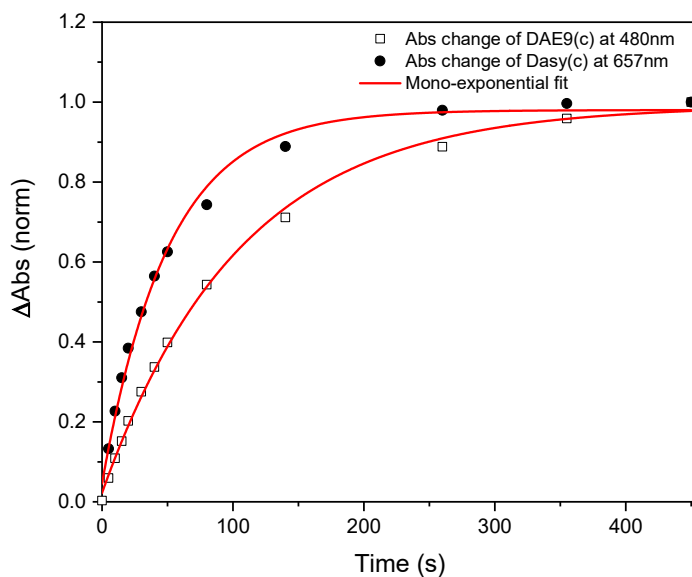


Figure S13. The kinetics of isomerization of **DAE9(o)** to **DAE9(c)** (solid circles) and **Dasy(o)** to **Dasy(c)** (hollow squares) in acetonitrile upon 381 nm irradiation. The kinetics is around twice as fast for **Dasy** (isomerization time constants = 50.5 s and 105.2 s for **Dasy** and **DAE9**, respectively). [**Dasy**] = ca. 35 μM , [**DAE9**] = 2.3 μM .

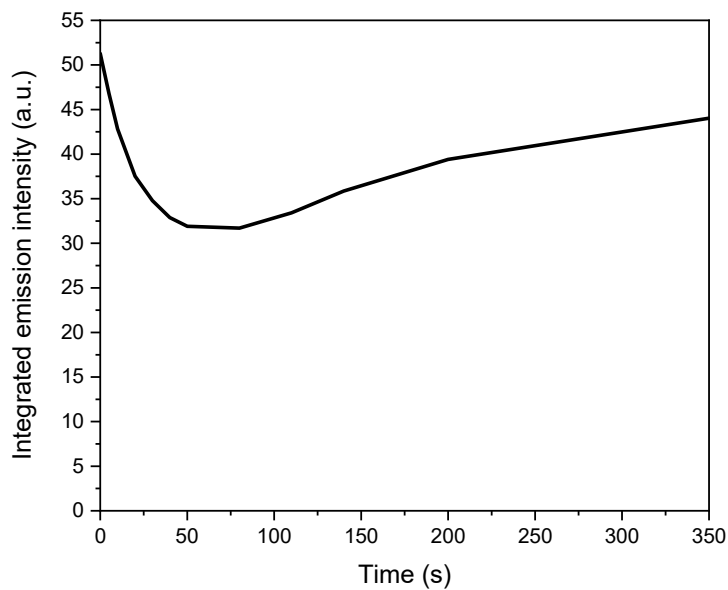


Figure S14. Changes in the overall integrated emission intensity for the **Dasy+DAE9** cocktail in acetonitrile upon increasing exposure time to 381 nm UV light. All spectra recorded upon excitation at 410 nm.

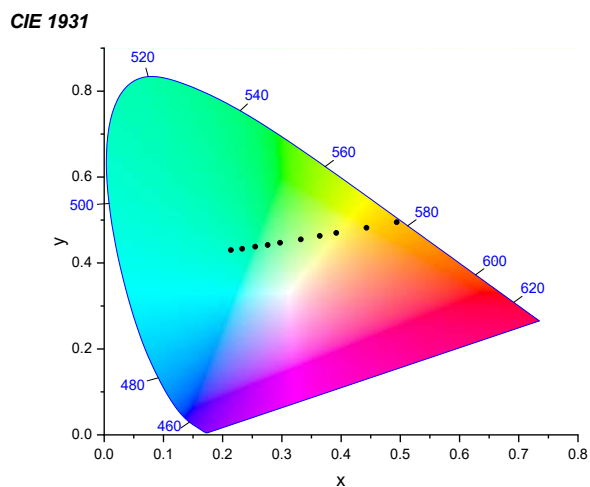


Figure S15. CIE coordinates for the spectra recorded upon isomerizing the **Dasy+DAE9** cocktail in acetonitrile using 381 nm light. Irradiation conditions from left to right: no irradiation, irradiation for 5s, 10s, 15s, 20s, 30s, 40s, 50s, 80s, and 350s. All spectra recorded upon excitation at 410 nm.

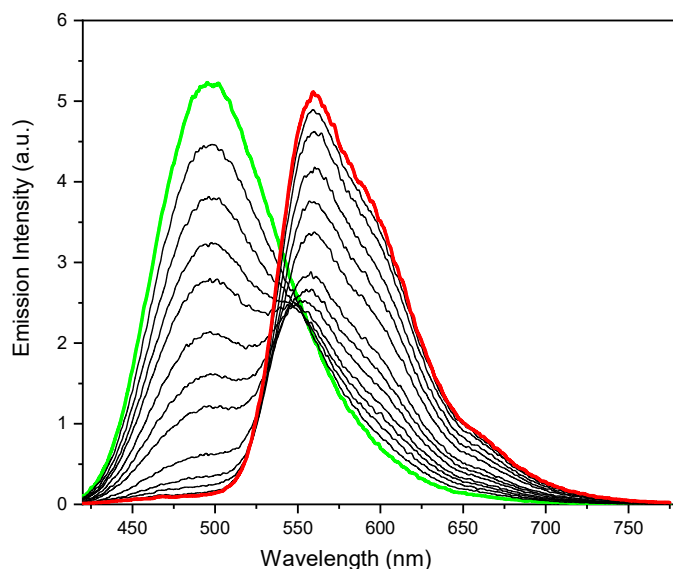


Figure S16. Second round of 381 nm isomerization to trigger the emission color changes for the cocktail. The sample has been reset to the initial form **Dasy(o)**+**DAE9(o)** using 523 nm light subsequent to the first round. All spectra recorded upon excitation at 410 nm after exposure to 381 nm light for 0 s, (green line), 5 s, 10 s, 15 s, 20 s, 30 s, 40 s, 50 s, 80 s, 110 s, 140 s, 200 s, 260 s, and 350 s (red line).

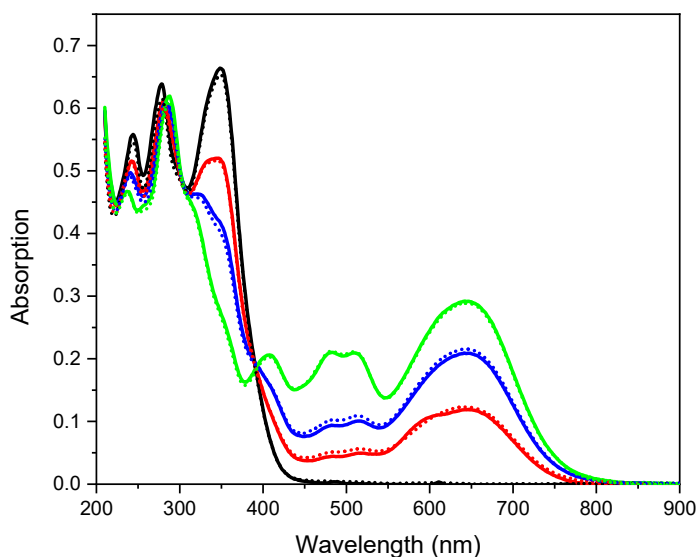


Figure S17. Absorption spectra of the **Dasy**+**DAE9** cocktail in acetonitrile recorded after exposure to 381 nm light for 0 s (black line), 20 s (red line), 50 s (blue line), and 350 s (green line). The solid lines are taken from the first isomerization cycle, and the dotted lines are taken from the second isomerization cycle.

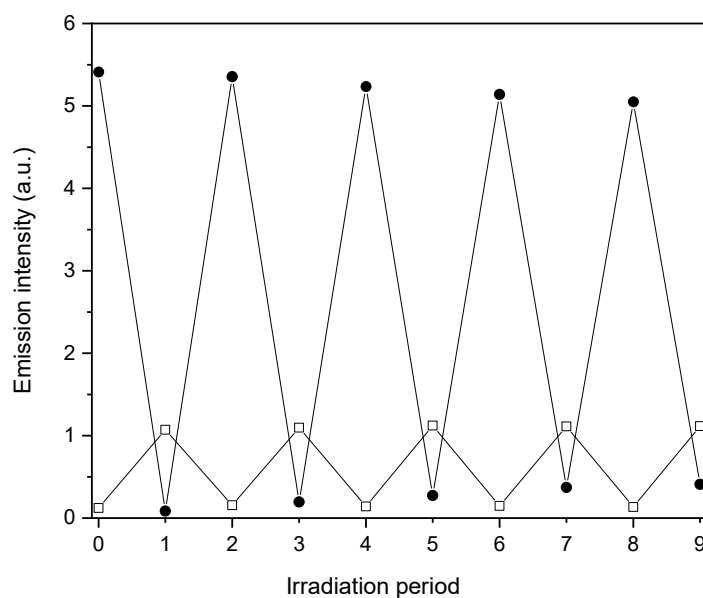


Figure S18. Photocycling of the cocktail. The emission intensity of **Dasy** and mainly **DAE9** was monitored at 494 nm (solid circles) and 649 nm (hollow squares), respectively. The sample was exposed to 381 nm light after irradiation periods 0, 2, 4, 6, and 8, while 523 nm light was applied after irradiation periods 1, 3, 5, and 7. All spectra were recorded upon excitation at 410 nm.

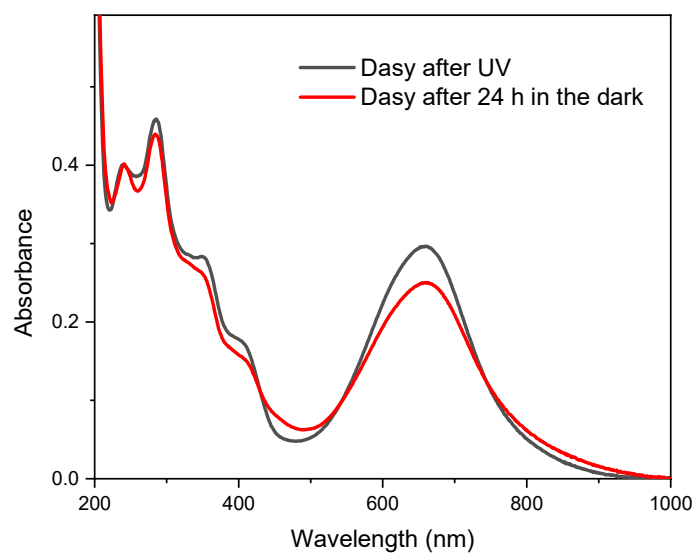


Figure S19. Absorption spectra of **Dasy** in acetonitrile after UV irradiation at 365 nm to yield the photostationary state (98.5:1.5 **Dasy(c):Dasy(o)**, black line) and after leaving the UV irradiated sample for 24 hours in the dark (red line).

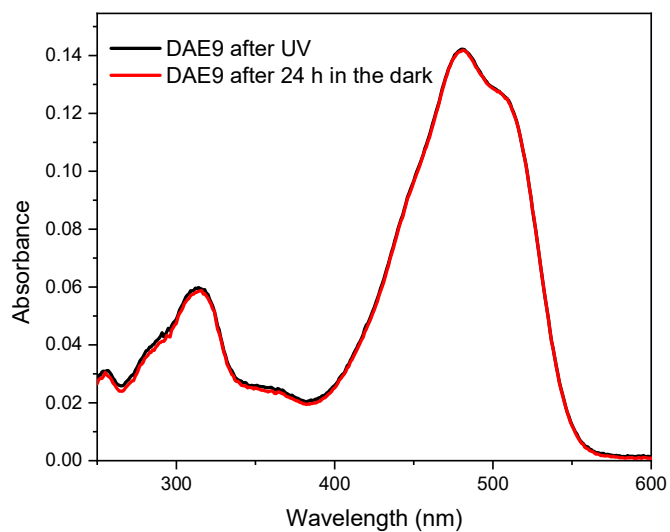


Figure S20. Absorption spectra of **DAE9** in acetonitrile after UV irradiation at 365 nm to yield the photostationary state (virtually 100% **DAE9(c)**, black line) and after leaving the UV irradiated sample for 24 hours in the dark (red line).

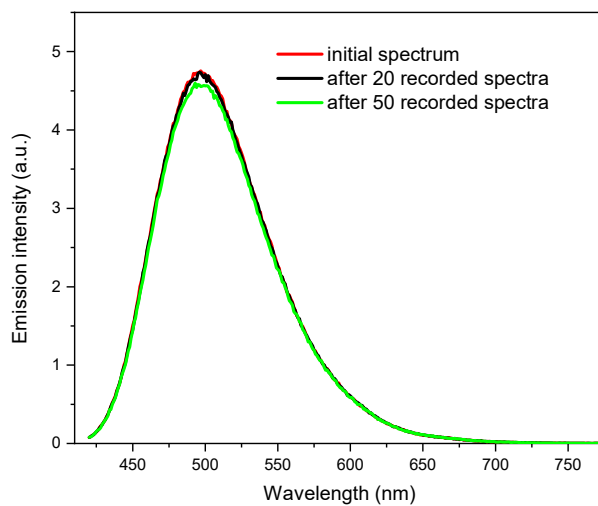


Figure S21. Color stability of the initial state (no exposure to 381 nm) for the cocktail **Dasy+DAE9**. The emission spectra in acetonitrile before (red line) and after exposure to 410 nm excitation light for a time period equivalent to recording 20 emission spectra (black line) and 50 emission spectra (green line) at this excitation wavelength.

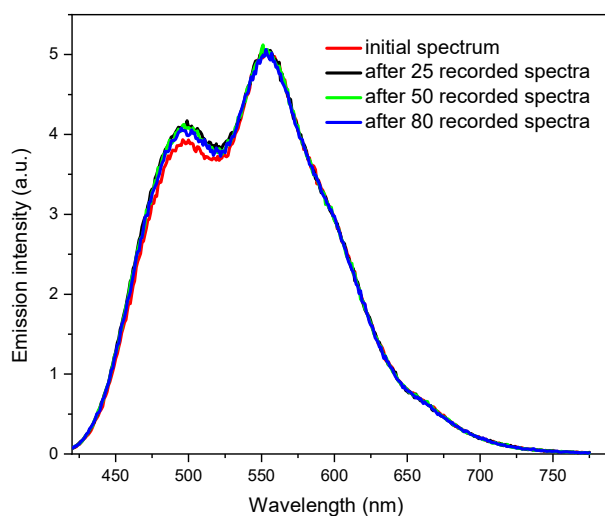


Figure S22. Color stability of an intermediate state (40 s exposure time to 381 nm light) for the cocktail **Dasy**+**DAE9**. The emission spectra in acetonitrile before (red line) and after exposure to 410 nm excitation light for a time period equivalent to recording 25 emission spectra (black line), 50 emission spectra (green line), and 80 emission spectra (blue line) at this excitation wavelength.

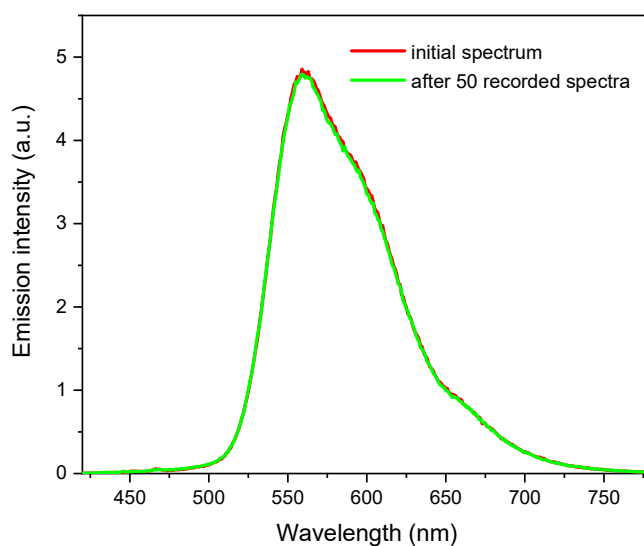


Figure S23. Color stability of the final state (350 s exposure time to 381 nm light) for the cocktail **Dasy**+**DAE9**. The emission spectra in acetonitrile before (red line) and after exposure to 410 nm excitation light for a time period equivalent to recording 50 emission spectra (green) at this excitation wavelength.

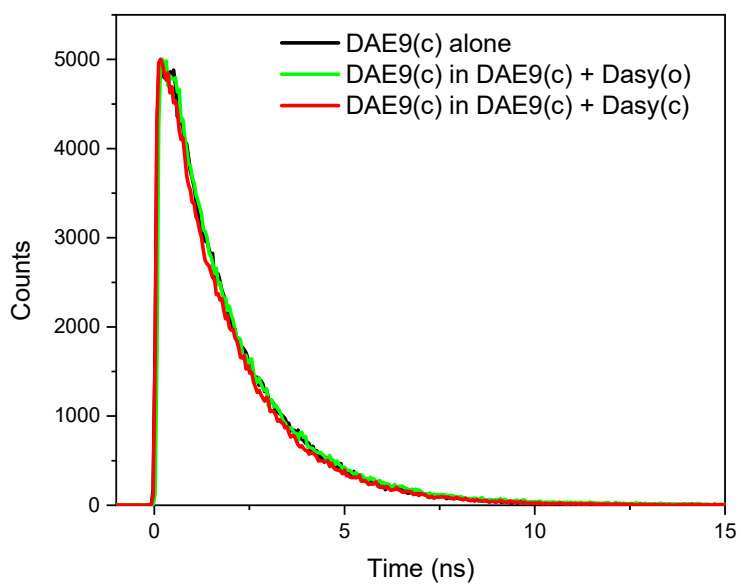


Figure S24. Time-resolved (SPC) fluorescence decays of **DAE9(c)**: alone (black line $\lambda_{\text{exc}} = 377$ nm, $\lambda_{\text{em}} = 560$ nm), **DAE9(c)+Dasy(o)** (green line $\lambda_{\text{exc}} = 377$ nm, $\lambda_{\text{em}} = 680$ nm) and **DAE9(c) in DAE9(c)+Dasy(c)** (red line $\lambda_{\text{exc}} = 377$ nm, $\lambda_{\text{em}} = 680$ nm).

Decay	τ (ns)	χ^2
DAE9(c) alone (black)	1.8	1.06
DAE9(c) in DAE9(c)+Dasy(o) (green)	1.8	1.27
DAE9(c) in DAE9(c)+Dasy(c) (red)	1.8	1.07

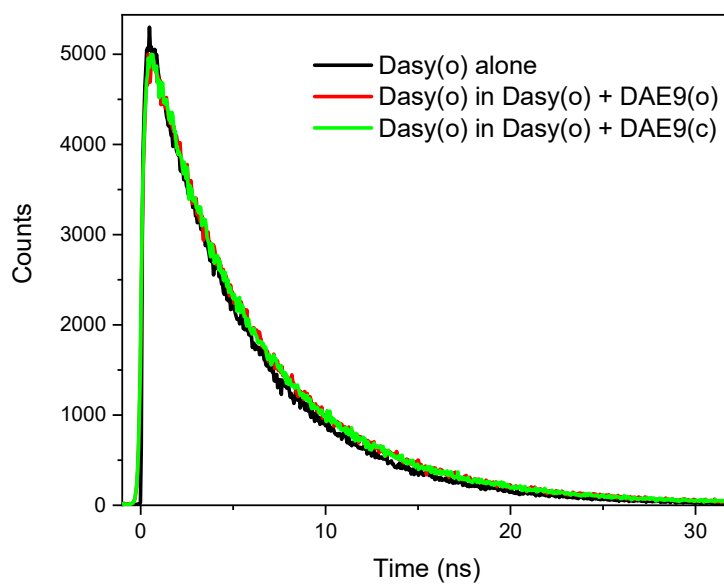


Figure S25. Time-resolved (SPC) fluorescence decays of **Dasy(o)**: alone (black line $\lambda_{\text{exc}} = 377$ nm, $\lambda_{\text{em}} = 495$ nm), **DAE9(c)+Dasy(o)** (green line $\lambda_{\text{exc}} = 377$ nm, $\lambda_{\text{em}} = 490$ nm) and **DAE9(c) in DAE9(c)+Dasy(c)** (red line $\lambda_{\text{exc}} = 377$ nm, $\lambda_{\text{em}} = 490$ nm).

Decay	τ (ns)	χ^2
Dasy(o) alone (black)	5.4	1.31
Dasy(o) in DAE9(o)+Dasy(o) (green)	5.8	1.15
Dasy(o) in DAE9(c)+Dasy(o) (red)	5.7	1.19

References

1. S. Hermes, G. Dassa, G. Toso, A. Bianco, C. Bertarelli and G. Zerbi, *Tetrahedron Lett.*, 2009, **50**, 1614-1617.
2. L. N. Lucas, J. J. D. de Jong, J. H. van Esch, R. M. Kellogg and B. L. Feringa, *Eur. J. Org. Chem.*, **2003**, 155-166.
3. K. Uno, H. Niikura, M. Morimoto, Y. Ishibashi, H. Miyasaka, M. Irie, *J. Am. Chem. Soc.* 2011, **133**, 13558-13564.
4. H. G. Heller, J. R. Lanagan, *J. Chem. Soc., Perkin Trans. 2.* **1981**, II, 341-343.
5. A. M. Brouwer, *Pure Appl. Chem.*, **2011**, 83, 2213-2228.