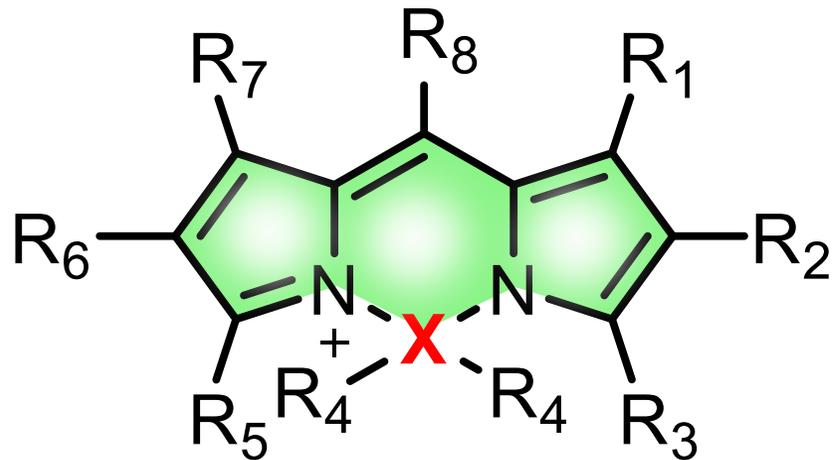


---Literature Reports

Heteroatom Doped Dipyrromethenes



Bright fluorescence

Narrow emission bandwidth

Environment insensitivity

Stability

Highly lipophilic

Reporter: Qinglong Qiao

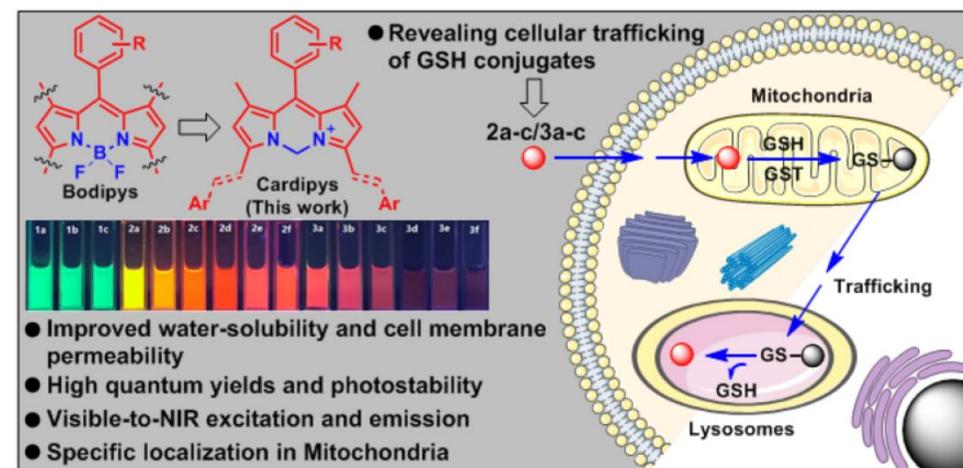
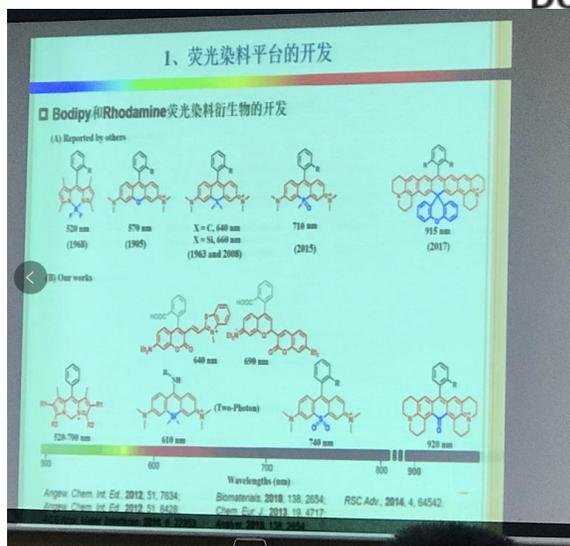
Date: 2020.09.24

Carbon-Dipyrromethenes: Bright Cationic Fluorescent Dyes and Potential Application in Revealing Cellular Trafficking of Mitochondrial Glutathione Conjugates

Hongxing Zhang, Jing Liu, Yuan-Qiang Sun, Mengxing Liu, and Wei Guo

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.0c06916 • Publication Date (Web): 18 Sep 2020

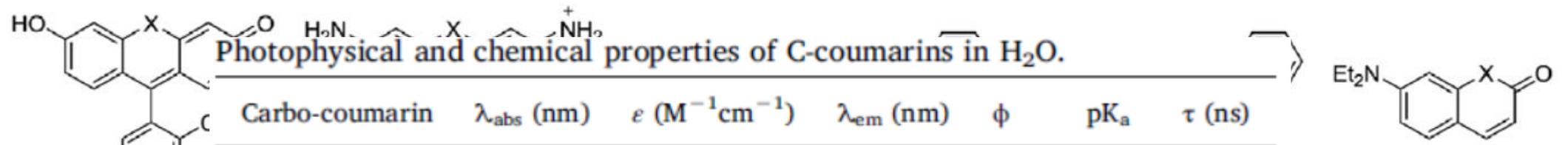
Downloaded from pubs.acs.org on September 19, 2020



C doped fluorophores

A

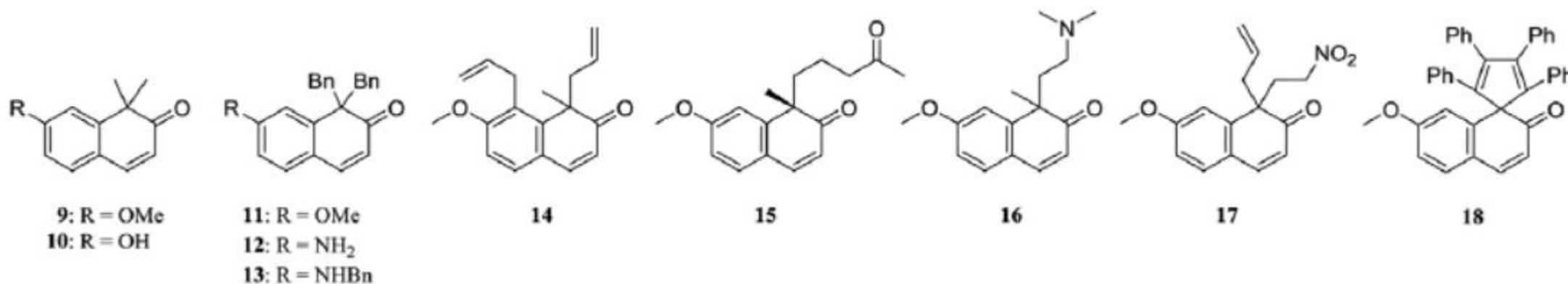
Photophysical and chemical properties of C-coumarins in H₂O.



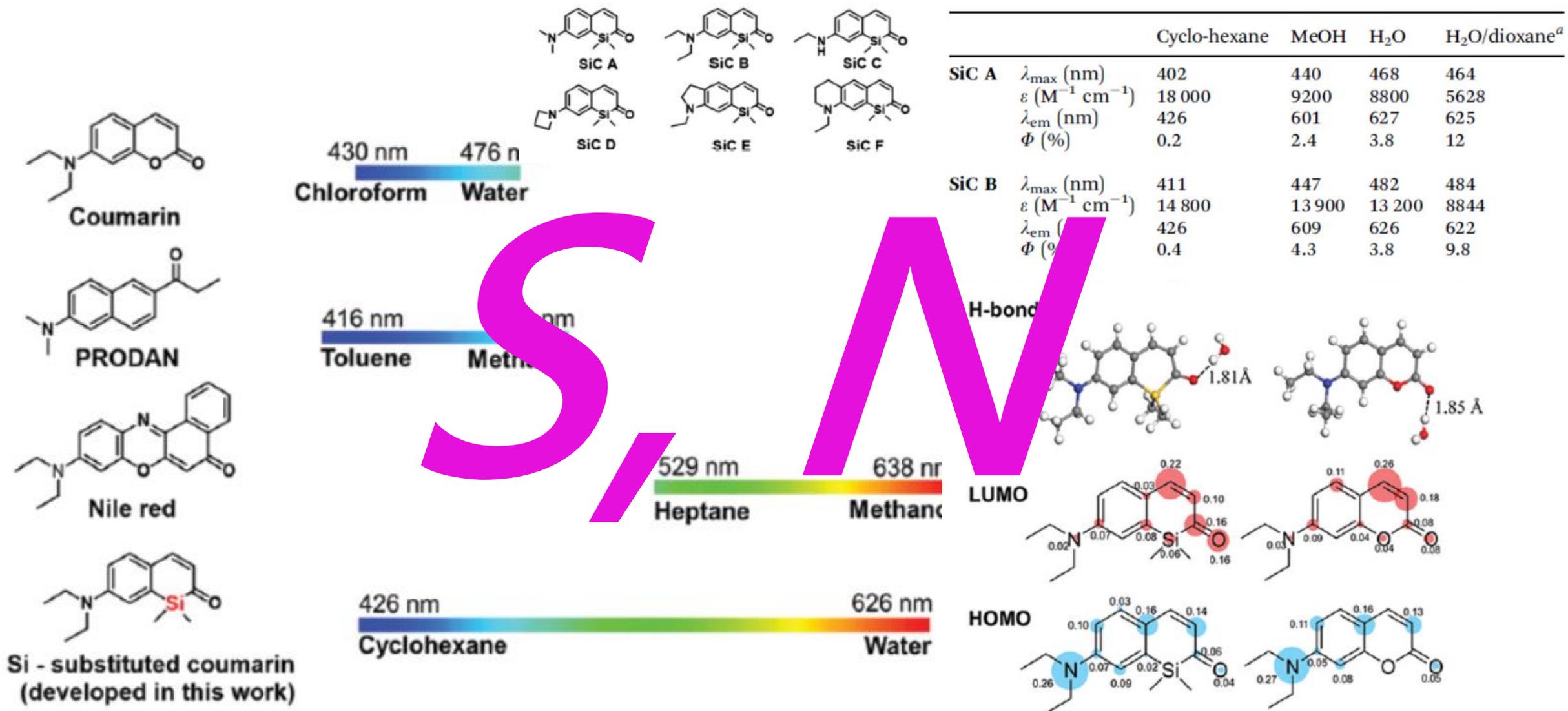
| Carbo-coumarin | λ_{abs} (nm) | ϵ (M ⁻¹ cm ⁻¹) | λ_{em} (nm) | ϕ | pK _a | τ (ns) | |
|---|-----------------------------|--|----------------------------|--------|-----------------|-------------|------|
| C1 | 341 | 8040 | 522 | 0.05 | 8.52 | 2.45 | |
| C2 | 377 | 10060 | 526 | 0.14 | 2.53 | 3.49 | |
| X=O 1 : $\lambda_{\text{abs}}/\lambda_{\text{em}} = 491/5$ | C3 | 402 | 12060 | 541 | 0.18 | 3.29 | 3.90 |
| | C4 | 413 | 12400 | 554 | 0.13 | 3.24 | 3.66 |
| X=CMe ₂ 2 : $\lambda_{\text{abs}}/\lambda_{\text{em}} = 544/5$ | C5 | 429 | 13440 | 552 | 0.09 | 4.60 | 2.56 |
| | C6 | 387 | 12880 | 555 | 0.13 | 2.97 | 3.83 |

O-coumarin:
 $\lambda_{\text{abs}}/\lambda_{\text{em}} = 388/476$ nm

C-coumarin:
 $\lambda_{\text{abs}}/\lambda_{\text{em}} = 429/552$ nm



Si doped Coumarin



Si-doped Dipyrromethenes

Structural Interconversion and Regulation of Optical Properties of Stable Hypercoordinate Dipyrin–Silicon Complexes

Naoya Sakamoto, Chusaku Ikeda, Masaki Yamamura, and Tatsuya Nabeshima*

Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

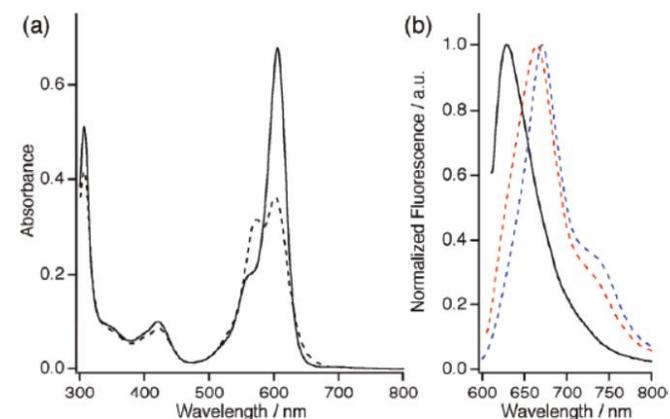
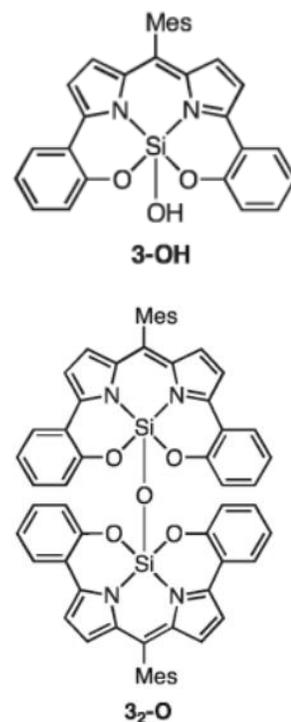


Figure 3. (a) Absorption and (b) fluorescence spectra of 3-OH (solid line) and 3₂-O (dashed line) in CHCl₃. The samples were excited at 605 nm (3-OH), 573 nm (3₂-O, blue line), and 601 nm (3₂-O, red line). (c, d) Photographs of 3-OH (left) and 3₂-O (right) were taken under (c) ambient light and (d) UV light (365 nm).



J. Am. Chem. Soc. **2011**, *133*, 4726–4729

Silicon Compounds of 1,1-Bis(pyrrol-2-yl)ethenes: Molecular Structures and Chemical and Spectroscopic Properties

Alexander Kämpfe, Edwin Kroke, and Jörg Wagler*

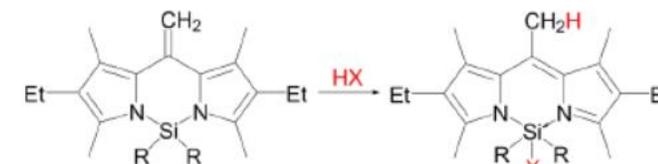
Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, D-09596 Freiberg, Germany

S Supporting Information

ABSTRACT: The first examples of silicon compounds of 1,1-bis(pyrrol-2-yl)ethenes have been synthesized via salt metathesis from a 2-fold lithiated dipyrromethene and different diorganodichlorosilanes (i.e., dimethyldichlorosilane, diphenyldichlorosilane, and 1,1-dichlorosilacyclobutane). Herein we report on their molecular structures, their optical properties, and some reactivity patterns.



| | λ_{\max} | ϵ |
|------|------------------|------------|
| 2/2' | 455 | 5133 |
| | 297 | 14069 |
| 4a | 466 | 819 |
| | 302 | 8546 |
| 4b | 503/410 | 1275/1286 |
| | 302 | 10649 |
| 4c | 502 | 224 |
| | 304 | 11753 |



Organometallics **2014**, *33*, 112–120

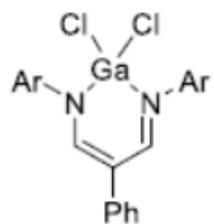
P,Ga-doped Dipyrromethenes

Highly Luminescent Heavier Main Group Analogues of Boron-Dipyrromethene

Wang Wan,[†] Mayura S. Silva,[†] Colin D. McMillen,[†] Stephen E. Creager,^{†,‡,Ⓢ} and Rhett C. Smith^{*,†,‡,Ⓢ}

[†]Department of Chemistry, Clemson University, Clemson, South Carolina 29634, United States

[‡]Center for Optical Materials Science and Engineering Technology, Clemson University, Anderson, South Carolina 29625, United States



Ar = 2,6-*i*-Pr₂C₆H₃

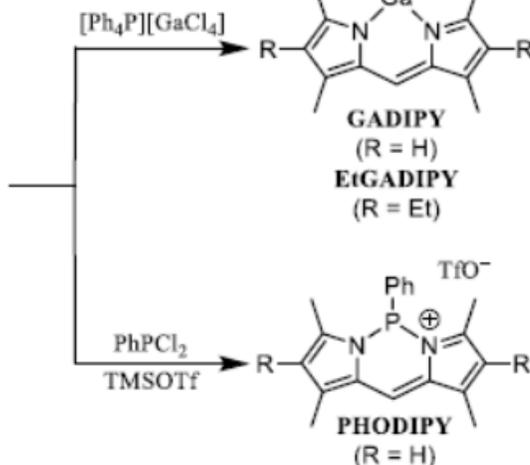
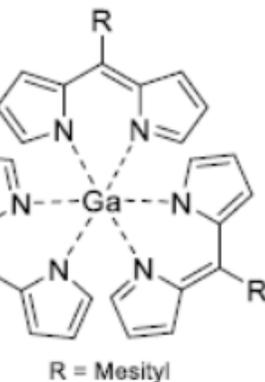
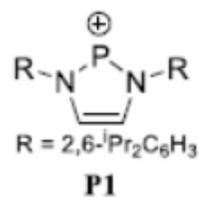
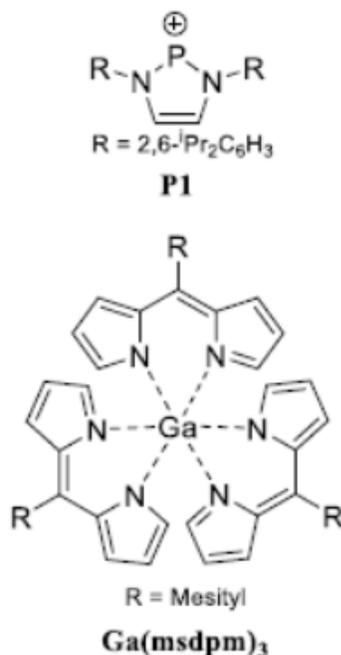
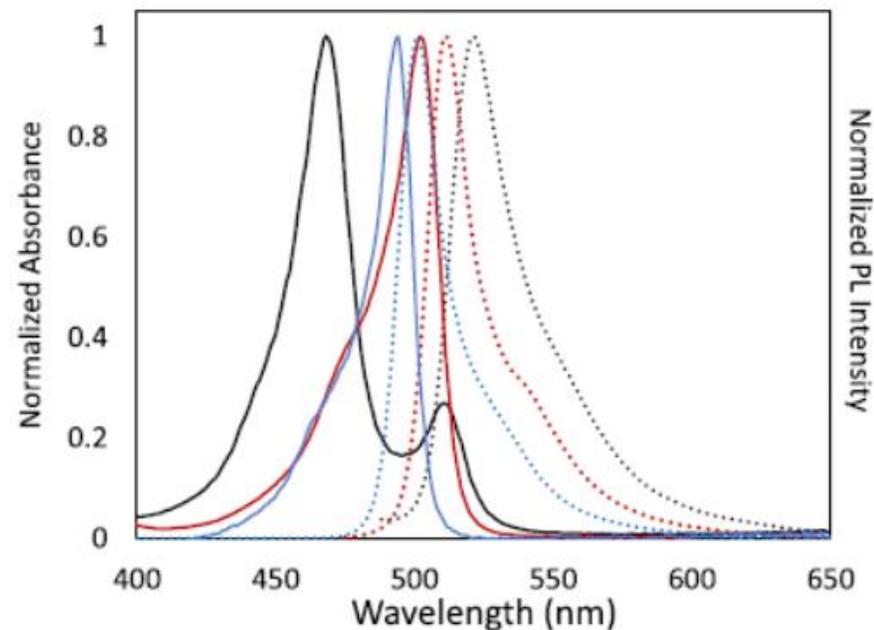
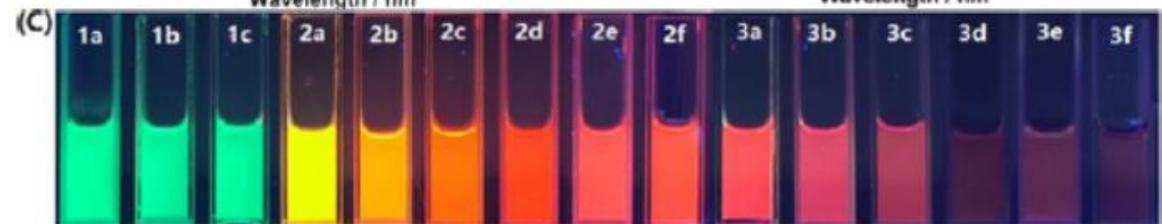
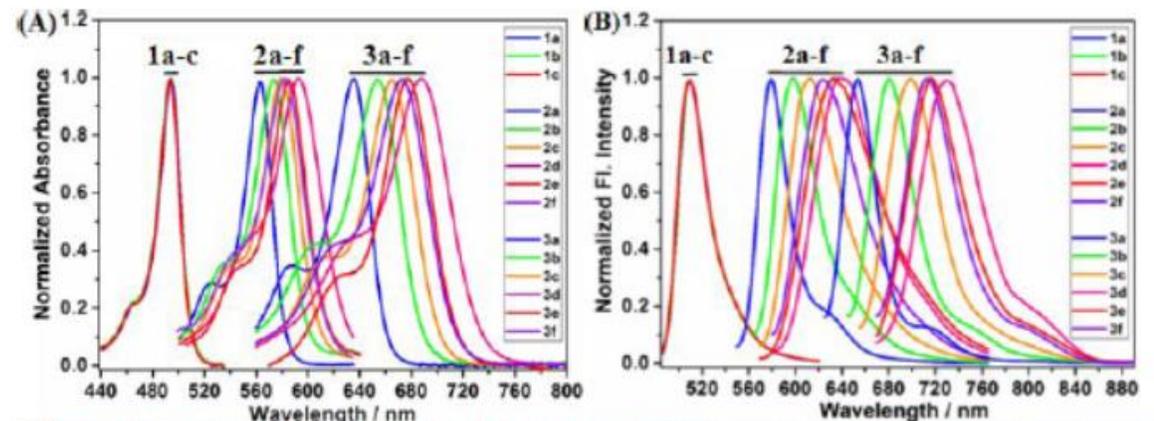
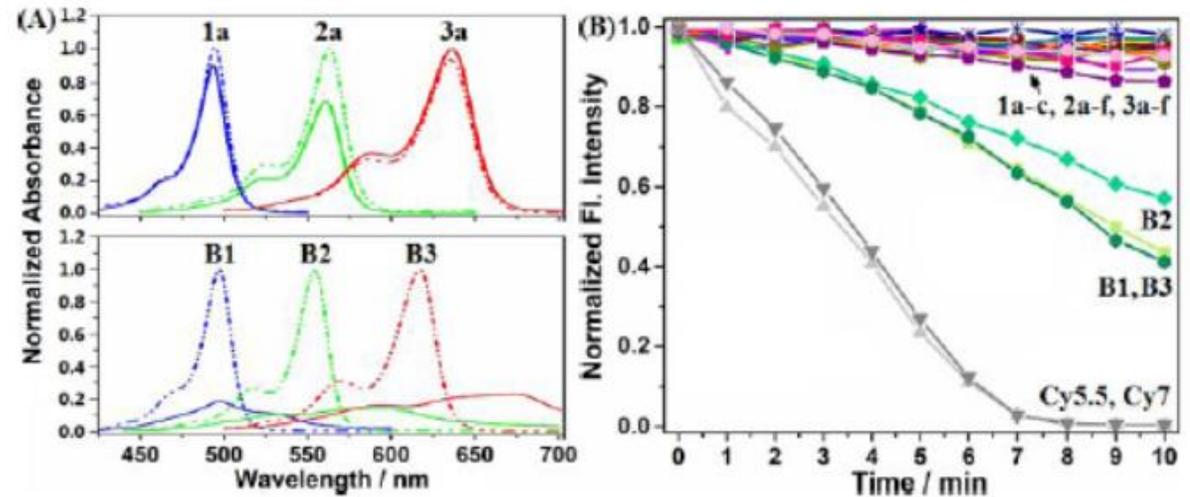
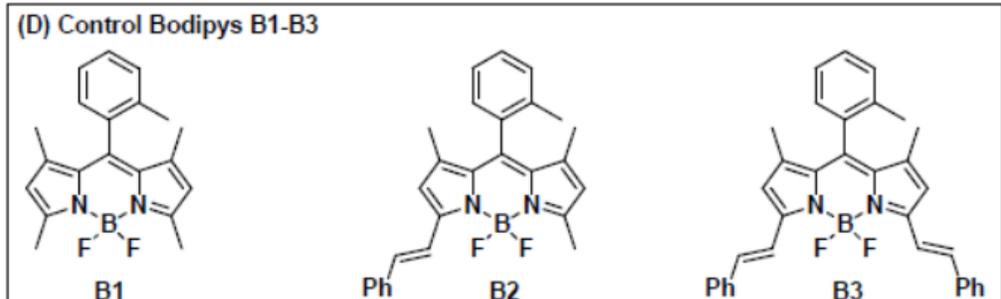
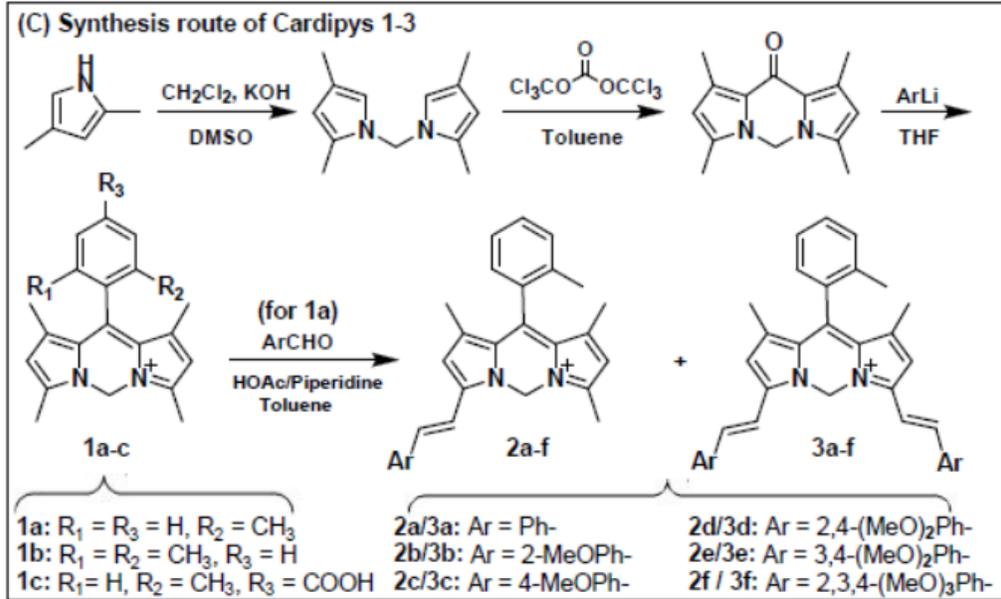
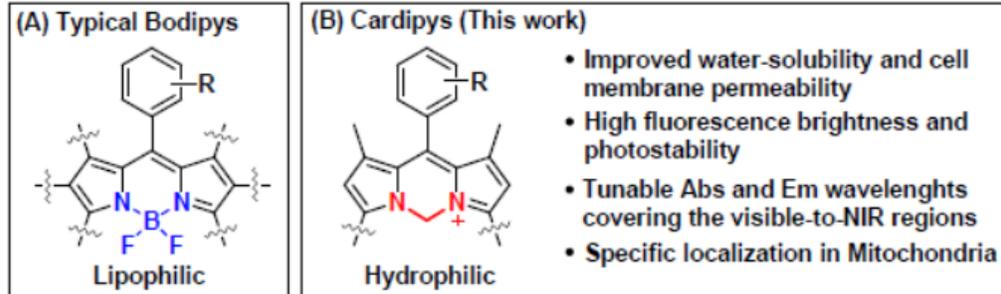


Table 1. Select Photophysical Properties

| | Φ (%) | λ_{\max} (nm) | λ_{em} (nm) | E_g (eV) ^c |
|---|------------------|-----------------------|----------------------------|-------------------------|
| BODIPY | 80 ^a | 505 ^a | 516 ^a | 2.9 |
| Ga(NacNac)Cl ₂ | <1 ^b | 382 ^b | ND | ND |
| Ga(msdpm) ₃ | 2.4 ^c | 496 ^c | 528 ^c | ND |
| GADIPY (CH ₂ Cl ₂) | 82 | 494 | 501 | 3.0 |
| GADIPY (Toluene) | 91 | 497 | 505 | 3.0 |
| PHODIPY ^d | 80 | 467 | 510 | 3.1 |



Different between OPA and TPA *advantages and disadvantages*

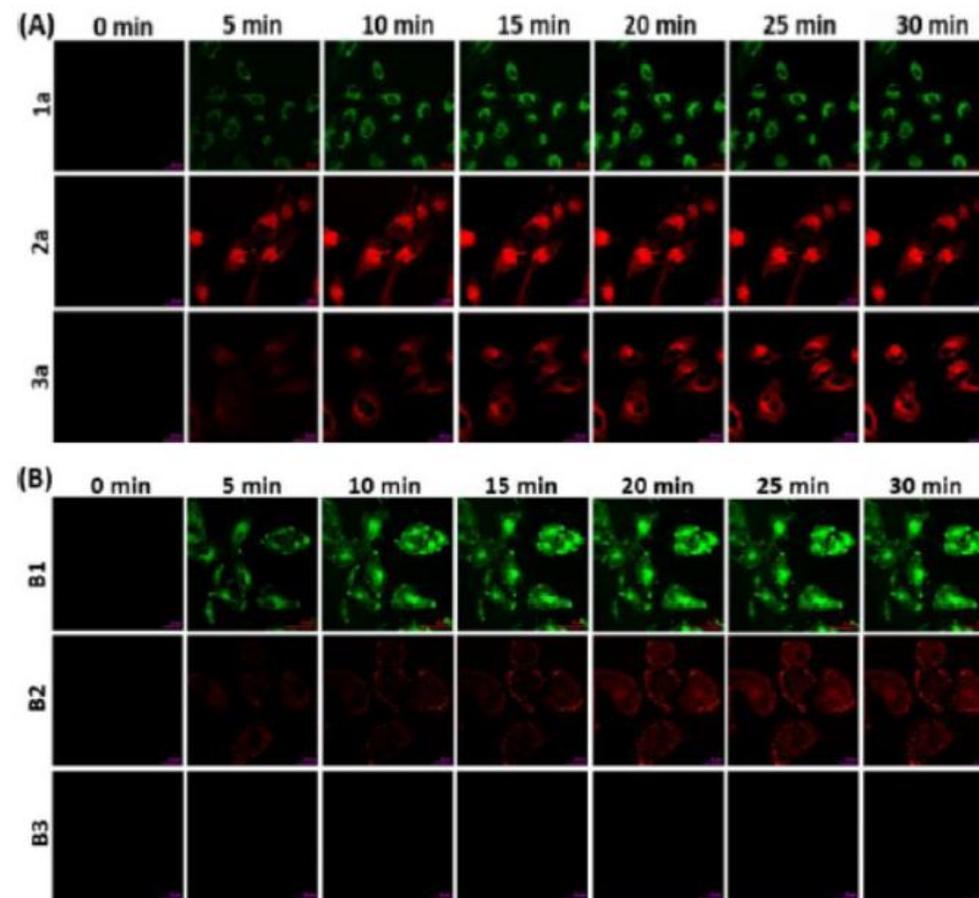
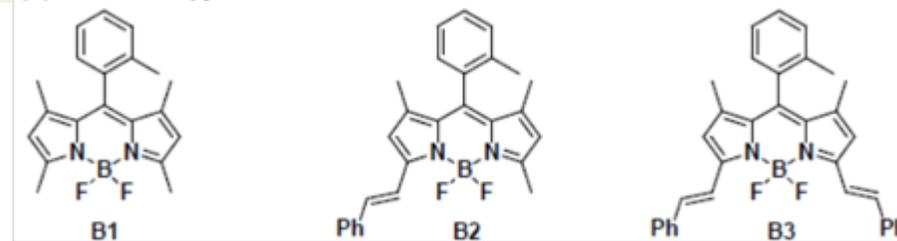


High QE and membrane-permeable

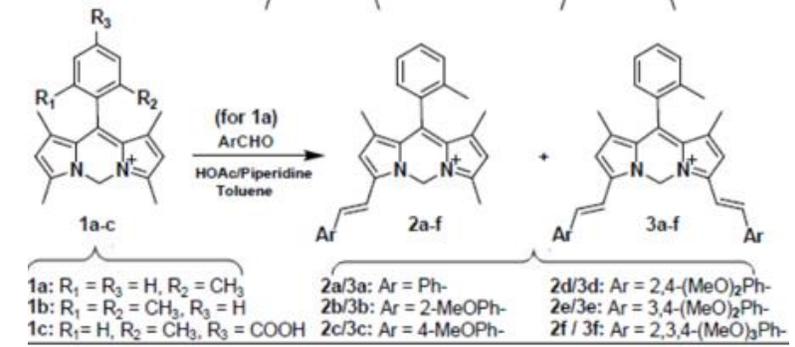
passive diffusion or endocytosis

Table 1 Photophysical properties of Cardipys 1a-c, 2a-f, and 3a-f in CH₂Cl₂, CH₃CN, and PBS, respectively.

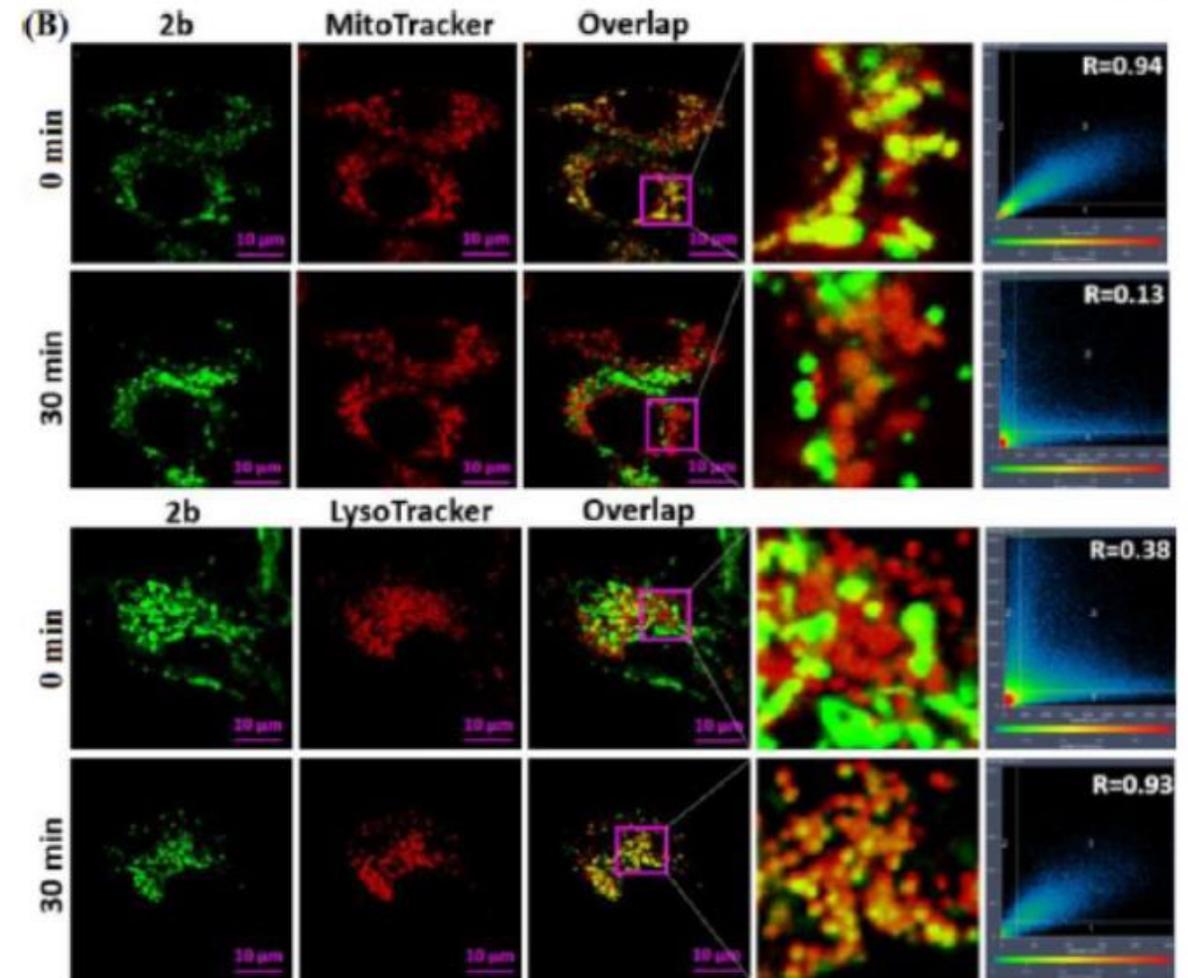
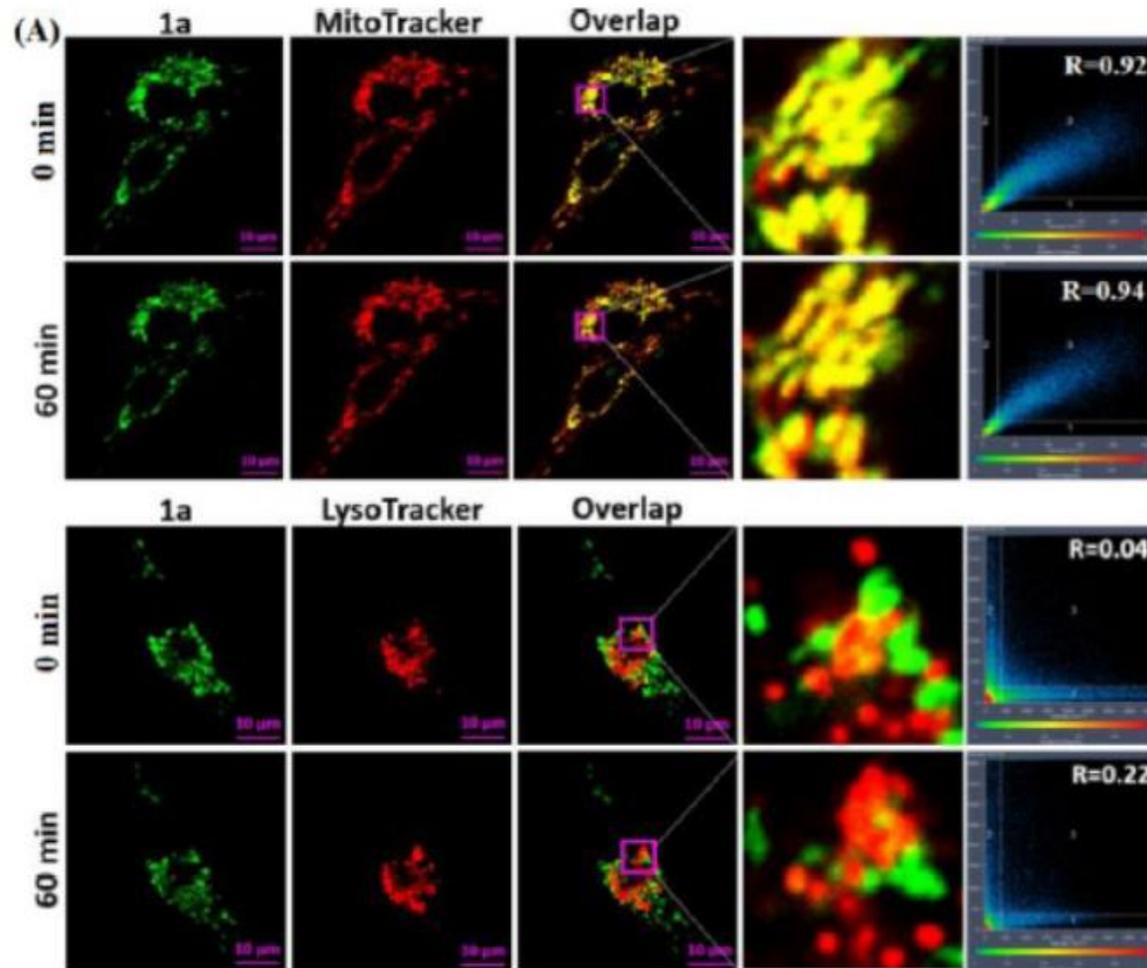
| Dyes | Sol. | $\lambda_{\text{abs}}/\lambda_{\text{em}}$ (nm) | Stoke s shift | ϵ (M ⁻¹ cm ⁻¹) | Φ | τ (ns) |
|-----------------|---------------------------------|--|------------------|---|-----------|----------------|
| 1a ^a | CH ₂ Cl ₂ | 497/511 | 14 | 75600 | 1.03±0.05 | 5.84 |
| | CH ₃ CN | 494/510 | 16 | 57700 | 0.93±0.02 | |
| | PBS | 493/509 | 16 | 62500 | 0.91±0.01 | |
| 1b ^a | CH ₂ Cl ₂ | 496/511 | 15 | 62500 | 0.96±0.04 | 7.53 |
| | CH ₃ CN | 494/509 | 15 | 46800 | 0.97±0.08 | |
| | PBS | 493/509 | 16 | 56800 | 0.98±0.05 | |
| 2a ^b | CH ₂ Cl ₂ | 571/587 | 16 | 102700 | 0.53±0.09 | 7.28 |
| | CH ₃ CN | 563/579 | 16 | 81700 | 0.57±0.03 | |
| | PBS | 561/577 | 16 | 69400 | 0.58±0.03 | |
| 2b ^c | CH ₂ Cl ₂ | 583/607 | 24 | 77900 | 1.01±0.05 | 5.99 |
| | CH ₃ CN | 573/598 | 25 | 57800 | 1.02±0.07 | |
| | PBS | 570/593 | 23 | 41400 | 0.96±0.04 | |
| 2c ^c | CH ₂ Cl ₂ | 593/622 | 29 | 78800 | 0.73±0.09 | 5.32 |
| | CH ₃ CN | 580/612 | 32 | 70600 | 0.82±0.05 | |
| | PBS | 573/605 | 32 | 49500 | 0.77±0.03 | |
| 3e ^d | CH ₂ Cl ₂ | 695/728 | 33 | 95500 | 0.49±0.01 | 3.00 |
| | CH ₃ CN | 678/716 | 38 | 77900 | 0.48±0.04 | |
| | 80% PBS | 670/710 | 40 | 75500 | 0.32±0.03 | |
| 3f ^d | CH ₂ Cl ₂ | 690/725 | 35 | 79500 | 0.47±0.03 | 3.21 |
| | CH ₃ CN | 673/714 | 41 | 81000 | 0.48±0.01 | |



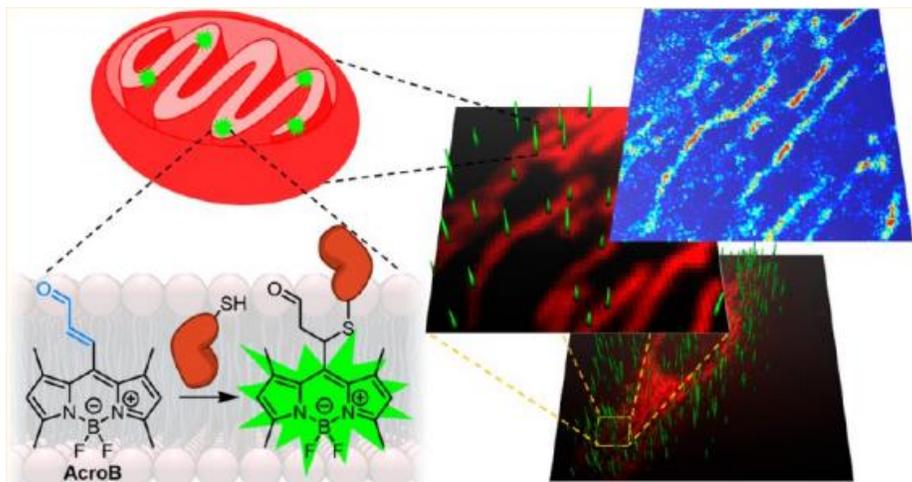
Location in vivo – Mito transfer to Lyso



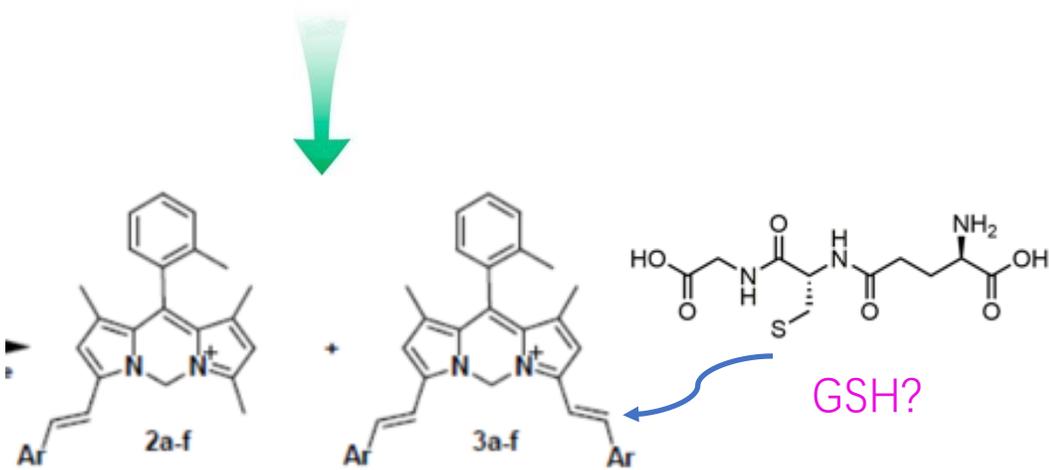
damaged mitochondria by fusing with lysosomes ????



Ideal TP Dyes



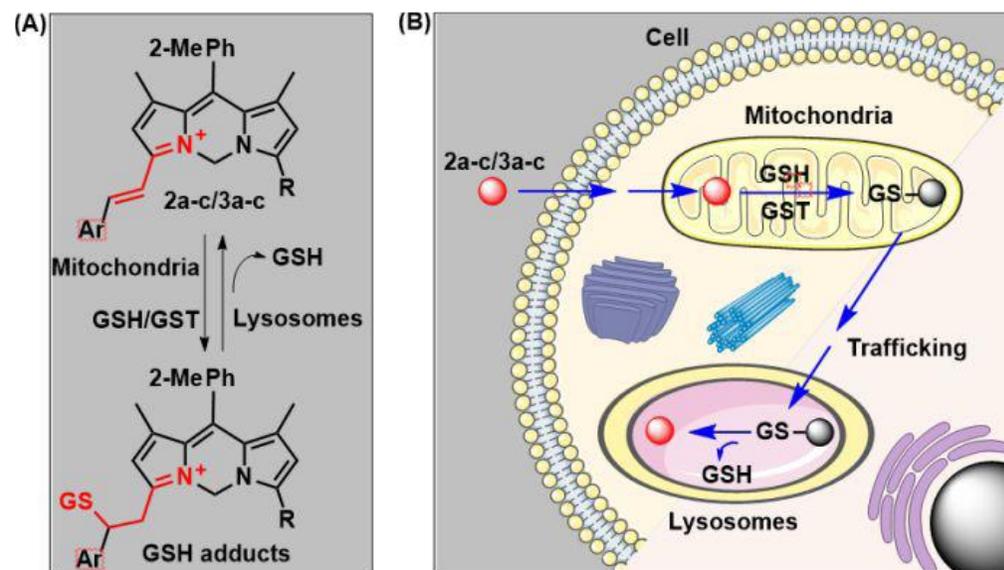
J. Am. Chem. Soc. **2017**, *139*, 16273–16281



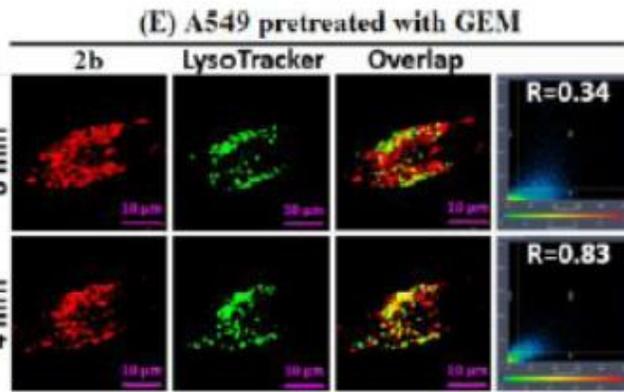
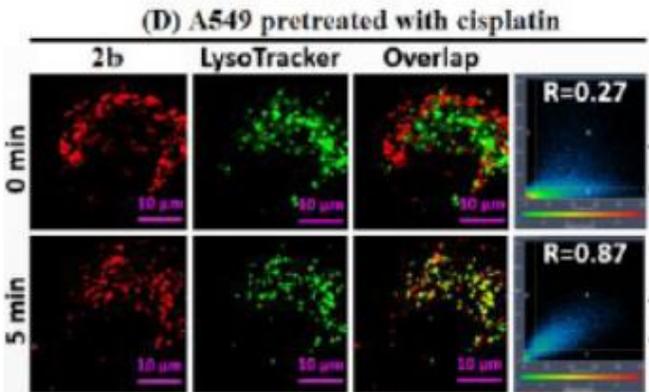
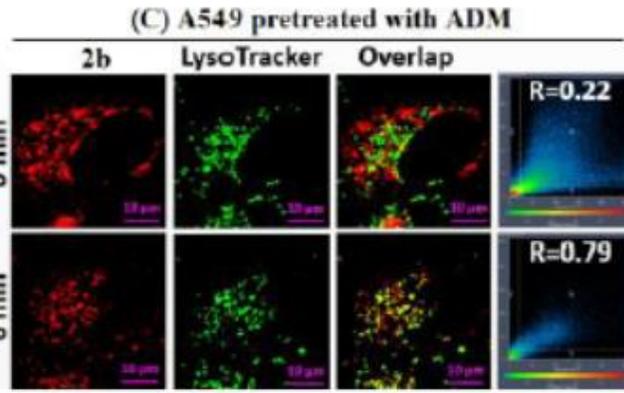
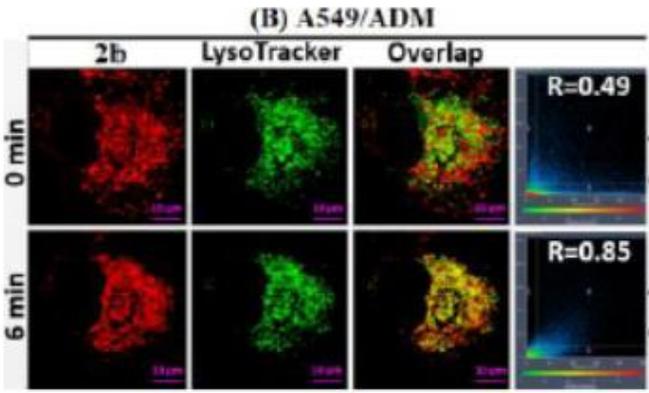
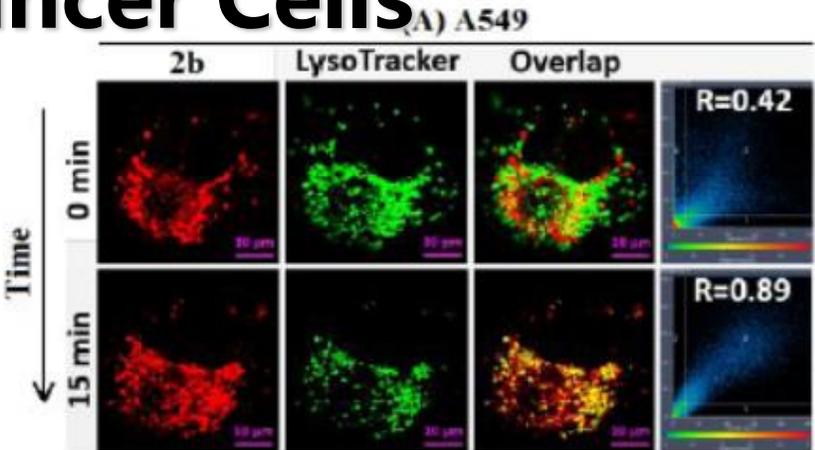
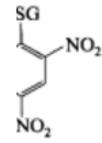
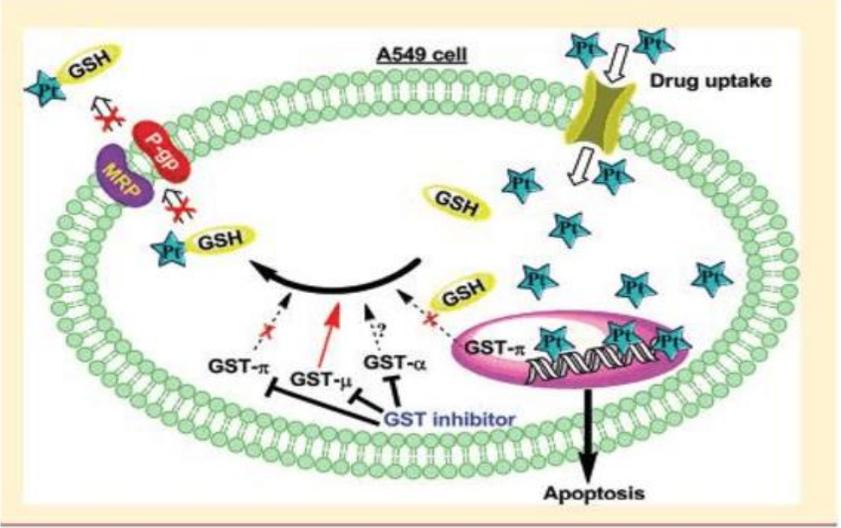
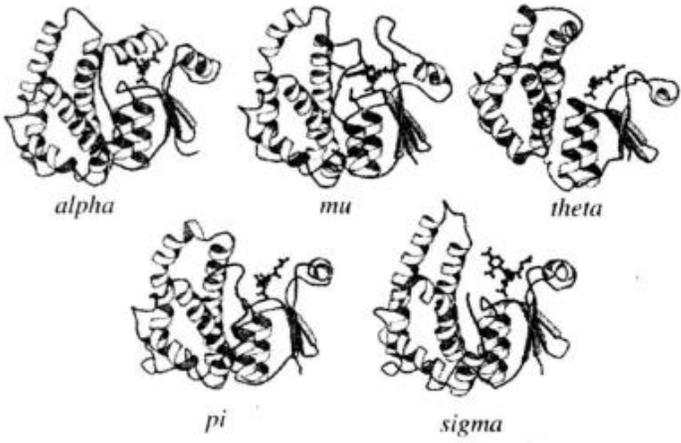
This paper by Guo

lysosomal disposal of the compromised mitochondrial biomolecules

To figure out which biothiol is involved in the mitochondria-to-lysosome translocation of **2a-c/3a-c**, we tested the reactivity of **2a** toward various biothiols, including Cys, GSH, glutathione S-transferase (GST), thioredoxin (Trx), glutathione reductase (GR), and glutaredoxin (Grx), all of which play crucial roles in controlling redox balance to defend against oxidative stress,^{52,53} in B-R buffer (pH = 8.0) at 37 °C by absorption spectra. Note that, the selection of pH = 8.0 is in order to simulate the weakly basic mitochondrial macroenvironment.⁵⁴ Unfortunately, none of them could

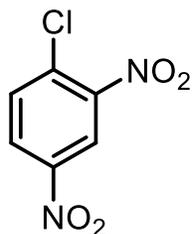


Evaluating Drug-Resistance of Cancer Cells

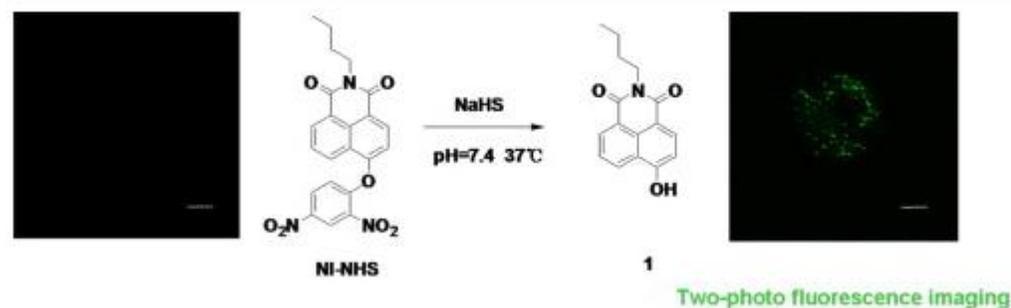


CDNB

CDNB with our group



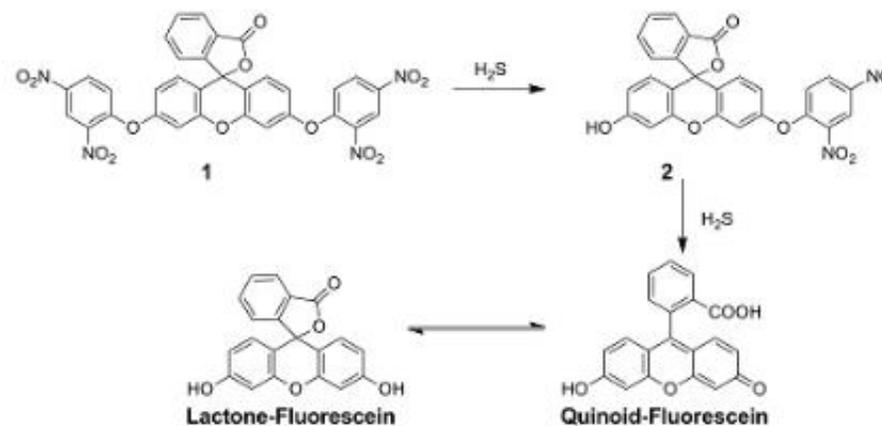
CDNB for GST kit



Dyes and Pigments. **2013**, *99*, 537-542

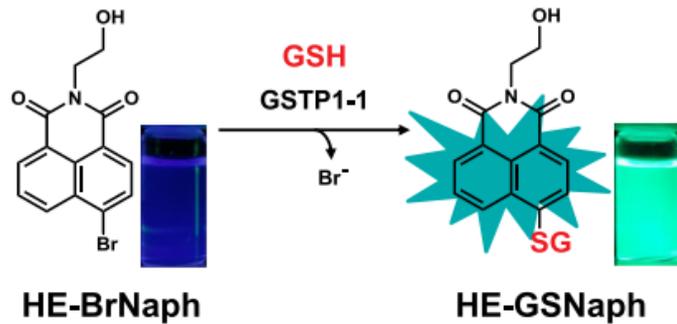


Org. Lett., **2013**, *15*, 2310- 2313.



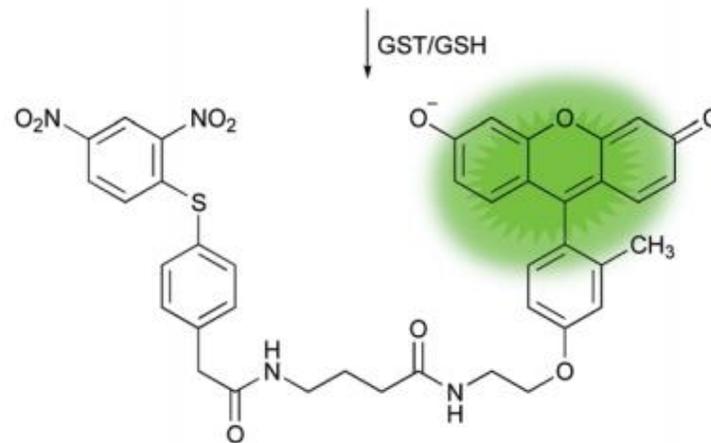
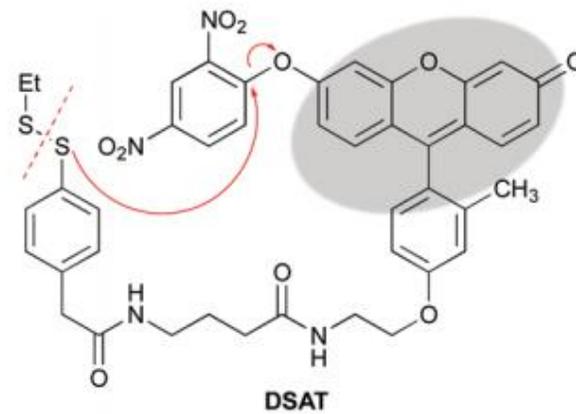
Chin. Chem. Lett., **2014**, *25*, 1060-1064.

Different probes toward GST

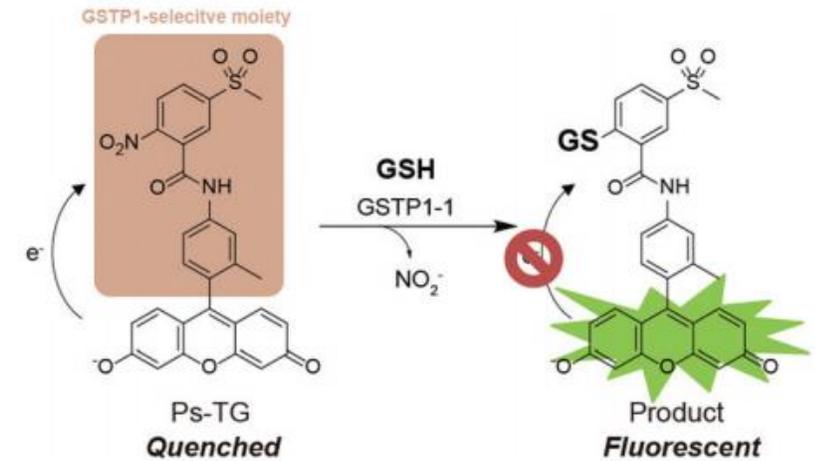


Scheme 1. Sensing mechanism of HE-BrNaph for the GSTP1-1 catalyzed S_NAr reaction.

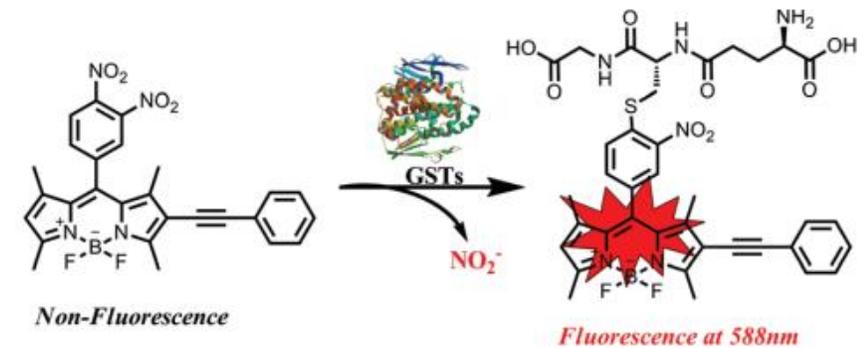
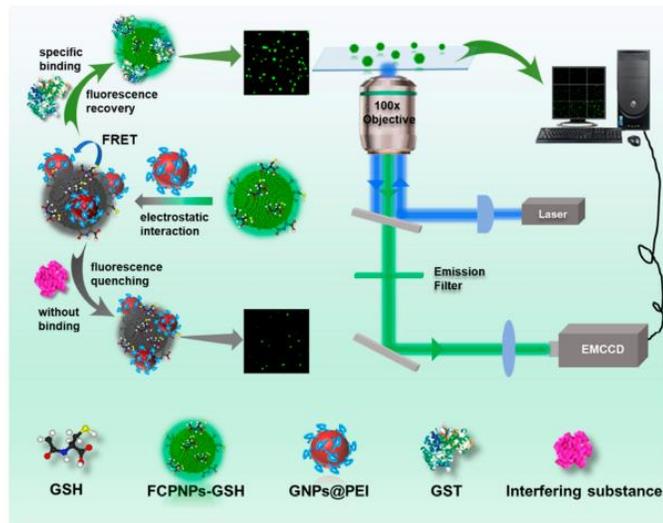
Talanta, 2019, 204, 633–640



Chem. Commun., 2019, 55, 7219--7222

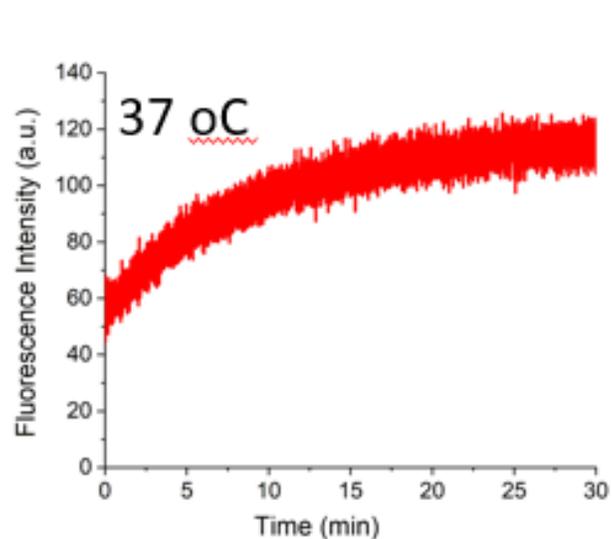
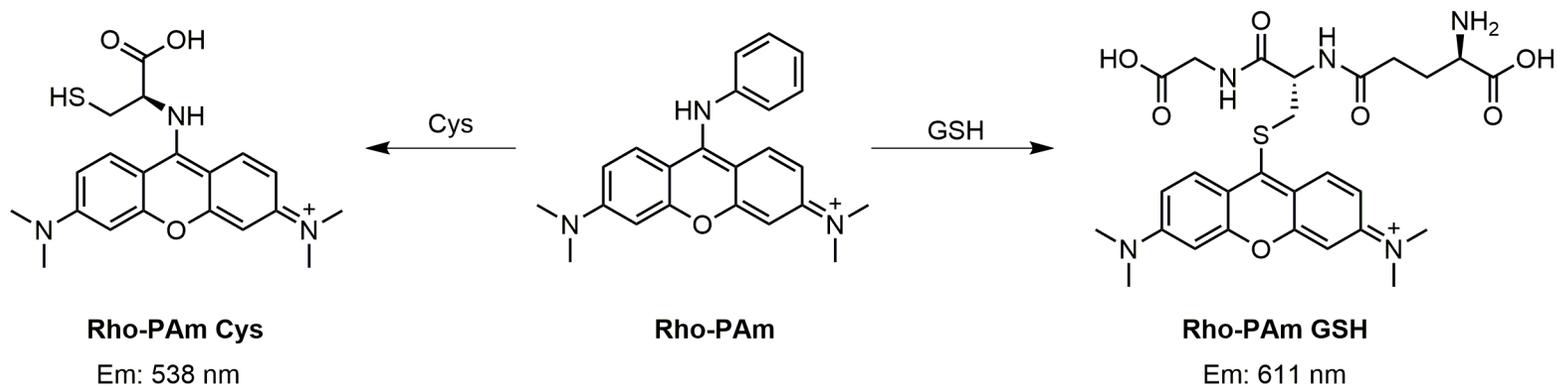


Chem. Commun., 2019, 55, 8122--8125



J. Mater. Chem. B, 2019, 7, 4983--4989

What we can do



动力学：存在问题，
反应慢，效率低
室温反应在2小时达到平衡

x10³
4.25
4
3.75
3.5
3.25
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
x10⁴
3.1
3
3.2
2.1
2
2.3
1.1
1

3Q **3Q** **3Q** **3Q**