

## PRF # 57379-DN14

### Desulfurization of crude oil by fluorous extraction

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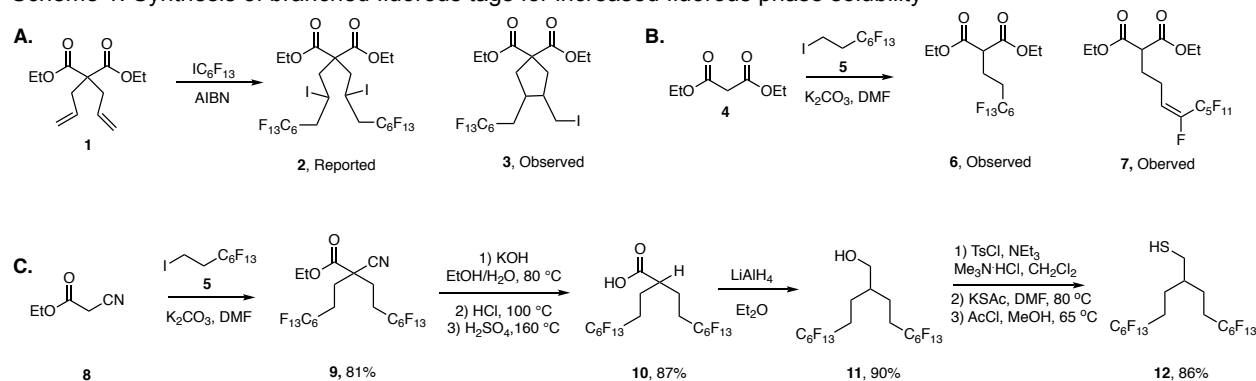
Our PRF put forth a new approach to hydrodesulfurization of crude oil using fluorous extraction. The key to the success of this work is the development of selective chemistries to append fluorous tags to sulfur containing molecules such that they can be sequestered from the oil and partition into perfluorocarbon. In the past year, we have 1) synthesized new fluorous tags with branched motifs to increase the partition coefficients into perfluorocarbons 2) investigated novel strategies for tagging disulfides using strained hydrocarbons and 3) developed an optical readout regarding the separation of the hydrocarbon and perfluorocarbon layers.

#### 1) Enhanced fluorous tags

To render compounds soluble in perfluorocarbons, ~60 wt% fluorine must be achieved. This can be accomplished through the addition of long chain fluorinated tags ( $C_8F_{17}$  or greater); however, there is mounting environmental concern regarding these long chain perfluorocarbons. Thus, we have focused on the preparation of branched fluorous tags which have less than eight consecutive ( $CF_2$ ) groups. The addition of branched hydrocarbon moieties is an established method to increase the solubility of organic compounds and we expect this strategy will extend to fluorous materials.

We first attempted to follow previously published literature to access a branched fluorous tag (Scheme 1A). Diethyl 2,2-diallylmalonate was subjected to perfluoroiodohexane and azobisisobutyronitrile which was reported to yield **2** but in our hands gave cyclic compound **3** with only one fluorous chain installed. Our next attempt involved the direct alkylation of diethyl malonate (**4**) with commercially available iodide **5**; however, only monoalkylation was observed (**6**) and when forcing conditions were employed fluoride elimination (**7**) occurred rather than dialkylation. Successful dialkylation was achieved when diethyl malonate (**4**) was combined with ethyl cyanoacetate (**8**). Dialkylation of **8** with **5** proceeded in 81% yield to give **9**. Decyanation could be accomplished via sequential treatment with base and acid to give branched carboxylic acid **10**, which was reduced to **11**. The acid and alcohol functional handles on **10** and **11** facilitate their attachment to a variety of thiol-reactive species. To be able to use the branched tag for a desulfurization experiment, we transformed alcohol **11** into thiol **12** in 86% yield as seen in Scheme 1C. The branched fluorous tag work has been submitted for publication.

Scheme 1. Synthesis of branched fluorous tags for increased fluorous phase solubility



#### 2) Strategies for tagging disulfides using strained hydrocarbons

Compound **12** is effective at removing thiols from hydrophobic media; however, thiols are commonly oxidized to the disulfide, in which case a simple compound such as **12** will not be effective. Furthermore, all existing methods to modify disulfides first involve the reduction to the thiol. This is not feasible in crude oil and therefore direct disulfide modifications are necessary. We are developing an approach for the direct modification of disulfides using bicyclobutane motifs. We have prepared bicyclobutanes **13–15**

according to literature procedures. Unfortunately, when combined with both diphenyldisulfide and dihexyldisulfide no reactivity was observed, even at elevated temperatures (Scheme 2). In efforts to observe the desired reactivity, we irradiated **14** in the presence of disulfides **20** and **21** with 365 nm light in the presence or absence of 2,2-dimethoxy-2-phenylacetophenone (DMPA) initiator. Under these conditions, we start to observe our desired reactivity with the diphenyldisulfide, although the major product is mono addition product **22** rather than desired product **19**. We found that the addition of DMPA or an electron donating group (**15**) improved the ratio of double addition:mono addition products (table 1). We are in the process of further optimizing this chemistry.

Scheme 2: Bicyclobutanes and direct disulfide addition

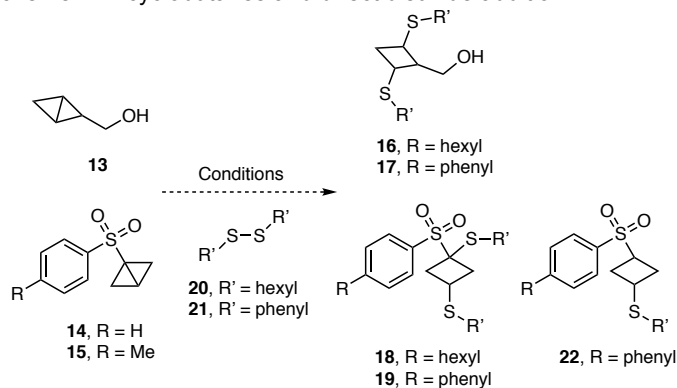


Table 1: Selected result for disulfide addition

Cm pd	Disulfide (R' =)	Conditions	Result
<b>13</b>	<i>n</i> -Hexyl ( <b>20</b> )	Heat	No reaction
<b>14</b>	<i>n</i> -Hexyl ( <b>20</b> )	Heat	No reaction
<b>15</b>	<i>n</i> -Hexyl ( <b>20</b> )	Heat	No reaction
<b>13</b>	Phenyl ( <b>21</b> )	Heat	No reaction
<b>14</b>	Phenyl ( <b>21</b> )	Heat	No reaction
<b>15</b>	Phenyl ( <b>21</b> )	Heat	No reaction
<b>14</b>	<i>n</i> -Hexyl ( <b>20</b> )	365 nm light	No reaction
<b>14</b>	Phenyl ( <b>21</b> )	365 nm light	20% <b>19</b> ; 80% <b>22</b>
<b>14</b>	Phenyl ( <b>21</b> )	365 nm light, DMPA	40% <b>19</b> ; 60% <b>22</b>
<b>15</b>	Phenyl ( <b>21</b> )	365 nm light	30% <b>19</b> ; 70% <b>22</b>

### 3) Optical readout for separation of hydrocarbon and perfluorocarbon

A key feature of the desulfurization approach is the lower consolute temperature of perfluorocarbons and hydrocarbons such that they become miscible. It can be difficult to determine when complete phase separation has been achieved. We have prepared the first non-aqueous J-aggregate (**23**, Figure 1A, *J. Am. Chem. Soc.* **2018**, *140*, 2727), which is highly sensitive to the percentage of fluoruous solvent. Compound **23** has distinctive photophysical properties in organic, semifluorinated, and fluoruous solvent (Figure 1B). Furthermore, the absorbance of **23** is extremely responsive to the percentage of fluoruous solvent, providing a readout on phase separation. Work is underway to increase the scope of fluoruous and organic solvents that **23** can report on.

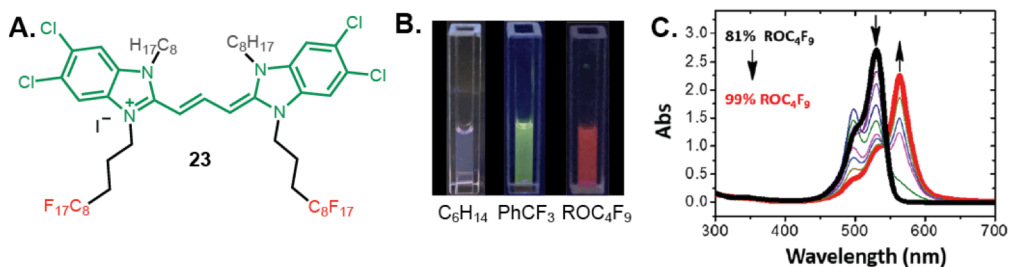


Figure 1. (A) First non-aqueous cyanine dye J-aggregator. (B) Solvent-dependent emission due to aggregation. (C) Aggregation is sensitive to percent fluoruous solvent.

### Impact

The simple preparation of biocompatible branched fluoruous tags will the expand the utility of the fluoruous phase, as concerns regarding the bioaccumulation of perfluorocarbons are mitigated by the use of C<sub>6</sub>F<sub>13</sub> chains. The branched nature also imparts fluoruous solubility with less wt% fluorine. Direct disulfide modification is a novel approach but still requires chemical optimization. Lastly, the first non-aqueous J-aggregate provides opportunities for advanced optical sensors as well as easy fabrication of devices with J-aggregates as active components. Furthermore, students and postdocs working on these projects have gained valuable training in organic synthesis, reaction screening and photophysical analysis.