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Glycols as novel solvents for synthesis of squaraine dyes

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ABSTRACT

Glycols are non-volatile, non-flammable solvents for efficient, facile, and environmentally benign syntheses of various types of symmetric and non-symmetric squaraine dyes, thus providing a viable alternative to conventionally used n-butanol/toluene system.

1. Introduction

Squaraine dyes (Fig. 1) are considered privileged small-molecule fluorescent dyes due to their unique and tunable photophysical properties. Their applications extend across various fields, including chemical, biological, materials, and energy-related areas of modern sciences [1]. Thus, the development of versatile, efficient, and sustainable synthetic methods for these dyes is crucial. This should not only enhance the utilization of these materials, but also facilitate a broader integration of squaraine dyes into various fields. For example, squaraines were recently shown to be photocatalysts for several organic reactions [2].

Squaraine dyes are commonly synthesized via condensation reactions involving squaric acid (or alkyl squarate or dichloro-derivative) with various nucleophiles, employing n-butanol/toluene (n-BuOH/PhMe) mixtures as solvents, with azeotropic removal of water (Scheme 1, top; for some syntheses that employ other solvents and alternative heating methods, see Table S1) [1,3]. While both solvents are deemed "acceptable" from the industrial point of view [4], their high volatility, flammability (for n-BuOH and PhMe), and toxicity (for PhMe) warrant a search for alternatives (Fig. S1). It is noteworthy that several protocols relying on deep-eutectic solvents and mechanochemical approaches had been explored for the "greener"/more environmentally friendlier syntheses of squaraine dyes [5]. However, the limited scope and moderate efficiencies, especially when compared to the conventional n-BuOH/PhMe solvent mixture, necessitate further studies. Additionally, given the escalating demands for a) larger quantities of squaraine type scaffolds, and b) increase of structural/functional diversity of squaraines in line with their expanding applications, there is a need for the development of alternative, benign, facile and efficient synthetic approaches towards squaraine dyes.

2. Results and discussion

During our studies on the synthesis of pyrrole-containing semisquaraines [6], we discovered that condensation of 2,4-dimethylpyrrole with squaric acid produces symmetric squaraine **1** in water as the major product even in the presence of large excess of squaric acid (Scheme 1, bottom). This suggested that water could be a viable solvent for the synthesis of **1**. It should be noted that synthesis of some amino-containing semisquaraines and squaraines (i.e., N/N-squaraines, Fig. 1) in water was reported [7], yet synthesis of C/C-squaraines in water has not been explored. Thus, we decided to investigate the synthesis of **1** in water in more detail (Tables 1 and S2).

By varying the reaction time and concentration (Table S1), allowed to obtain dye **1** in good yield within 75 min of reflux in water (Table 1, entry 1). However, we noted that reactions in water often proceeded with the formation of "sticky" oily solids, which caused some inconvenience during the work-up/isolation step. Furthermore, recognizing that many other organic nucleophiles that are suitable for making squaraine dyes might have a limited solubility in water, we decided to explore the use of various hydroxyl-containing solvents for the synthesis of **1**. Notably, the use of EtOH, and n-BuOH as solvents for the synthesis of squaraine dyes was reported in several accounts [6,8], yet other hydroxy-containing solvents were not explored. Therefore, we investigated the ability of several hydroxy-containing liquids to act as solvents for the synthesis of **1** (Table 1, entries 2–14).

We found that **1** could be produced in relatively high yields in EtOH, i-PrOH, n-BuOH, and n-decanol in a relatively short period of time (Table 1, entries 2–5). The use of ethylene glycol (EG, entry 6), and propylene glycol (PG, entry 7) gave **1** in moderate, and similar yields. However, when reaction temperature was increased to 150 °C, dye **1** was obtained in 90 % yield using EG as the solvent (Table 1, entry 8). The process was found to be scalable without any impact on the yield as

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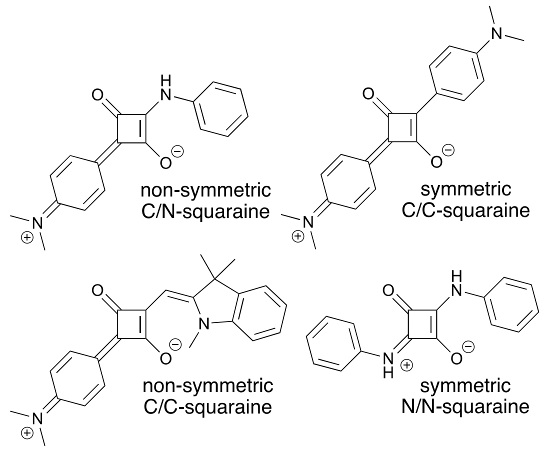
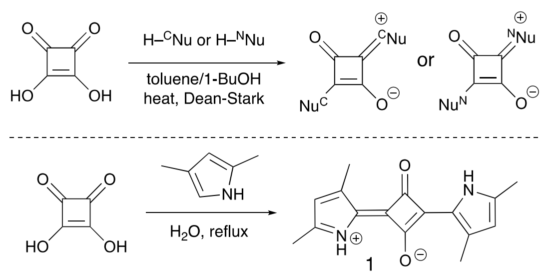
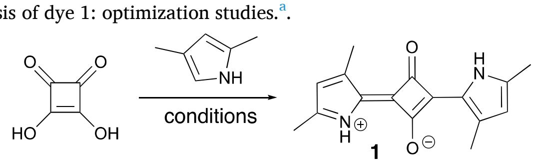


Fig. 1. General structures of symmetric and non-symmetric squaraine dyes. C–C and C–N connections to the four-membered core designated as C/C, C/N and N/N.



Scheme 1. Top: literature, general routes to symmetric squaraines; ^{C}Nu and ^{N}Nu refer to nucleophiles that form either C–C or C–N bonds to the squaraine core. Bottom: synthesis of squaraine **1** in water as a solvent.

Table 1
Synthesis of dye 1: optimization studies.[a].



entry	Solvent	Temp., °C	Time, min	Yield, %
1	H_2O	100	75	85
2	EtOH	78	15	75
3	i-PrOH	82	15	77
4	n-BuOH	118	15	71
5	n-decanol	120	15	68
6	EG[b]	120	15	72
7	PG[c]	120	15	75
8	**EG**	**150**	**15**	**90**
9[d]	**EG**	**150**	**15**	**87**
10	EG	200	15	–[g]
11	DEG[e]	150	15	62
12	PEG200[f]	150	15	82
13	PEG400[f]	150	15	67
14	glycerol	150	15	77

a) 0.10 M;b) EG = ethylene glycol.
c) PG = propylene glycol.
d) 1 g-scale reaction.
e) complex mixture (**1** was not isolated).
f) DEG = diethylene glycol.
g) PEG200 and PEG400 are polyethylene glycols with an average MW of 200 and 400 g/mol, respectively.

judged by the high yield of the scaled-up reaction for dye **1** (entry 9). Further increase in temperature (entry 10) proved detrimental. Other glycols (entries 11–13) and glycerol (entry 14) appeared to be viable solvents for the synthesis of **1** as well, albeit inferior to EG.

The use of glycols as solvents in organic synthesis is well documented [9]. Furthermore, glycols are non-volatile and possess low-toxicity, making them potentially greener and more sustainable alternatives to the conventionally used n-BuOH/PhMe solvent system for the synthesis of squaraine dyes (Fig. S1). Furthermore, glycols might be a better solvent fit within the 12 principles of Green Chemistry, specifically those that are related to waste, solvents, reaction times, and inherently safer processes (Table S3). Additionally, adopting a single solvent rather than a mixture of solvents enhances robustness and operational simplicity of the process, especially for larger scale reactions.

In view of promising results (Table 1, entries 8 and 9), we decided to explore the notion as to whether glycols could be used as general solvents for syntheses of various squaraine dyes. In order to cover most widely used types of squaraine dyes, the following nucleophiles were considered: pyrroles, indoles, electron-rich benzene derivatives, and indolenine/indolinium-based compounds. Notably, the choice of nucleophiles was primarily driven by the accessibility of starting materials, electronic effects of the substituents, etc rather than by the perceived photophysical properties of the final dyes, in order to establish viability of glycols as solvents for various types of squaraine dyes.

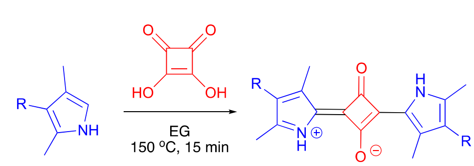
Pyrrole-containing squaraines have found numerous applications in sensing, photovoltaics and photocatalytic processes 8a,10. Thus, several pyrrol-2-yl containing dyes were prepared using EG as the solvent (Scheme 2). Specifically, 3-ethyl-2,4-dimethylpyrrole (i.e., kryptopyrrole) and 3-acetyl-2,4-dimethylpyrrole produced the corresponding squaraine dyes **2** and **3** (Scheme 2) in good yields and significantly shorter period of time (minutes versus hours) when compared to literature accounts [11].

Indole-containing dyes have been a relatively underexplored class of squaraine dyes, yet based on the properties of some reported compounds [12], these dyes would be a valuable addition to the family of squaraine dyes. Thus, we examined the synthesis of indole-containing squaraine dyes in the glycols (Scheme 3).

Various substituted indoles provided the corresponding squaraines **4**–**9** in moderate yields upon simply heating the indoles with squaric acid in EG (Scheme 3). Indoles bearing strong electron-withdrawing groups proved to be inefficient nucleophiles, and dyes **10** and **11** were not obtained (the starting materials were recovered). Furthermore, to our surprise, reaction between indole and squaric acid produced minute amounts of dye **12** only upon some optimization (Table S4). Arguably, the incurred issues with the synthesis of some indol-3yl-containing squaraine dyes might be more related to the specific substrates, rather than to the nature of the solvent.

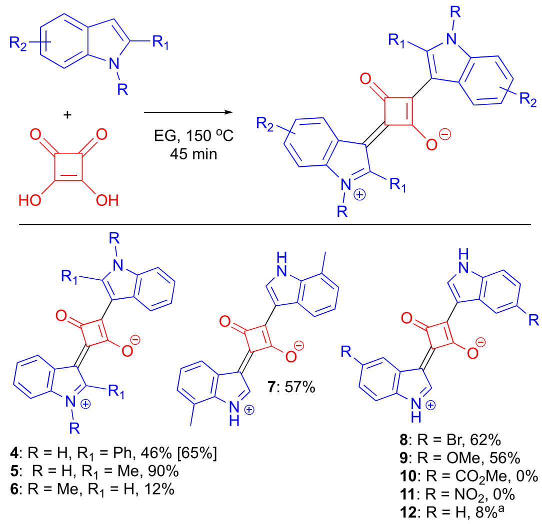
Recently, indolizine-containing squaraine dyes have been a valuable addition to the family of small molecule probes and imaging agents [13]. Here, when indolizine was used as a nucleophile towards squaric acid in EG, the corresponding squaraine **13** was obtained in a relatively short period of time and a good yield (Scheme 4).

Electron-rich nucleophiles have been shown to be viable substrates for preparing squaraine dyes with wide utility [14]. Thus, we used several electron rich C–H nucleophiles for the synthesis of the corresponding squaraine dyes (Scheme 5). Specifically, dyes **14**–**16** were

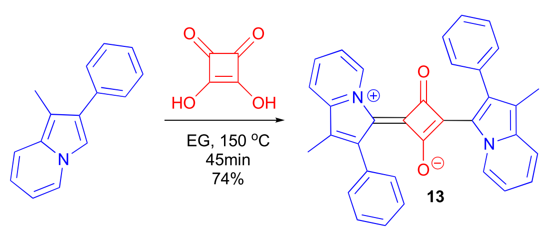


2: R = Et; 90%
3: R = CO_2Et; 59%

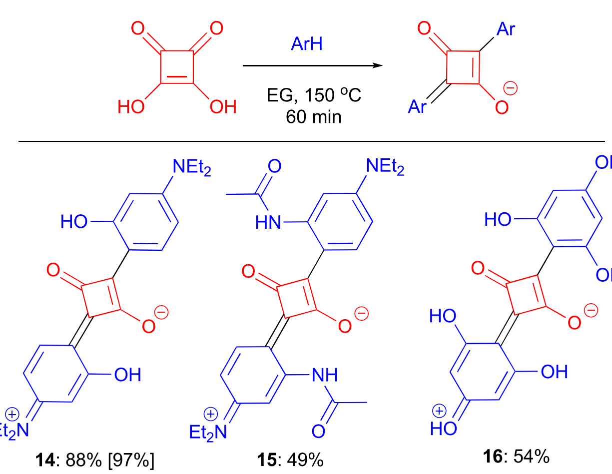
Scheme 2. Synthesis of pyrrole-containing symmetric squaraine dyes.



Scheme 3. Synthesis of indol-3-yl-containing symmetric squaraine dyes in EG. The yield of a 1g-scale reaction for dye **4** is given in brackets. [a] Reaction time: 5 min; see Table S4 for details.



Scheme 4. Synthesis of indolizine-based squaraine dye **13** in EG.

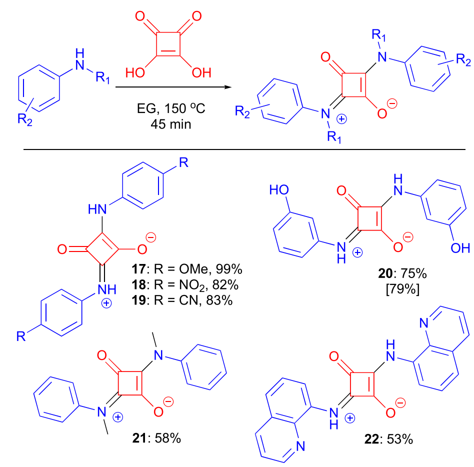


Scheme 5. Synthesis of squaraine dyes **14**–**16** in EG. The yield of a 1g-scale reaction for dye **14** is given in brackets.

obtained in moderate yields. These results are in line with many literature accounts that use n-BuOH/PhMe solvent mixtures [14].

In addition, we examined the synthesis of N-containing squaraines in EG (Scheme 6). These types of squaraine dyes have been shown to exhibit some interesting properties 15a–c, in addition to their use as photoinitiators 15d–f. Primary aromatic amines appeared to work well as nucleophiles toward squaric acid in EG, and regardless of the electronic demands of the amine, the corresponding squaraine dyes were obtained in good yields (e.g., dyes **17**–**20**).

Using secondary amine, *i.e.*, N-methylaniline, afforded the corresponding squaraine **21**, albeit in moderate yield (Scheme 6). It is of interest to note, that using EG as a solvent afforded squaraine **22** in 53 % yield by simply quenching the reaction with water, and isolating the product by filtration as opposed to the use of n-BuOH/PhMe system, which required multiple recrystallizations to obtain pure product in only *ca.* 15 % yield [15c].



Scheme 6. Synthesis of N-aryl-containing squaraine dyes in glycols. The yield of a 1g-scale reaction for dye **20** is given in brackets.

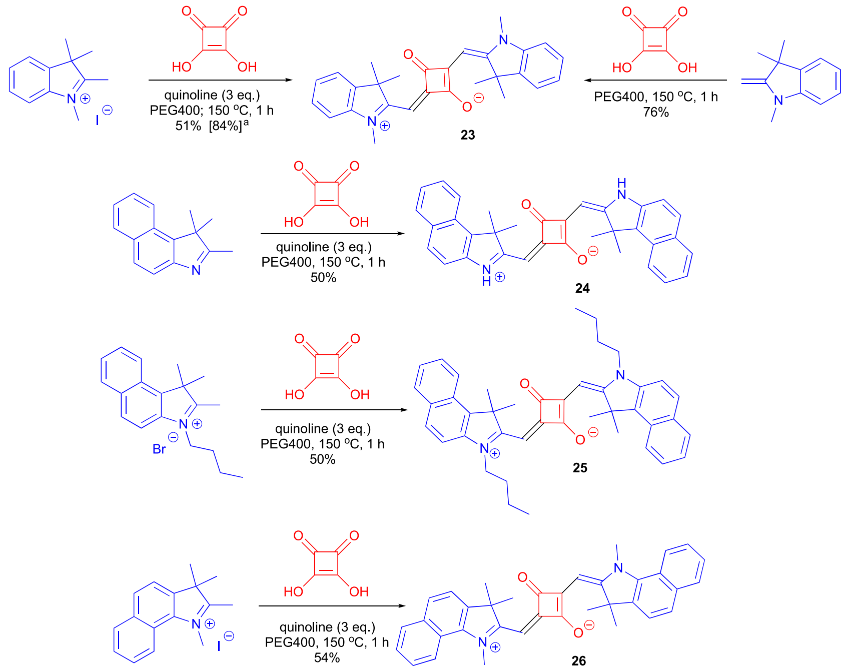
Squaraine dyes that incorporate indolenine and benzo-indolenine moieties are among the most widely used squaraines with a diverse range of applications [16]. Thus, we also investigated the synthesis of indole-2-ylidene-containing squaraine dyes in glycols (Scheme 6). Unlike the previous cases, EG and relatively short reaction times (i.e., 15 or 45 min) did not lead to acceptable yields of squaraine dye **23**, and as such, we conducted some optimization studies (Table S5). It was found that PEG400 was the most viable solvent in the presence of a typical base, such as quinoline. Furthermore, similar to literature account 5c,17, we found that dye **23** could also obtained from 2-methylene-1,3,3-trimethylindoline (Fischer base) in PEG400 (Scheme 7). Overall, squaraines **23**–**26** were obtained in moderate, yet comparable to literature [16] yields (Scheme 7).

In order to demonstrate suitability of glycols for the synthesis of non-symmetric squaraine dyes, we considered two easily accessible precursors [6,18]. Specifically, kryptopyrrol-2-yl-containing semisquaraine A was found to be a viable synthon for non-symmetric squaraine dyes using n-BuOH as the solvent [6]. Here, PEG400 was used as the solvent for the synthesis of non-symmetric squaraine dyes **27**–**30** (Scheme 8), and these dyes were obtained in moderate yields using either conventional heating (dyes **27** and **28**) or microwave (MW) heating (dyes **29** and **30**).

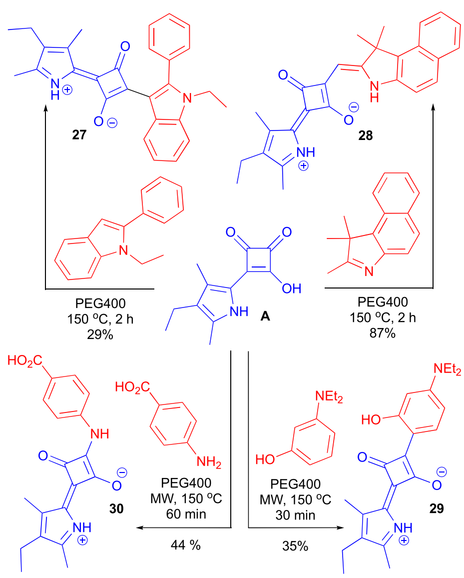
Finally, we used indolin-2yl-containing semisquarate **B**[18] to prepare non-symmetric squaraine dyes **31** and **32** (Scheme 9). These dyes were obtained either under conventional and MW-irradiation heating in good and moderate yields, respectively (Scheme 9). Notably, using semisquarates [19] increases the overall synthetic efficiency in obtaining non-symmetric squaraines by eliminating the hydrolysis step, which leads to semisquarate (a typical precursor for making non-symmetric squaraines).

3. Conclusions

As non-volatile, relatively non-toxic, and relatively inexpensive solvents, various glycols appeared to be a more environmentally benign and sustainable alternative to conventionally used n-BuOH/PhMe system, allowing for facile and efficient syntheses of various types of symmetric and non-symmetric squaraine dyes. On average, the reaction times in glycols appeared to be appreciably shorter (minutes to hours)



Scheme 7. Synthesis of indolinium-containing squaraine dyes in PEG400 as the solvent. The yield of a 1g-scale reaction for dye **23** is given in brackets; the reaction time was 6 h.

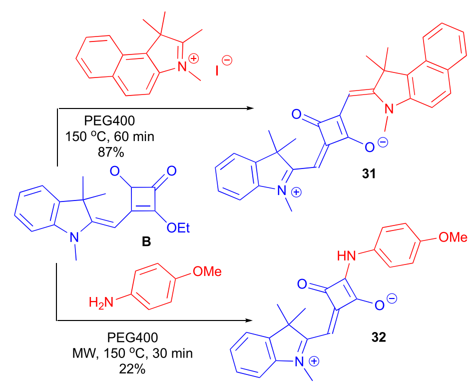


Scheme 8. Synthesis of non-symmetric squaraine dyes in PEG400 using kryptopyrrol-2-yl-semisquaraine **A** as one the starting materials.

than those observed when using the conventional n-BuOH/PhMe solvent system (hours to days). Synthesis of various types of symmetric and non-symmetric squaraine dyes in glycols also appeared to be scalable, and in many cases, the dyes were obtained quite efficiently (quenching with water, filtration and water wash), without the use of column chromatography (see SI).

CRediT authorship contribution statement

Daniel D. Ta: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Ernesto Rodriguez:** Writing – review & editing, Methodology, Investigation. **Sergei V. Dzyuba:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.



Scheme 9. Synthesis of non-symmetric squaraine dyes in PEG400 using indolin-2-yl-semisquarate **B** as one the starting materials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

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