Electronic supplementary information for

The Effect of Methylation on the Intrinsic Photophysical Properties of Simple Rhodamines by Jocky C. K. Kung, Adam Forman, and Rebecca A. Jockusch* Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada

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Figure S1 Fluorescence Emission spectra of all of the rhodamine derivatives (a) (λ_{ex} for Rh123 and Rh-10M: 430 nm, for the others: 450 nm) and fluorescence excitation spectra of Rh123, Rh-10M, Rh-21M and TMRM (b). The dashed line on each excitation spectrum is a guide to the eye, generated by reflecting and scaling the emission spectrum of each derivative by a factor of 1, 0.96, 0.88 and 0.76 respectively.



Figure S2 Time-resolved fluorescence of gaseous Rh123 (a), m/z 373 ions from fraction 2 (b), Rh-21M (c) and TMRM (d) with the coloured line representing the best fit and residuals for the fit shown below each curve. Bumps present after 12.5 and 25 ns of the initial rise in signal are due to incomplete pulse picking and has been accounted for in our fitting function.



Figure S3 Fluorescence excitation (dashed lines) and emission (solid lines) spectra of a) Rh123 in the gas phase, b) Rh123 in methanol,¹ c) TMRM in the gas phase and d) tetramethylrhodamine in methanol.²

- 1. Rhodamine 123, 25 mg Thermo Fisher Scientific https://www.thermofisher.com/order/catalog/product/R302.
- 2. Tetramethylrhodamine, Methyl Ester, Perchlorate (TMRM) Thermo Fisher Scientific https://www.thermofisher.com/order/catalog/product/T668.



Figure S4 Fluorescence emission spectra of gaseous Rh123 (a), Rh-10M (b), Rh-21M (c) and TMRM (d) (transparent) which have been fitted with a function (solid line) that is the sum of two Gaussian functions (orange and red solid line).

Function for the Gaussian fits of emission spectra, as shown in Figure S4:

$$y = y_0 + \frac{A}{w\sqrt{\pi/2}}e^{-2\frac{(x-x_c)^2}{w^2}}$$

Where x_c is the centre of the Gaussian function, A is the area, w is the Full width at half maximum. In the fits, maximum width of Peak 1 and 2 were fixed at 950 and 1500, respectively.

	Peak 1			Peak 2			
	X _c	W	A	X _c	w	Α	A_1/A_2
Rh123	21000	950	855	20000	1500	978	0.87
Rh-10M	20500	852	881	19500	1500	850	1.04
Rh-21M	19400	867	947	18400	1500	673	1.41
TMRM	18900	944	1047	17900	1500	548	1.91

Table S1 Fitted values for the two Gaussian fits shown in Figure S4.