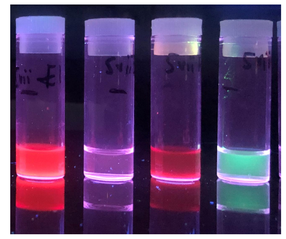
ARE GREEN ROUTES TO RED MOLECULES REAL?
Sustainability and cost-effectiveness studies on the synthesis of high-value infrared emitting materials



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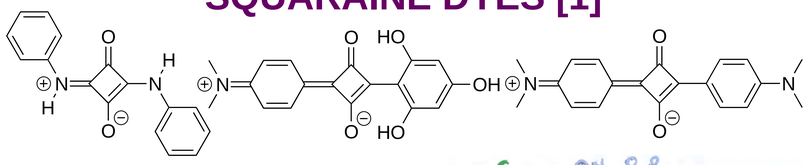
SQUARAINE DYES [1]



APPLICATIONS

(BIO)IMAGING

(BIO)SENSORS, LABELS & PROBES

OPTOELECTRONICS

PHOTODYNAMIC & PHOTOTHERMAL THERAPIES

RATIONALE FOR BETTER SYNTHESES

In general, the costs associated with the synthesis, isolation, and purification of high value molecules & materials as well as environmental & health concerns related to the overall process are disregarded due to perceived profits that could be obtained from the use of the final products.

As the scale of production of these materials increases, the amounts of toxic waste will increase as well! Thus, there is an urgent need for more environmentally benign, sustainable, inexpensive, yet still facile and efficient synthetic routes.

GREEN METRICS THAT MATTER [2]

Environmental factor (**E-factor**)*

$$\textbf{E-factor} = \frac{\textbf{total mass of waste (g)}}{\textbf{mass of product (g)}}$$

Cost of Academic Methodology – All Inclusive (**CAM–AI**)*

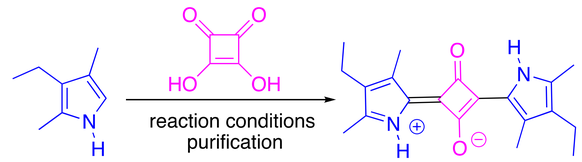
$$\textbf{CAM–AI} = \frac{\textbf{Σ cost of all chemicals \& solvents (\$ mol}^{-1}\textbf{)}}{\textbf{yield of product}}$$

Important (but should matter less): yield, atom economy, reaction mass efficiency; carbon efficiency

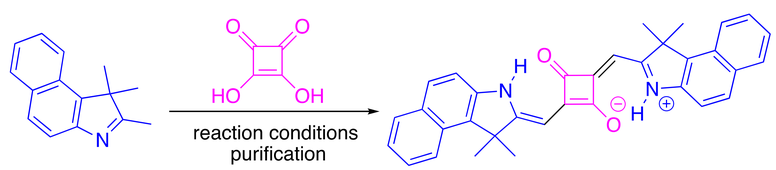
*** It is all relative; but the smaller numbers are desired!!**

GREEN SYNTHETIC METHODS
mechanochemistry/grinding & solvent-free

SOLVENTS FOR SQUARAINE SYNTHESIS



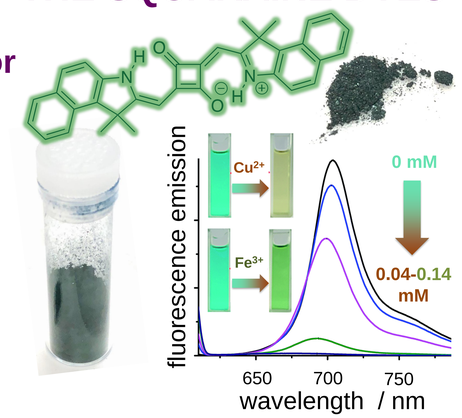
reaction conditions	purification	E-factor	CAM–AI
toluene/n-butanol Dean-Stark, 7h, reflux	precipitation & wash w/ org. solvents	874	**23,982**
ethylene glycol 150°C, 15min	precipitation & wash w/water	**1,001**	**9,245**
water, reflux, 7h	wash w/water, recrystallization	322	17,898
grinding, 15 min, rt	recrystallization	**57**	10,651



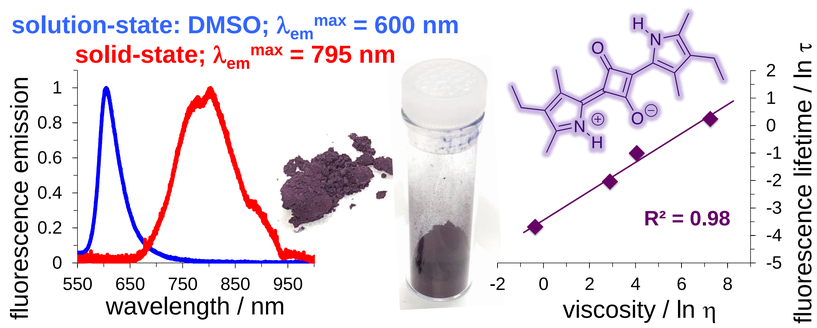
reaction conditions	purification	E-factor	CAM–AI
toluene/n-butanol Dean-Stark, 7h, reflux	precipitation & wash w/ org. solvents	715	**22,102**
polyethylene glycol 150°C, 5h	precipitation & wash w/water	**3,287**	28,668
polyethylene glycol 150°C, 5h	precipitation/wash, chromatography	2,962	75,256
solvent-free, 150°C, 2.5h	wash w/ org. solvents	**688**	**177,617**

APPLICATIONS OF THE SQUARAINE DYES

pH & metal ion sensor



dual-state emitter & molecular viscometer



"greenness" comes at a cost & generates waste

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[2] a) R.A. Sheldon, *ACS Sustainable Chem. Eng.* **2018**, *6*, 32; b) O. Berger, K.R. Winters, A. Sabourin, S.V. Dzyuba, J.-L. Montchamp, *Org. Chem. Front.* **2019**, *6*, 2095.

[3] a) Y. Wang, C. Wang, S. Xue, Q. Zhang, Z. Li, S. Xu, *RSC Adv.* **2016**, *6*, 6540; b) D.D. Ta, B. Lee, B.J. Janesko, Z.K. Gryczynski, S.V. Dzyuba, **2024**, *unpublished results*.

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