Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for

Ultrafast photophysics of the environment-sensitive 4′-methoxy-3-hydroxyflavone fluorescent dye

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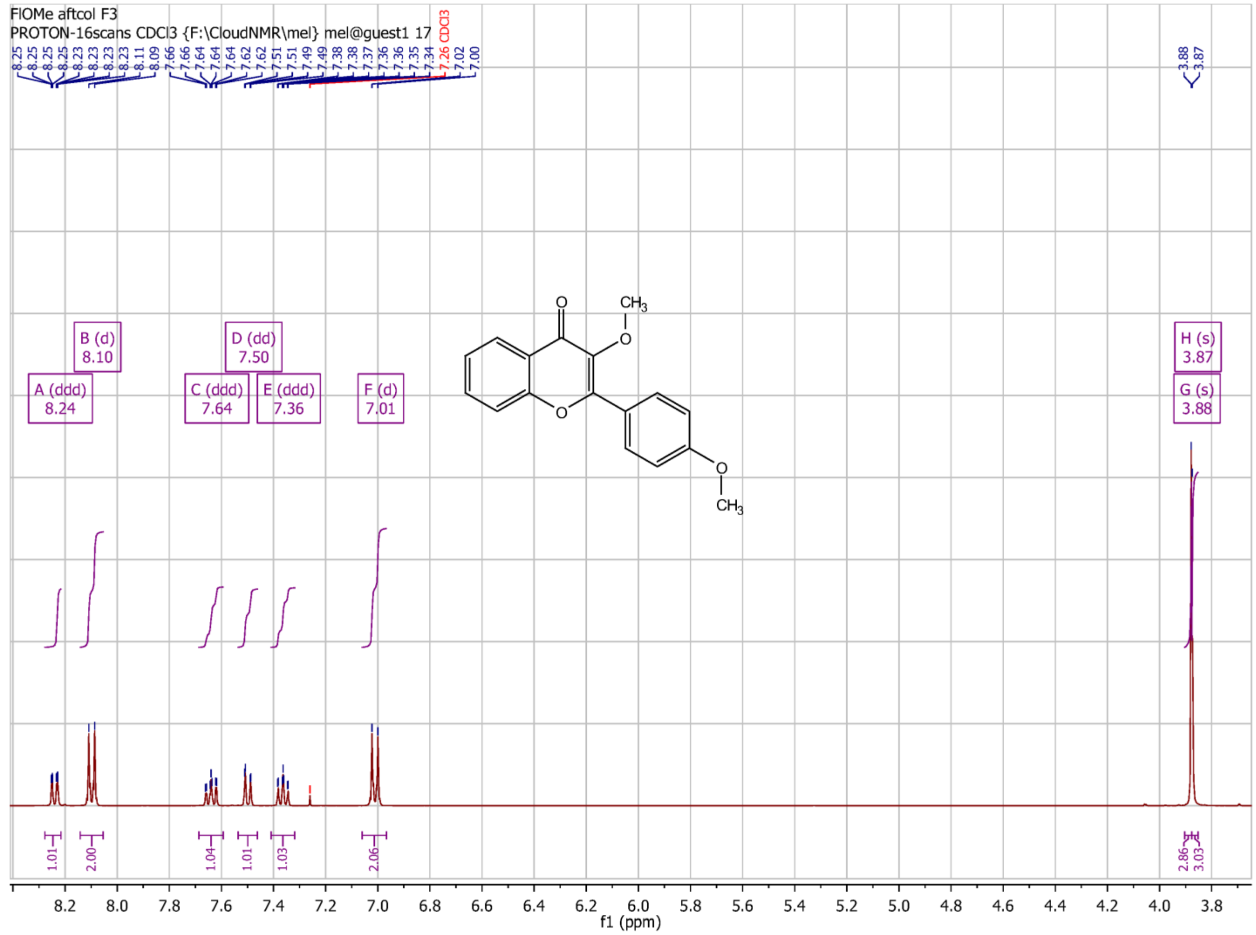


Figure S1. ^{1}H NMR spectrum of 4'-methoxy-3-methoxyflavone.

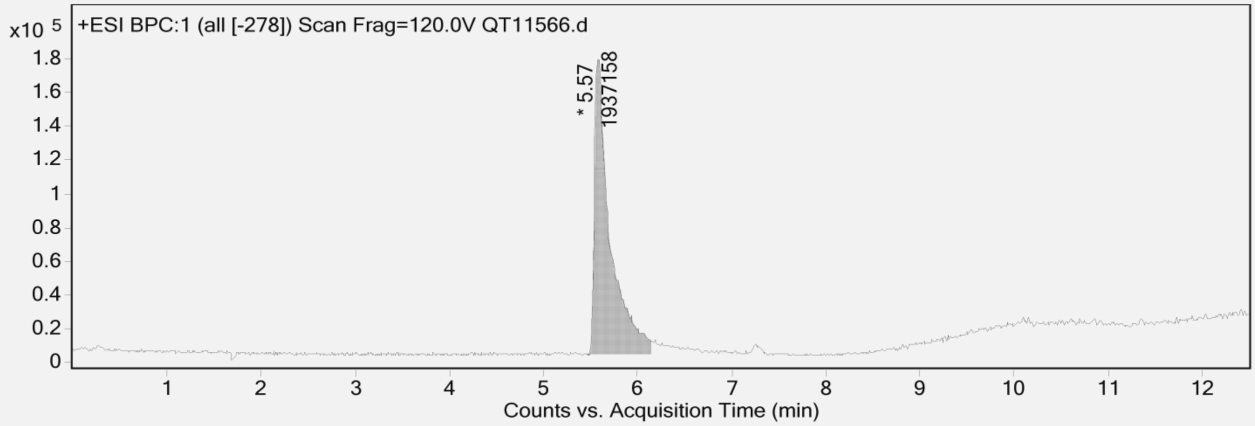
Qualitative Analysis Report

Data Filename	QT11566.d	**Sample Name**	FlOMe
Inj. Vol.	0.1	**Position**	P1-D1
Instrument Name	SCA Illkirch QToF	**User Name**	PW
Acq Method	C18-2,1x5x1,8.m	**Acquired Time**	12/18/2015 10:04:46 AM
IRM Calibration Status	Success	**DA Method**	C18-2,1x5x1,8.m
Comment			

Sample Group **Info.**

User Chromatograms

Fragmentor Voltage 120 **Collision Energy** 0 **Ionization Mode** ESI

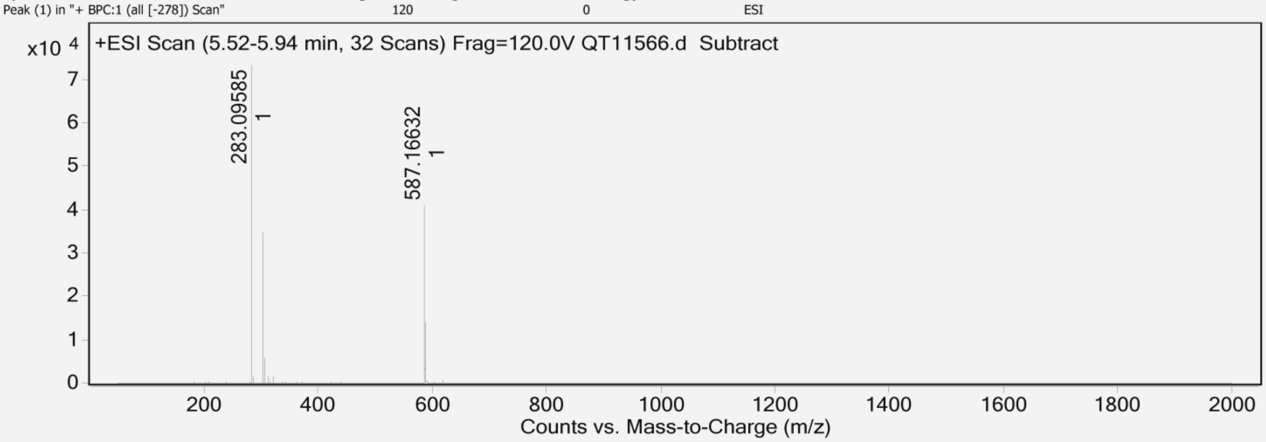


Integration Peak List

Start	RT	End	Height	Area	Area %	AreaSum%
5.46	5.57	6.14	174884	1937158	100	100

Qualitative Analysis Report

Spectrum Source	**Fragmentor Voltage**	**Collision Energy**	**Ionization Mode**
Peak (1) in "+ BPC:1 (all [-278]) Scan"	120	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
283.09585	1	76010.9	C17 H15 O4	(M+H)+
284.0991	1	12248.2	C17 H15 O4	(M+H)+
305.0776	1	34644.8		
306.0808	1	5931.1		
587.16632	1	41628.9	C34 H28 Na O8	(M+Na)+
588.16941	1	14080	C34 H28 Na O8	(M+Na)+

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Mz	Ion Species	Score
C17 H14 O4	TRUE	282.08857	282.08921	2.25	283.09585	C17 H15 O4	98.41
C34 H28 O8	TRUE	564.17709	564.17842	2.36	587.16632	C34 H28 Na O8	97.13

Figure S2. LCMS data of 4'-methoxy-3-methoxyflavone.

Supplementary Note 1: Relation between the ratio of the total N* and T* fluorescence intensities and the parameters of the rate equation model.

Within the model introduced in Figure 9, the time evolution of the excited state populations N*(t) and T*(t) can be written:

$$\frac{dN^*}{dt}(t) = -\frac{N^*(t)}{\tau_N} + k_- \, T^*(t)$$
$$\frac{dT^*}{dt}(t) = k_+ \, N^*(t) - \frac{T^*(t)}{\tau_T}$$

where τ_N and τ_T are the N* and T* lifetimes, i.e. the inverse of the sum of all radiative and non-radiative (nr) decay channels: ${\tau_N}^{-1} = k_N + k_+ + k_N^{nr}$ and ${\tau_T}^{-1} = k_T + k_- + k_T^{nr}$.

The ratiometric fluorescence detection approach measures the ratio $R=I_N/I_T$ between the measured fluorescence intensities of the N* and T* bands. By definition, the intensity of the N* band (and similarly for the T* band) can be written:

$$I_N = k_N \int_0^\infty N^*(t)\, dt$$

with k_N the radiative decay rate. Hence, instead of resolving the set of differential equations (as done e.g. in Shynhar et al., J. Phys. Chem. A, 2003, 107, 9522-9529), we may integrate both equations, which yields:

$$N_0 = \frac{I_N}{\tau_N \, k_N} - k_- \frac{I_T}{k_T}$$
$$0 = k_+ \frac{I_N}{k_N} - \frac{I_T}{\tau_T \, k_T}$$

with N_0, the population initially promoted to N* upon light absorption from N. The second line directly gives the ratio R between the total emission intensities in both bands:

$$R = \frac{I_N}{I_T} = \frac{k_N}{k_T} \frac{1}{\tau_T \, k_+}$$

Using in addition the first line allows us to conclude:

$$I_N = \frac{N_0 k_N \tau_N}{1 - k_+ k_- \tau_N \tau_T} \qquad \text{(Eq. 1)}$$

$$I_T = \frac{N_0 k_+ k_T \tau_N \tau_T}{1 - k_+ k_- \tau_N \tau_T} \qquad \text{(Eq. 2)}$$

Supplementary Note 2: Case study about the ratiometric detection of two sub-populations *a* and *b* characterized by distinct ESIPT rates

As described in the main text we may introduce:

$$R = \frac{I_{Na} + I_{Nb}}{I_{Ta} + I_{Tb}}$$

In the simplistic case of two subpopulations differing only by their ESIPT rates k_+ ($i.e. k_+^a \neq k_+^b$), with both ESIPT reactions occurring irreversibly ($k_- \sim 0$) and rapidly ($k_+ \tau_N \sim 1$ for each subpopulation), then Eq. 1 and 2 above can be written:

$$I_{Na} \sim \alpha N_0 k_N \tau_{Na} \sim \alpha N_0\, k_N / k_+^a, \qquad I_{Nb} \sim (1-\alpha) N_0 k_N \tau_{Nb} \sim (1-\alpha) N_0\, k_N / k_+^b$$

$$I_{Ta} \sim \alpha N_0 k_T \tau_T, \qquad I_{Tb} \sim (1-\alpha) N_0 k_T \tau_T$$

with α and $(1-\alpha)$ the relative proportions of species *a* and *b*, respectively.

And finally:

$$R \sim \alpha\, \frac{k_N}{k_T}\, \frac{1}{\tau_T\, k_+^a} + (1-\alpha)\, \frac{k_N}{k_T}\, \frac{1}{\tau_T\, k_+^b}$$