Computer-Guided Discovery of **pH-Responsive** Organic **PhotoCatalyst (OPC)**

Methodology

Chenyu Wu

The University of New South Wales

Supervisor:

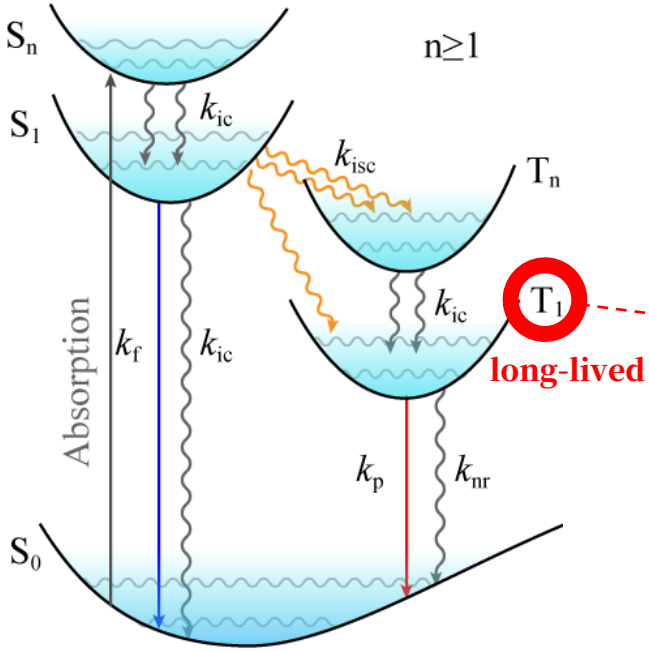
Prof Cyrille Boyer

boyerlab.com

Home Page: *kira.studio*

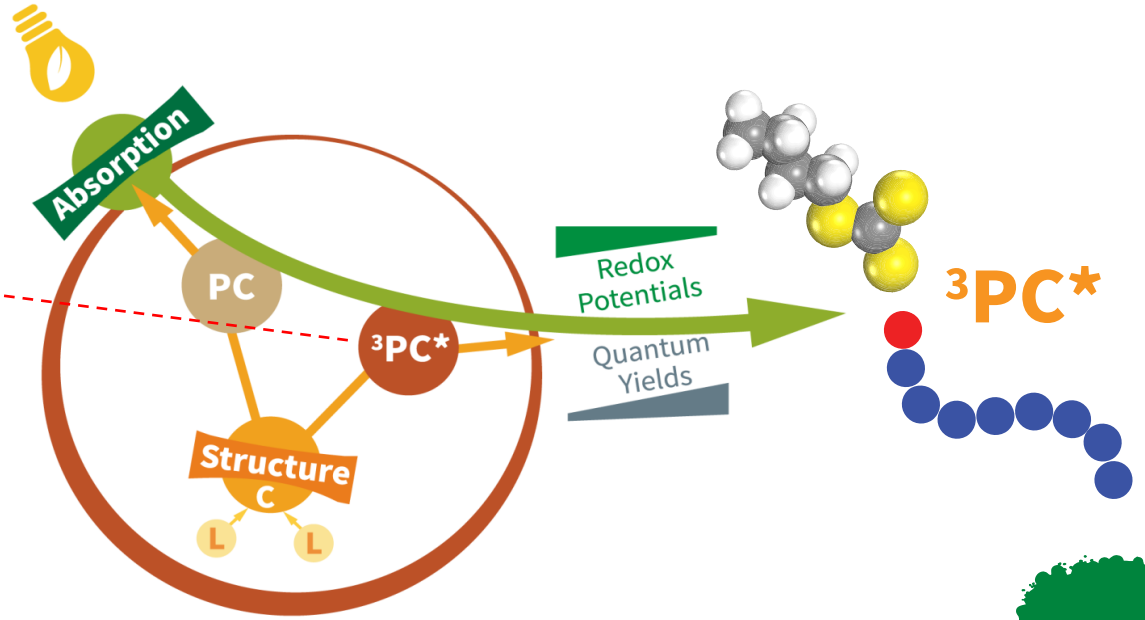
UNSW SYDNEY

What makes an OPC?



Jablonski diagram

Reproduced from ↓



Ma, H; Peng, Q; An, Z; Huang, Wei; Shuai, Z, Efficient and Long-Lived Room-Temperature Organic Phosphorescence: Theoretical Descriptors for Molecular Designs, *J. Am. Chem. Soc.* 2019, 141, 1010-1015.

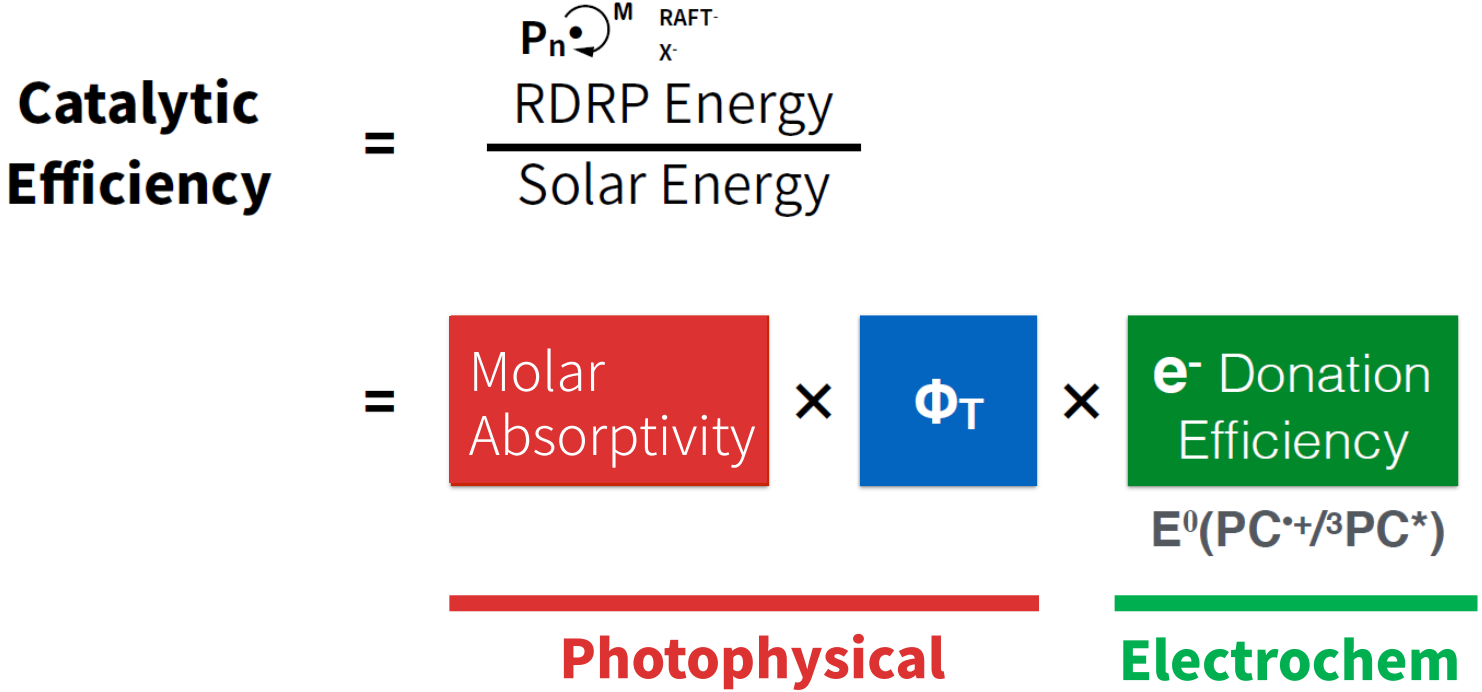
How OPC works?

Solar Energy → Chemical Energy

Light	Absorbed by PC (Absorbance)	Triplet Excited (Φ_T)	Donate e^- $E^0(PC^{\bullet+}/{}^3PC^*)$
		Fluorescence	*Phosphorescence*

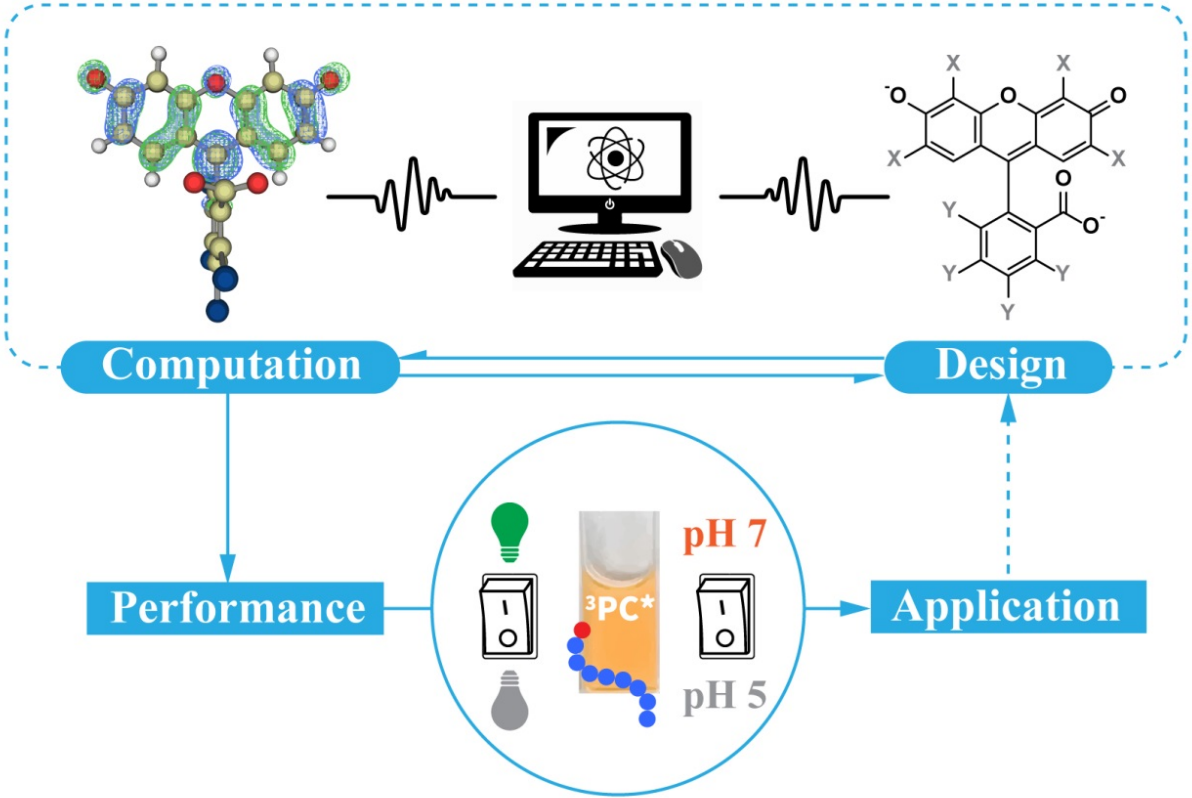
How OPC works?

Solar Energy — Chemical Energy



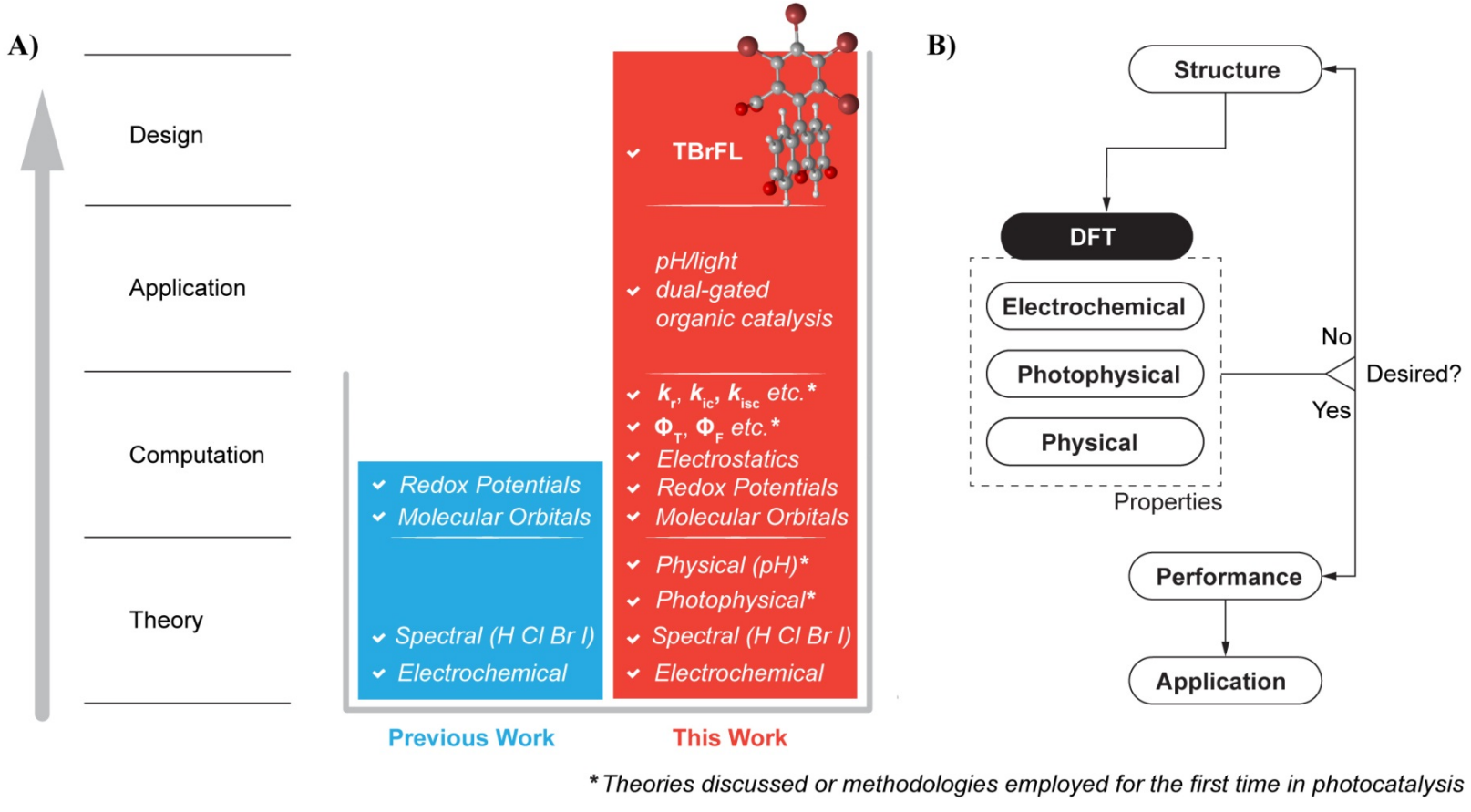
Introduction

GENERAL SCHEME

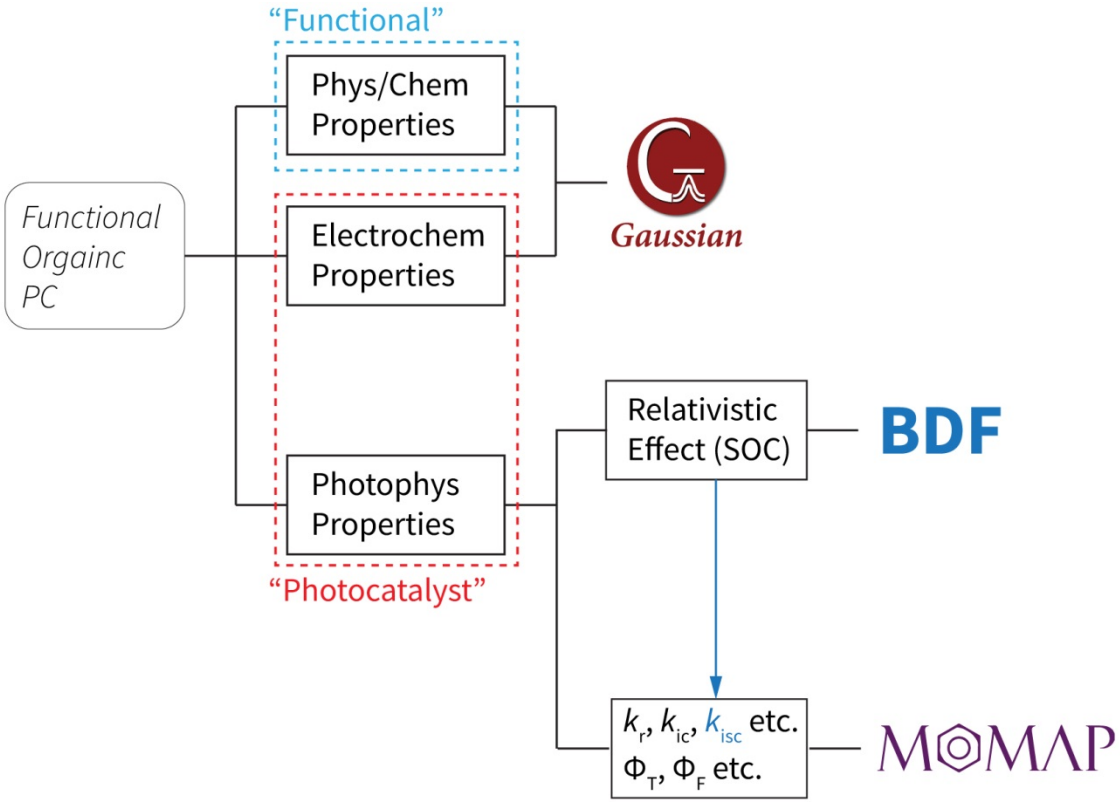


"Computer-Guided Discovery of a pH-Responsive Organic Photocatalyst and Application for pH and Light Dual-Gated Polymerization" ↓

Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.



Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.



Computational Screening

Prof Wenjian Liu
刘文剑 教授
Shandong University, China
山东大学 · 青岛

Prof Zhibo Li
李志波 教授
QUST, China
青岛科技大学

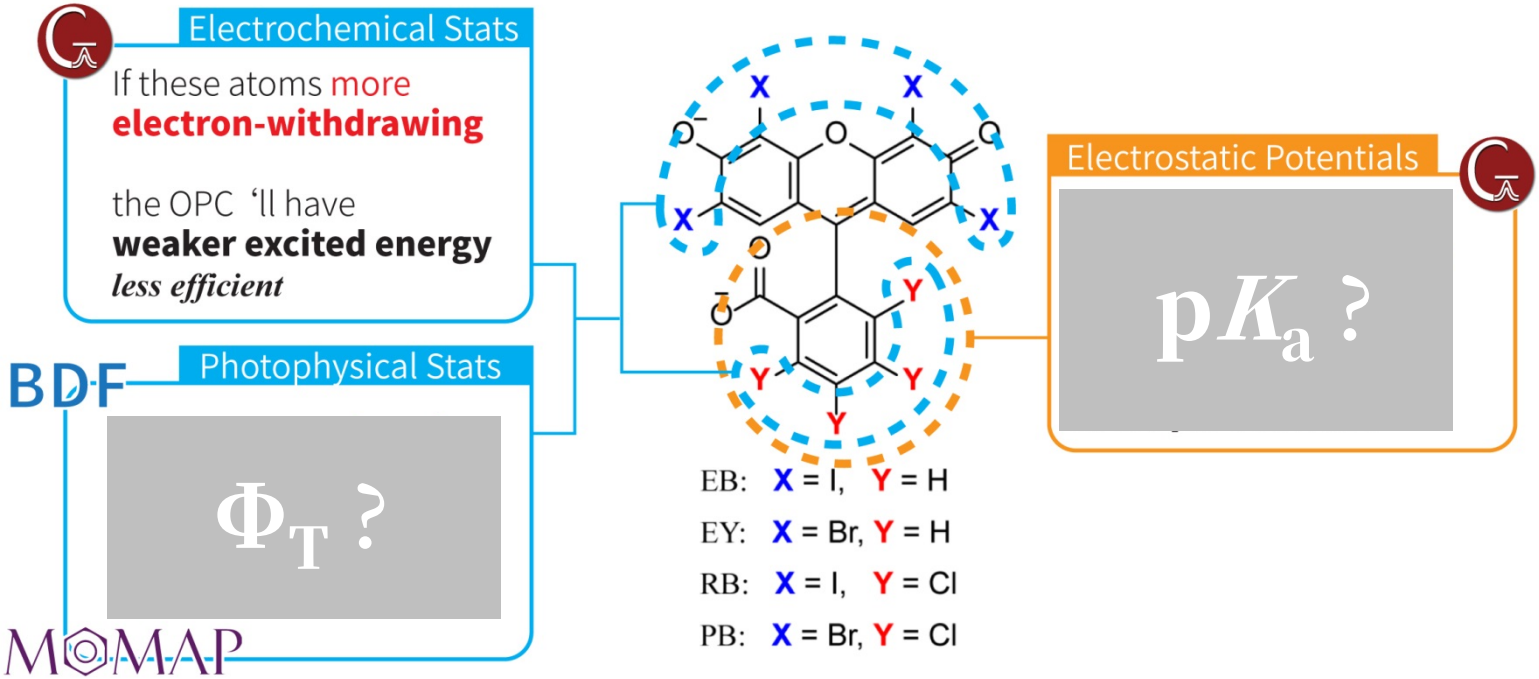
Dr Xiaonan Kan
阚晓楠 博士
QUST, China
青岛科技大学

Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

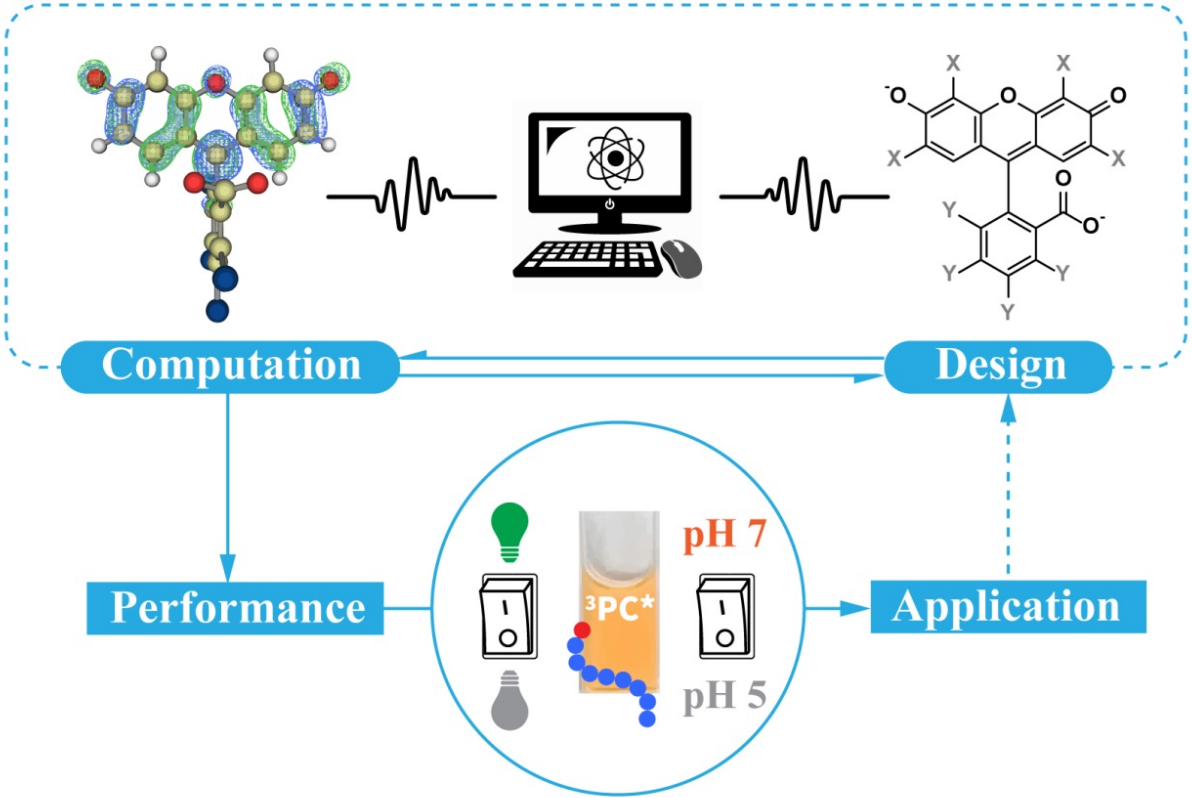
Theories and methodologies

DESIGN & PREDICT

Structure-Property Relationships



Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

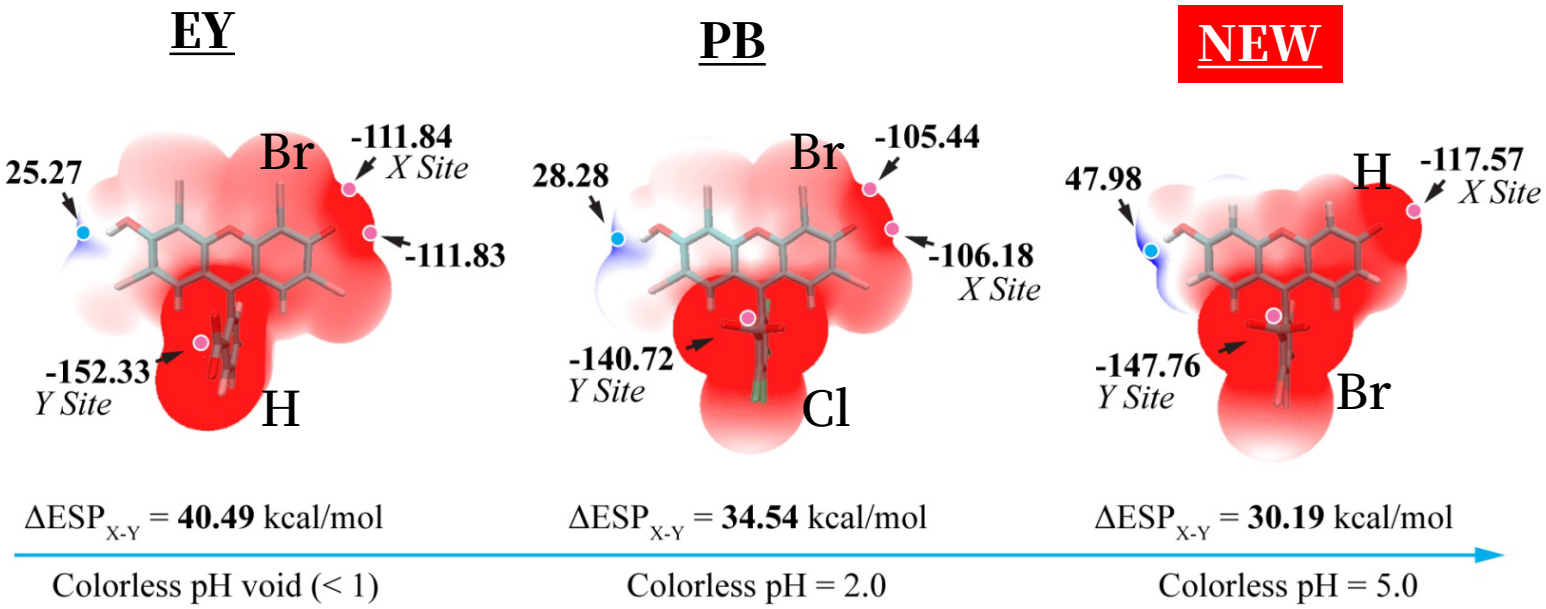


"Computer-Guided Discovery of a pH-Responsive Organic Photocatalyst and Application for pH and Light Dual-Gated Polymerization" ↓

Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

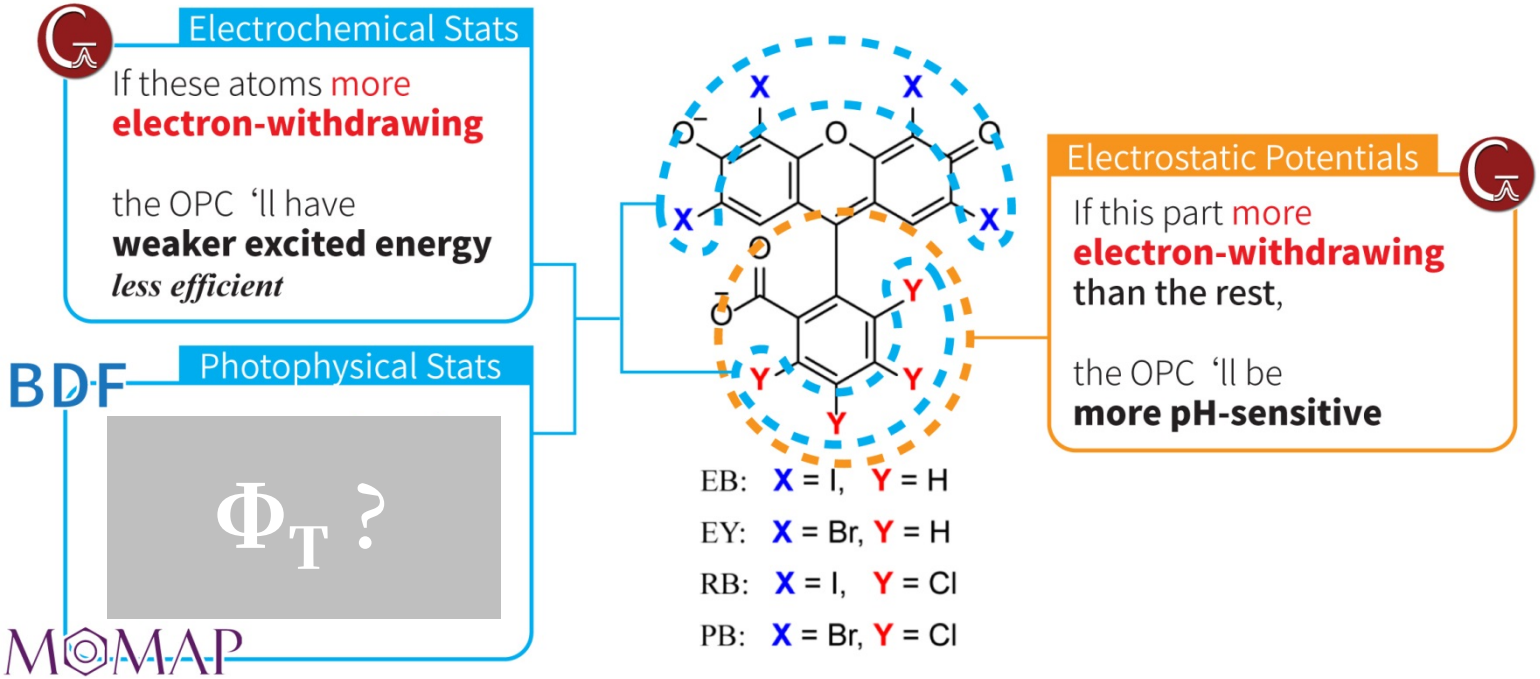
（略）

Physical Property Prediction



Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

Structure-Property Relationships



Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

（略）

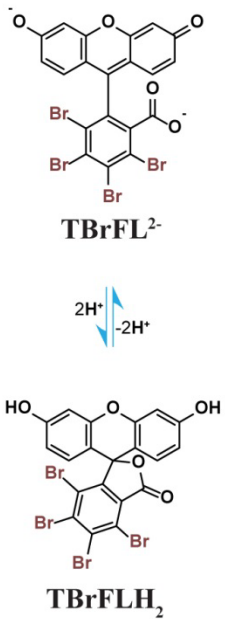
Spectral Property Prediction

TD-DFT ↓

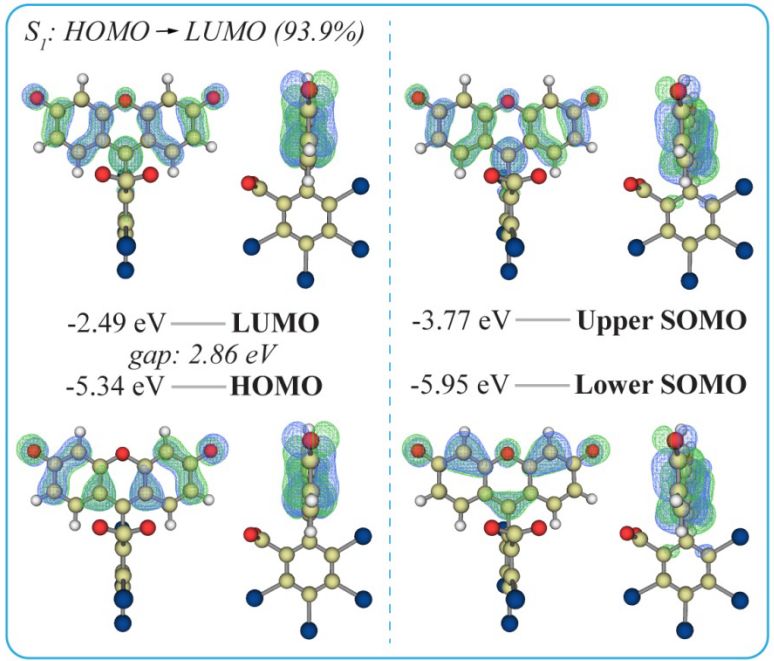
Green Light Absorption ~ 500 nm (f = 0.71)

UV Light Absorption ~ 300 nm

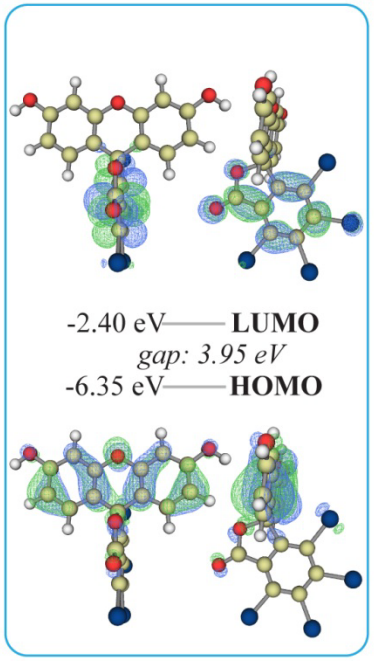
A)



B) $TBrFL^{2-}$

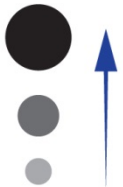


C) $TBrFLH_2$



Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

Heavy Atom Effect



spin orbit coupling (SOC) ↑

$S_1 \rightarrow T_n$ ISC rates ↑

Φ_T ↑

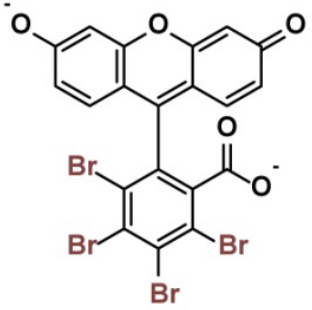
Relativistic effect scales like ~Z^2

SOC calculation: **sf-X2C-TDDFT/soc-DKH1** spin-free X2C Hamiltonian + 1st-order SOC by the DKH-type of SOC operator

Pyykkö, P., *Chem. Rev.* 1988, 88, 563-594; Li, Z.; Xiao, Y.; Liu, W., *J. Chem. Phys.* 2014, 141 (5), 054111.

（详）

BDF ➡ MOMAP



TBrFL^{2-}

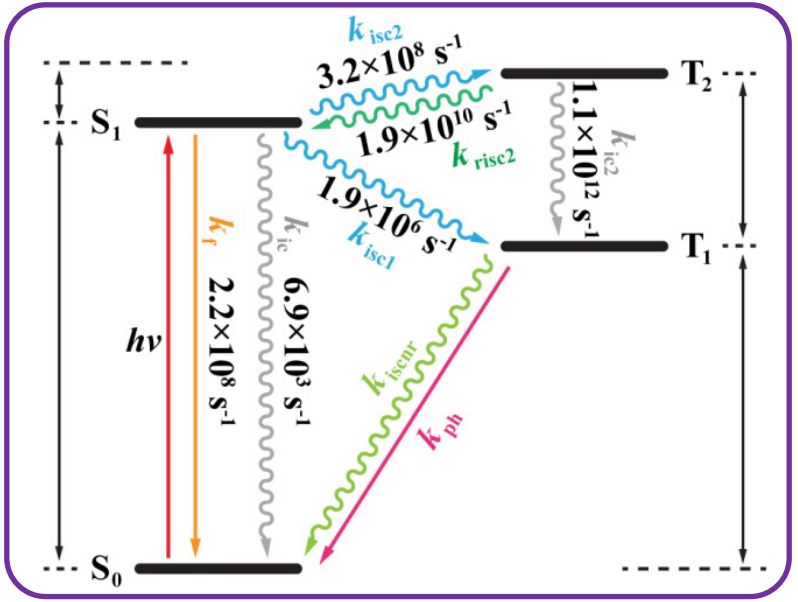
Spin-Orbit Coupling

$\langle S_1|H_{SOC}|T_1\rangle = 0.61\ cm^{-1}$

$\langle S_1|H_{SOC}|T_2\rangle = 28.33\ cm^{-1}$

$\langle S_1|H_{SOC}|T_3\rangle = 5.56\ cm^{-1}$

(T_3 high energy level)

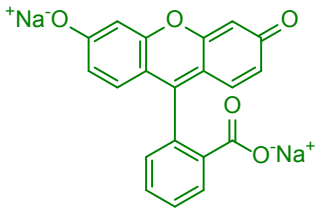


$$\Phi_T = \frac{k_{isc2}\left(1-\frac{k_{risc2}}{k_{risc2}+k_{ic2}}\right)+k_{isc1}}{k_f+k_{ic}+k_{isc2}\left(1-\frac{k_{risc2}}{k_{risc2}+k_{ic2}}\right)+k_{isc1}} = 0.58$$

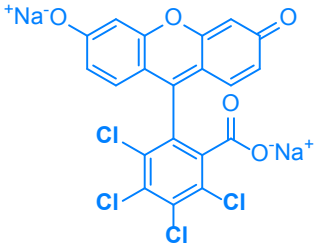
Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

Computed Measured

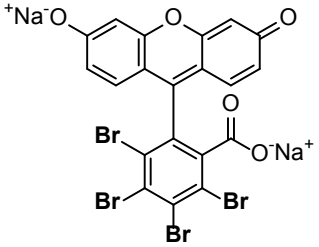
Dye	$E^0(PC^{\bullet+}/{}^3PC^*)$ V vs SCE	Φ_T	ΔESP_{X-Y} kcal/mol	Colourless pH
FL	**-1.45**	0.03	N/D	N/D
TClFL	N/D[a]	N/D	**29.99**	N/D
TBrFL	**-1.25**	**0.58**	**30.19**	**5**
EY	**-1.20**	0.57	**40.49**	**< 1**
PB	**-0.91**	0.65	**34.54**	**2**
RB	**-1.00**	0.79	N/D	**3.5**



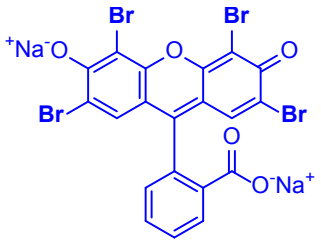
FL



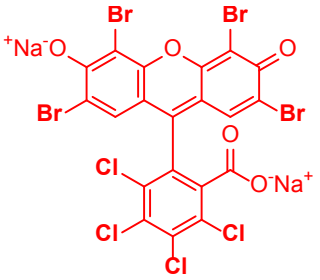
TClFL



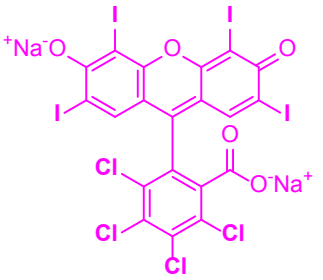
TBrFL



EY



PB



RB

Structure-Property Relationships

Electrochemical Stats

If these atoms more **electron-withdrawing**

the OPC 'll have **weaker excited energy** *less efficient*

Less ↑ ↓ More

Cl
Br
I
H

Photophysical Stats

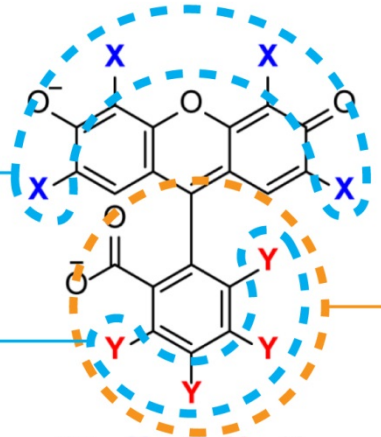
BDF

If these atoms **heavier**

the OPC 'll exihibit **higher Φ_T (heavy atom effect)**

More Br or I

MOMAP



EB: X = I, Y = H

EY: X = Br, Y = H

RB: X = I, Y = Cl

PB: X = Br, Y = Cl

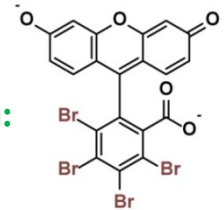
Electrostatic Potentials

If this part more **electron-withdrawing** than the rest,

the OPC 'll be **more pH-sensitive**

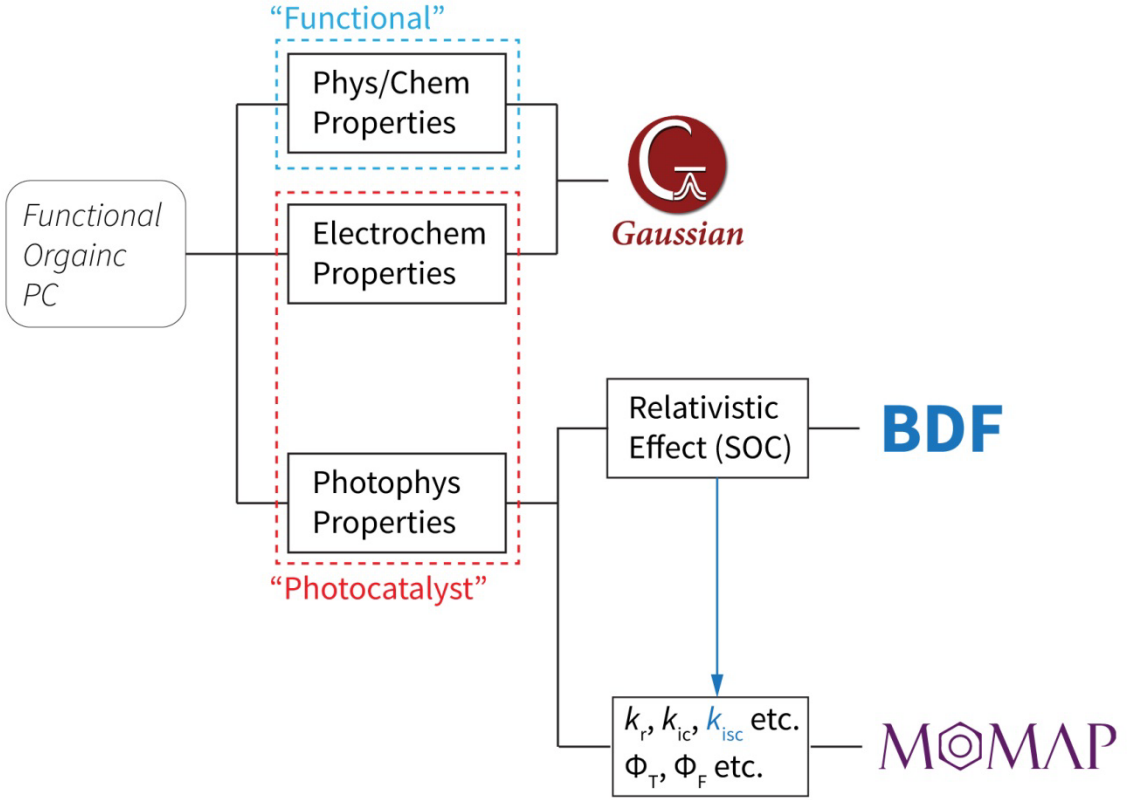
X = H
Y = Cl / Br

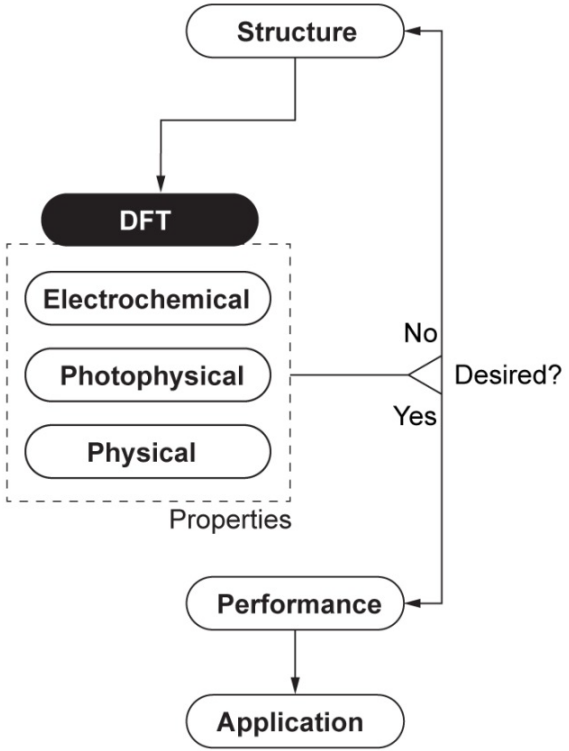
Overall BEST Design:



$TBrFL^{2-}$

Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

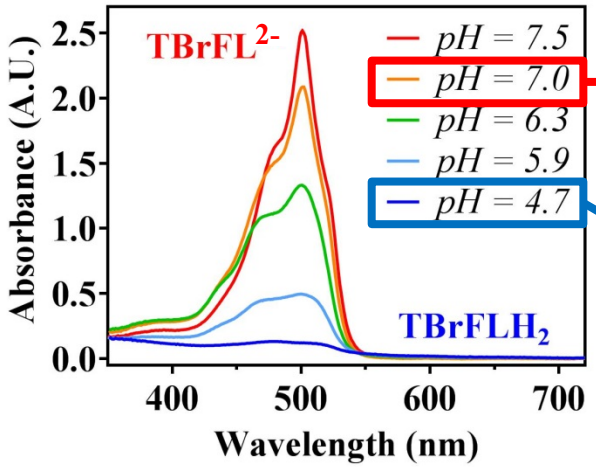




Computational Screening

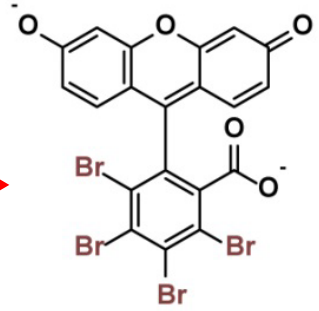
Results

THE NEW OPC

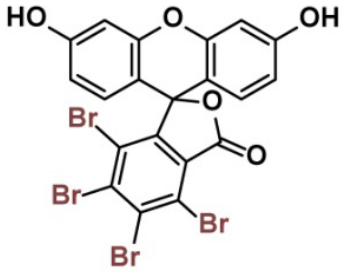


pH 7: "on"

pH 5: "off"



$TBrFL^{2-}$

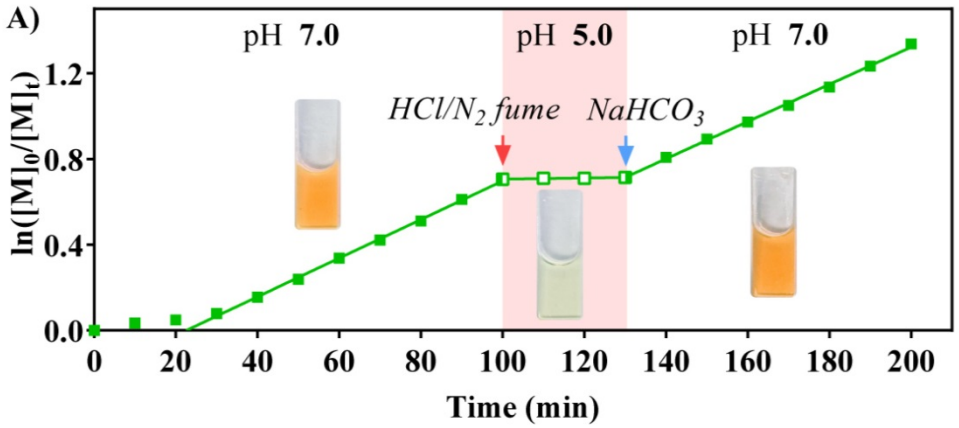


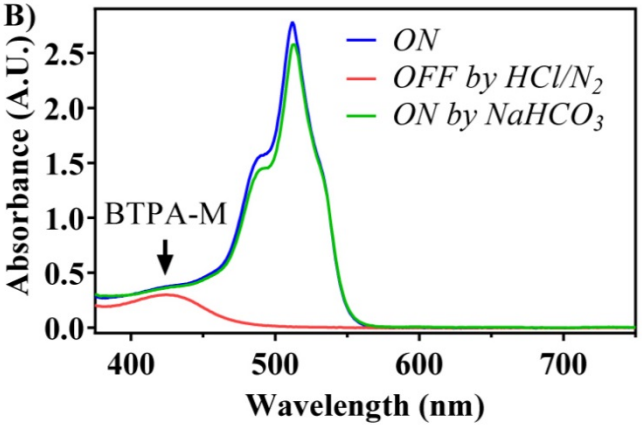
$TBrFLH_2$

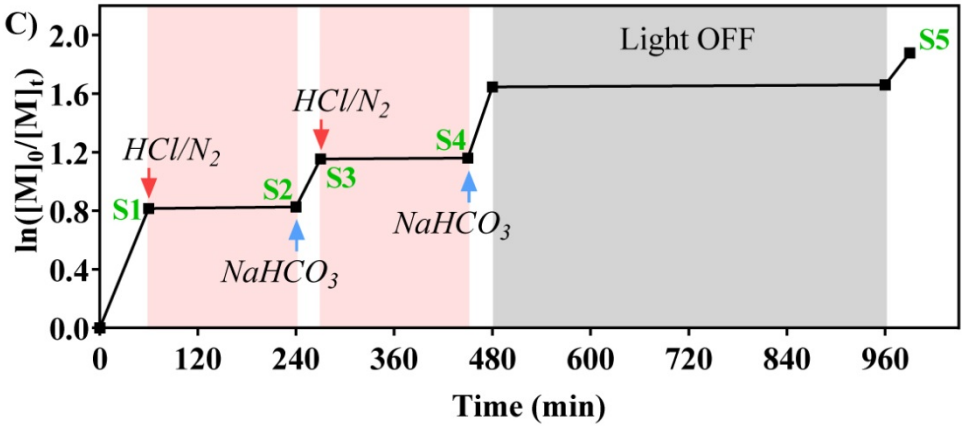
- ✓ Facile pH response
- ✓ High Efficiency
- ✓ Biocompatible

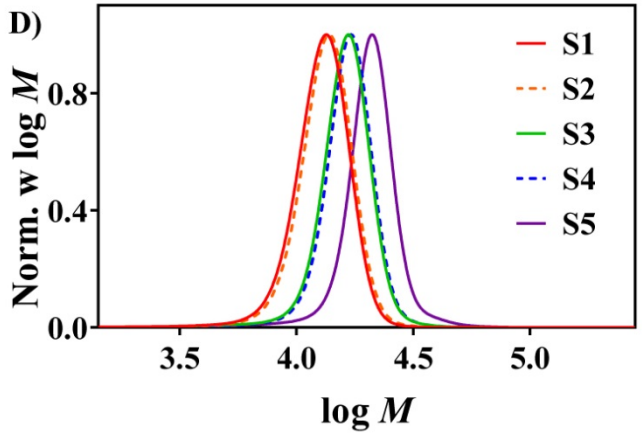
Best Candidate of pH-responsive OPC

Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.









Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

*Check my homepage at **kira.studio** for more info and future updates*

Acknowledgement

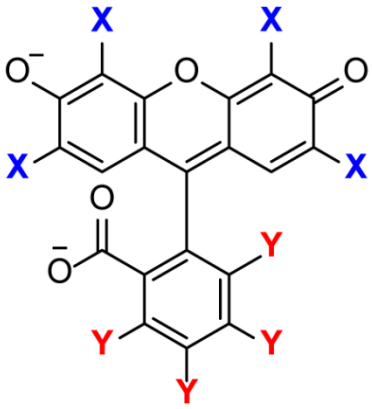
- Prof Cyrille Boyer
- Dr Jiangtao Xu
- Dr Nathaniel Corrigan
- Dr Kenward Jung
- Hengqi Chen
- Junchen He
- Dr Sivaprakash Shanmugam
- Dr Jordan Theriot
- Prof Wenjian Liu
- Prof Bingbing Suo
- Prof Garret Miyake
- Dr Chern-Hooi Lim
- Prof Jian Zhu
- Dr Xiaonan Kan
- Prof Zhibo Li
- Eu Hau Pan

Special thanks to the MOMAP Team, HZWTECK Beijing Density Functional (BDF) HPC Katana Team, UNSW

Wu, C.; Chen, H.; Corrigan, N.; Jung, K.; Kan, X.; Li, Z.; Liu, W.; Xu, J.; Boyer, C., *J. Am. Chem. Soc.* 2019, 10.1021/jacs.9b01096.

Structructure-Property Relationships

A)



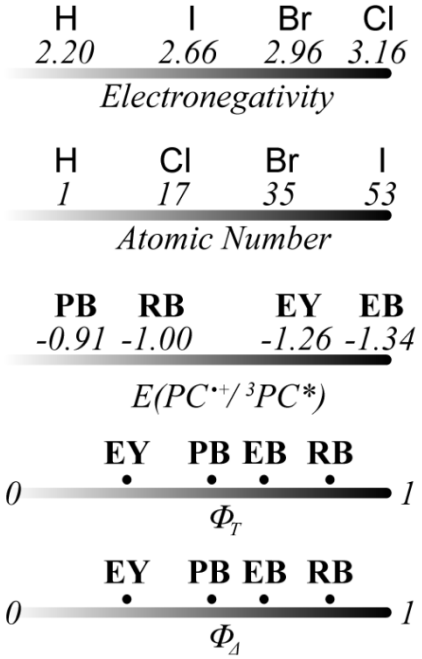
EB: X = I, Y = H

EY: X = Br, Y = H

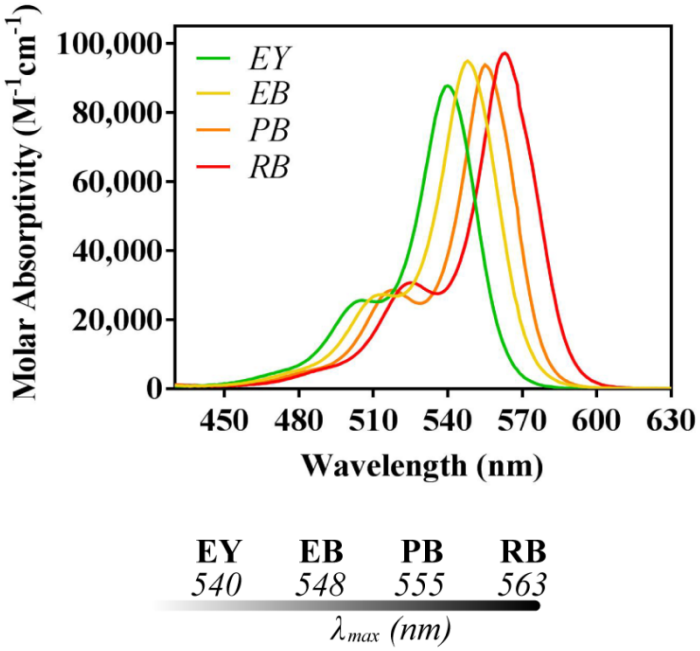
RB: X = I, Y = Cl

PB: X = Br, Y = Cl

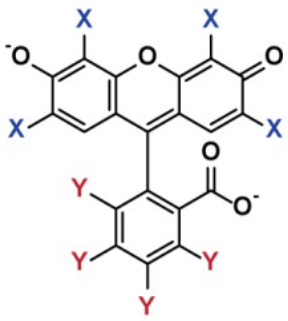
B)



C)



Structructure-Property Relationships



FL: X = H, Y = H
EY: X = Br, Y = H
PB: X = Br, Y = Cl
TBrFL: X = H, Y = Br

EY **PB** **TBrFL**
< 1 *2* *5*
0 *7*
Colourless pH

H I Br Cl
2.20 *2.66* *2.96* *3.16*
Electronegativity

H Cl Br I
1 *17* *35* *53*
Atomic Number

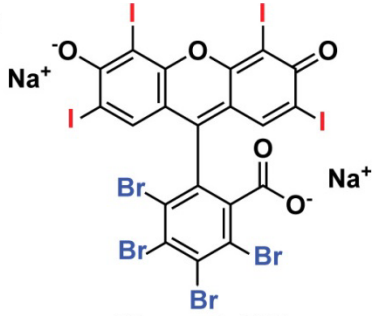
PB **EY/TBrFL** **FL**
-0.91 *-1.20/-1.25* *-1.45*
$E(PC^{\bullet+}/{}^3PC^*)$ vs SCE

FL **EY** **TBrFL** **PB**
0.03 *0.39-0.57* *0.58* *0.59-0.65*
Φ_T

Structure-Property-Performance

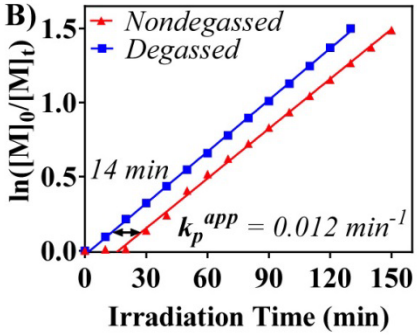
Dye	EY	PB	EB	RB	H1
Φ_T	0.28-0.32	0.40	0.62-0.69	0.76-0.86	0.82-0.90
Φ_Δ	0.39-0.57	0.59-0.65	0.62-0.63	0.75-0.79	
Oxygen Inhibition	90 min	47 min	41 min	23 min	14 min
$E^0(PC^{\bullet+}/^3PC^*)$ (V, vs. SCE)	-1.26	-0.91	-1.34	-1.00	-1.07
$k_{p,app}$ (min^{-1})	0.014	0.007	0.023	0.010	0.012

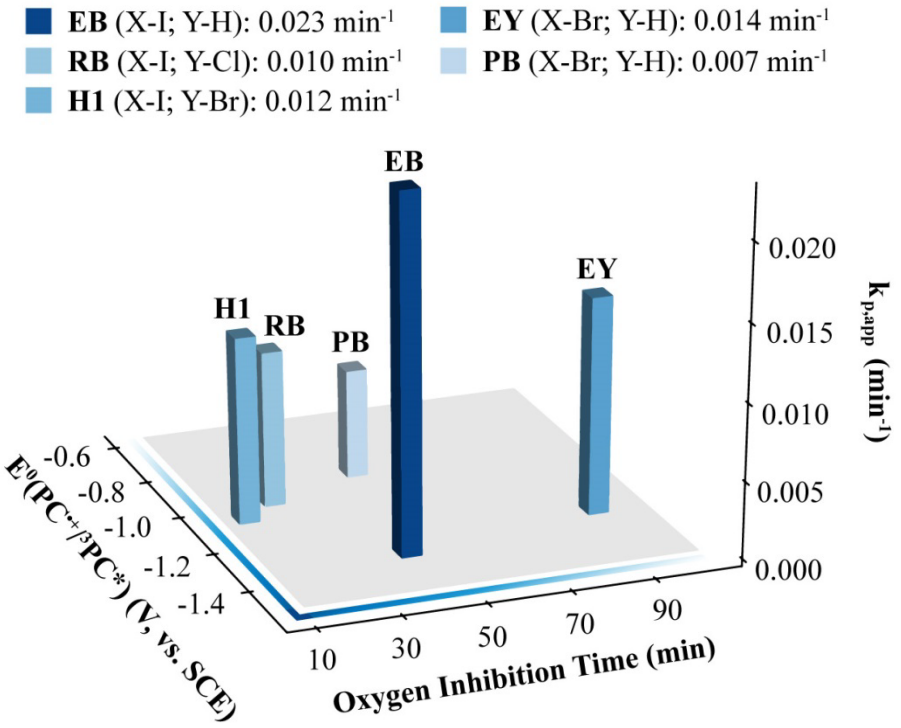
A)



Henry-1 (H1)

B)





Structure-Property-Performance

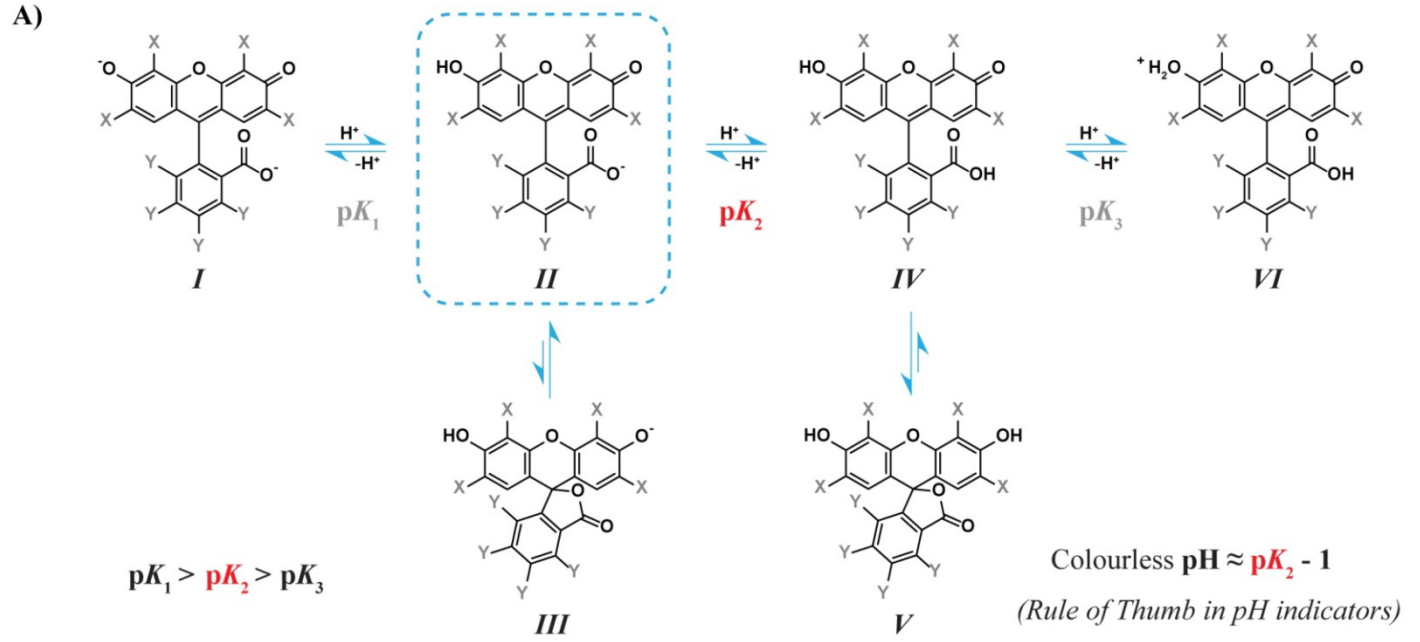
S

P

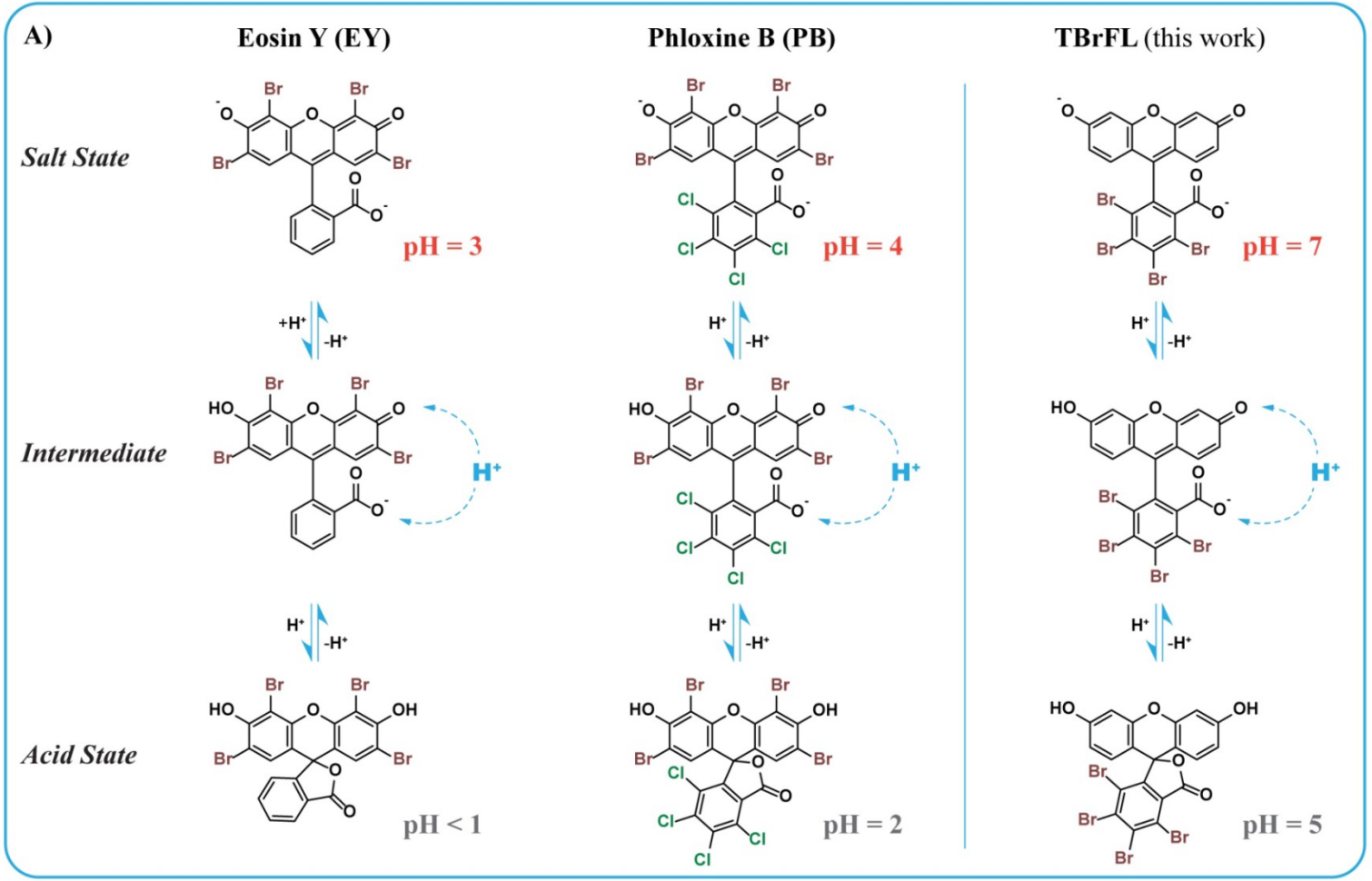
P

	EY	EB	PB	RB
X-position	Br × 4	I × 4	Br × 4	I × 4
Y-position	H × 4	H × 4	Cl × 4	Cl × 4
$\lambda_{max,\ abs}$ (nm)	540	548	555	563
$\varepsilon_{max,\ abs}$ ($M^{-1}cm^{-1}$)	87800	95000	93800	97300
Φ_T	0.28-0.32	0.62-0.69	0.4	0.76-0.86
Φ_Δ	0.39-0.57	0.62-0.63	0.59-0.65	0.75-0.79
$E^0(PC^{\cdot +}/{}^3PC^*)$ (V, vs. SCE)	-1.26	-1.34	-0.91	-1.00
k_p^{app} (min^{-1})	0.014	0.023	0.007	0.010
O_2 inhibition period (min)	90	41	47	23

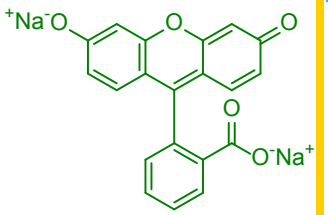
Supporting Slides



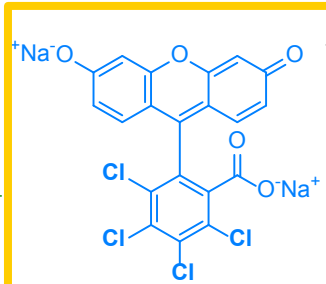
Supporting Slides



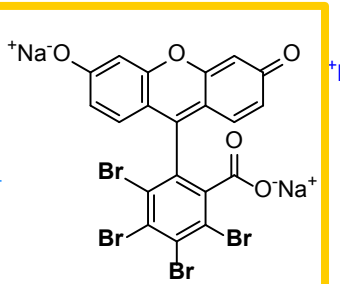
X less EW, Y more EW = colorless pH ⬆



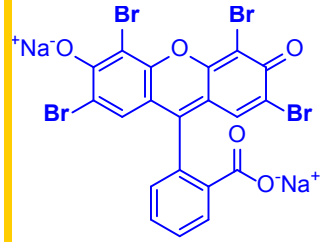
FL



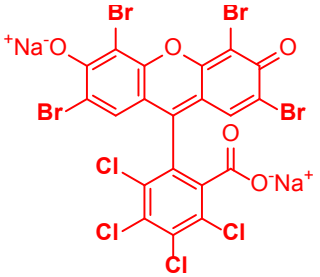
TClFL



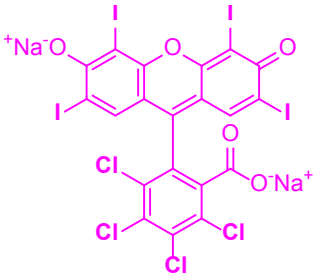
TBrFL



EY



PB

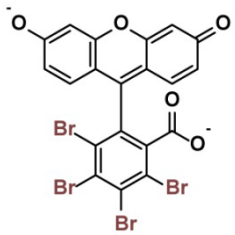


RB

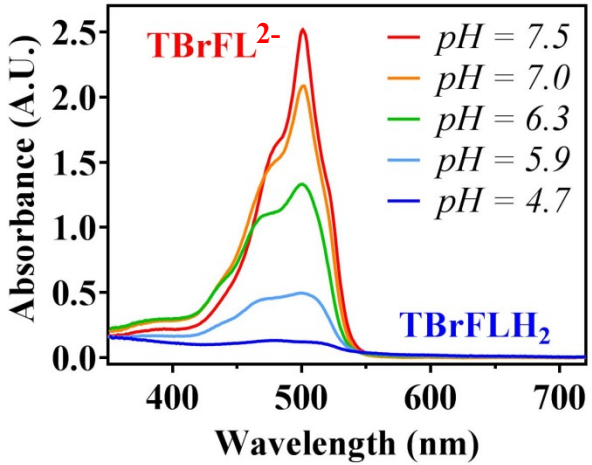
H	I	Br	Cl	F
2.20	2.66	2.96	3.16	3.98

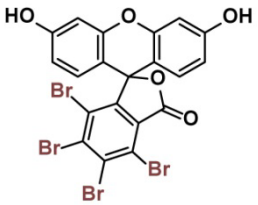
Electronegativity

Spectral Properties ✓



$TBrFL^{2-}$





$TBrFLH_2$

TBrFL-Catalysed PET-RAFT