Intrinsically Stretchable pCO_2 Sensor Enabled by Multi-functional Block Copolymer Matrices

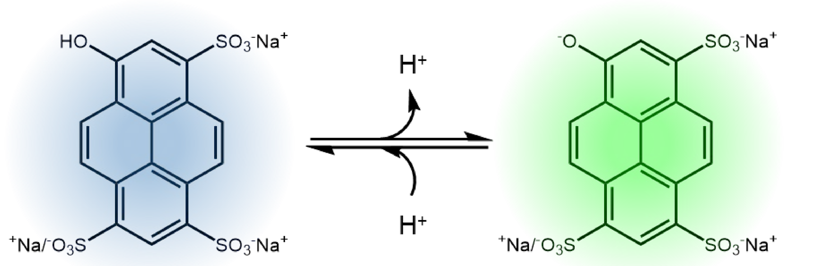
MinJae Kim[1], Emmanouil Rousakis[2], Victoria Lozano[2], Conor Evans[2*]

[1] Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea
[2] Wellman Center for Photomedicine, Massachusetts General Hospital, Harvard Medical School, Charlestown, MA, United States
E-mail: mj3259@kaist.ac.kr, *Corresponding: evans.conor@mgh.harvard.edu

Introduction

pCO_2 sensing by HPTS

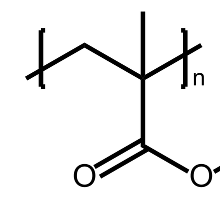
CO_2 *(g)* + H_2O *(l)* → H_2CO_3 *(aq)*



Fluorescence under 405 nm excitation (DH)

Fluorescence under 405 and 470 nm excitation (D^-)

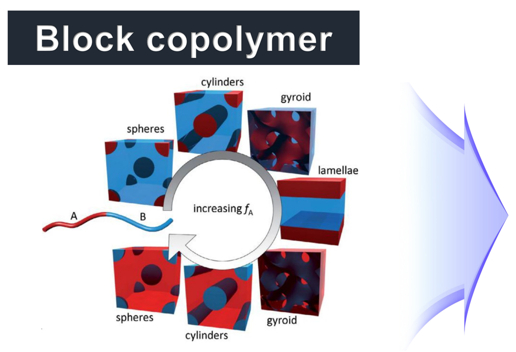
Conventional polymer matrix: PPMA



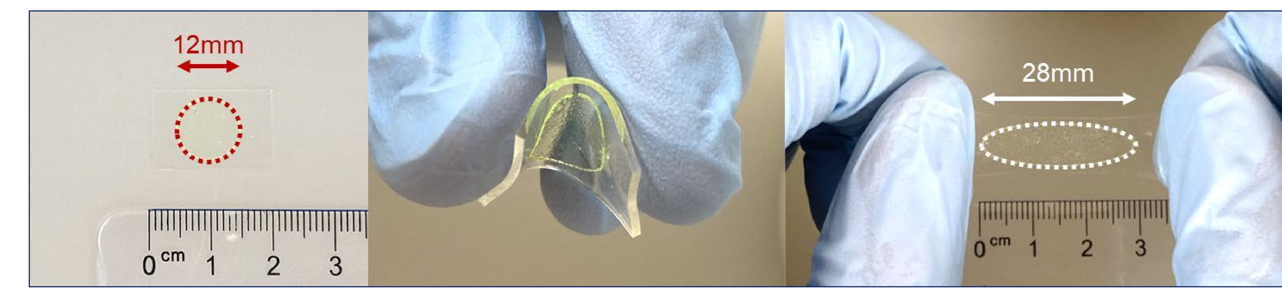
Challenges

- High Young's modulus ~ 1 GPa → Rigid sensor
- Easily dried → Loss of sensing capability
- Fast photobleaching → Signal changes over time

Block copolymer



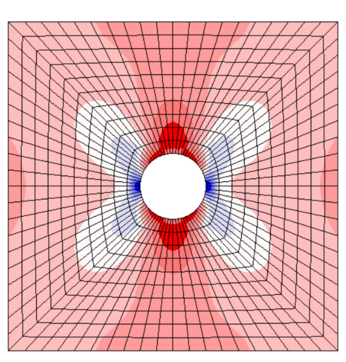
Intrinsically flexible and stretchable pCO_2 sensor



- Block copolymer with large chemical differences between blocks spontaneously undergoes microphase separation to minimize total energy and forms a nanostructure
- The multi-functional block copolymer matrices overcome the limitations of the previous PPMA-based and composite matrix

Theoretical

Finite Element Analysis (FEM) for composite stretchable sensor



Effective stress mapping for PDMS – HPTS@SiO_2

- FEM revealed that conventional stretchable PDMS – HPTS@SiO_2 composite pCO_2 sensor undergoes severe stress concentration of over 600% compared to an intrinsically stretchable sensor
- The stress concentration would induce mitigation on mechanical stability, as well as gas permeability
- Therefore, intrinsic stretchability is imperative

pCO_2-dependent fluorescence signal

pCO_2 change → pH change → Fluorescence change

$$Q^+D^- \cdot xH_2O + CO_2(g) \rightleftharpoons Q^+HCO_3^- + HD \cdot (x-1)H_2O \quad \text{(Equilibrium constant: } K = \frac{[HD]}{[D^-]\cdot pCO_2}\text{)}$$

$$R = \frac{I_{470}}{I_{405}} = \frac{\text{contributions of HD and } D^- \text{ to emission @470nm excitation}}{\text{contributions of HD and } D^- \text{ to emission @405nm excitation}} = \frac{\Gamma_{470}^{HD}[HD] + \Gamma_{470}^{D^-}[D^-]}{\Gamma_{405}^{HD}[HD] + \Gamma_{405}^{D^-}[D^-]}$$

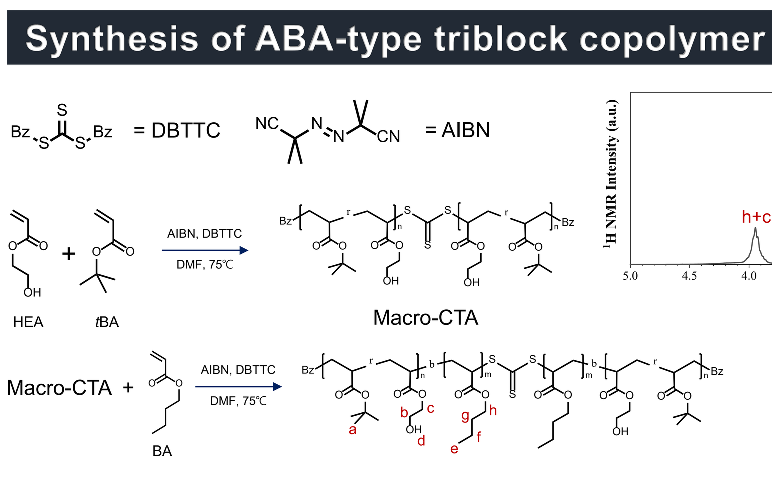
$$pCO_2 = \frac{1}{K}\cdot\frac{[HD]}{[D^-]} = \frac{1}{K}\cdot\frac{\Gamma_{470}^{D^-} - R\Gamma_{405}^{D^-}}{R\Gamma_{405}^{HD} - \Gamma_{470}^{HD}} \simeq \frac{k'}{R} - k'' \quad (\because \Gamma_{470}^{HD} \to 0 \text{ experimentally})$$

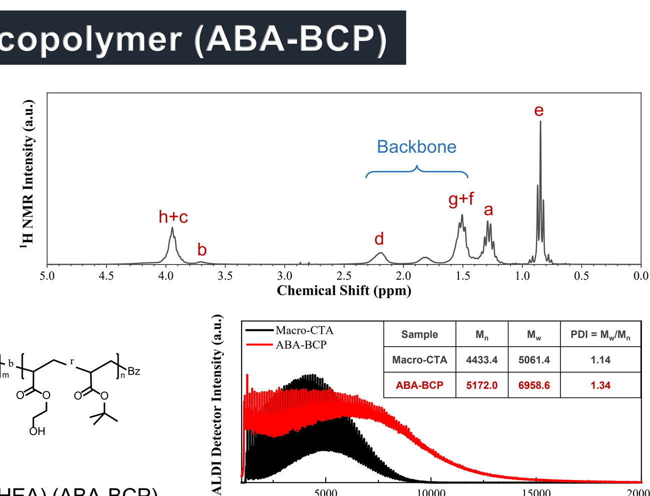
$R \simeq \frac{I_{470}}{I_{405}} = \frac{k'}{pCO_2 + k''}$ matches well with experimental data (dotted lines on the R - pCO_2 graphs)

Note: Γ = Oscillator strength, TOA = Q^+ = Tetraoctylammonium

Experimental

Synthesis of ABA-type triblock copolymer (ABA-BCP)

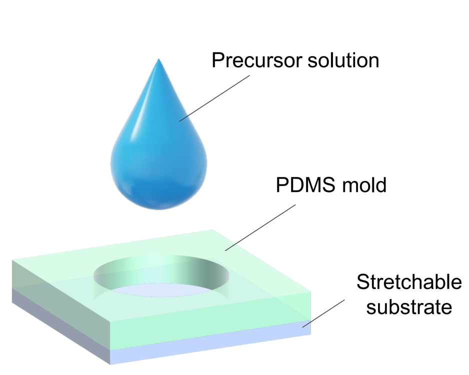




Sensor fabrication

Fabrication condition

- Precursor solution is made by mixing $HPTS^{4-}\cdot(TOA^+)_4$, TOA^+OH^-, NaOH, and polymer in methanol (or if required, tetrahydrofuran is mixed with methanol)
- Drop-casting of the precursor solution into PDMS mold, and sequential detaching of the mold



Conclusion

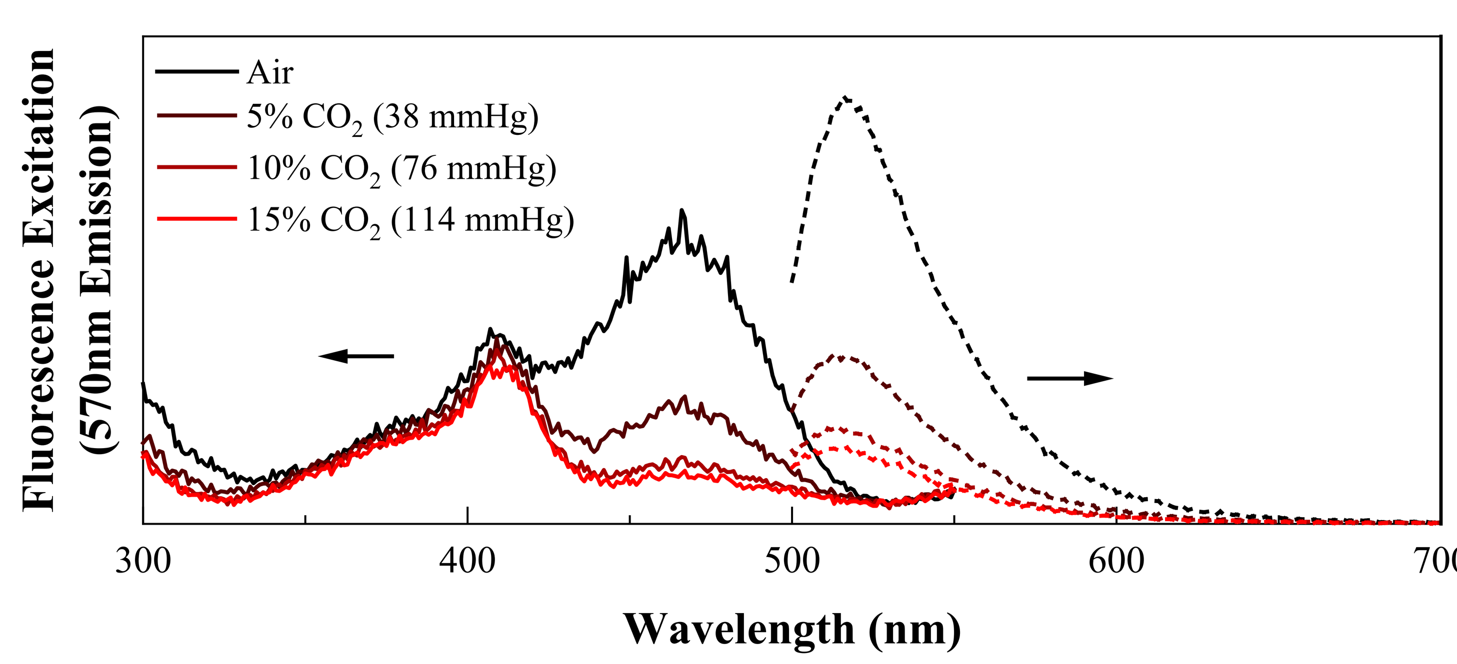
- By adopting a multifunctional matrix for the fluorescent molecule HPTS, we enabled **the first intrinsically flexible and stretchable pCO_2 sensor**
- The stretchable sensors showed excellent mechanical stability, reversibility, and sensing capability
- This work enables a novel modality for Point-of-Care for respiratory and metabolic diseases like hypercapnia

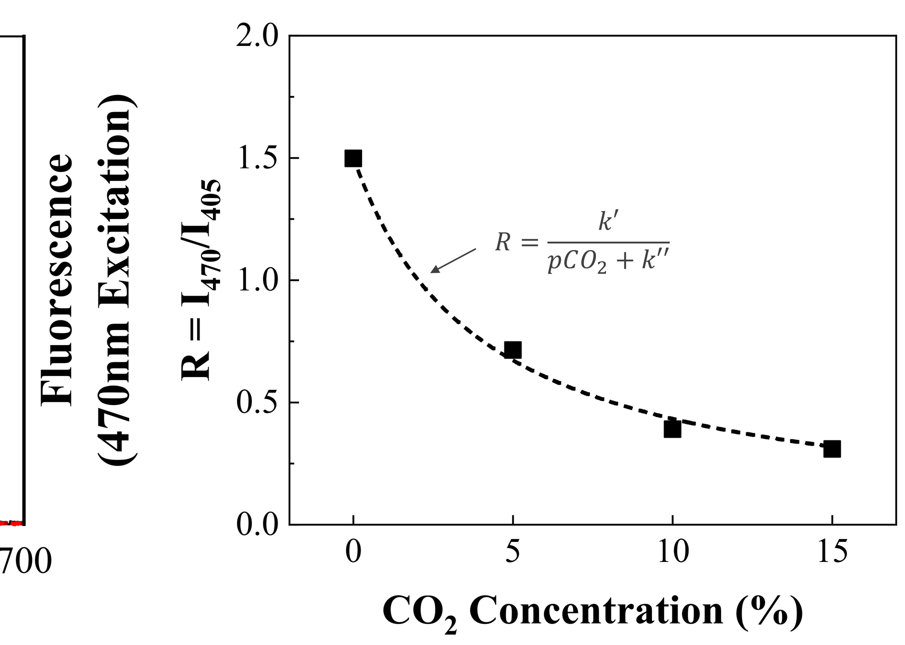
Acknowledgements

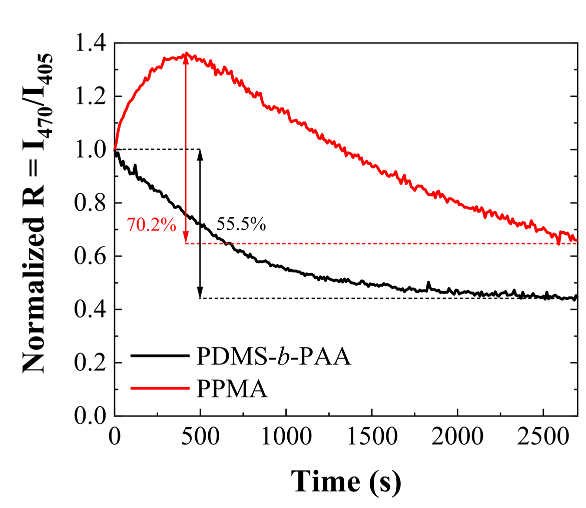
This summer was like *Komorebi* because of all of you in Evans Lab and the program. First, my gratitude goes to my PI, Conor, who made this summer a truly dazzling experience for me. The two months of experience revigorated my passion for science. At every juncture in the lab, I was awed a lot by the ardor, expertise, and experiences that Manolis has, and learned so much from him. I am indebted so much to Victoria for not only her kind guidance but also the competence and techniques she taught me. You were the best advisor and mentors that I could have. Also, the discussions we had in the chemistry group left unforgettable lessons for me. I remember the happy times that all the other group members including Wonsang made for me. Last but not least, I am grateful to Andy and Fred for making this wonderful opportunity.

Results

PDMS-*b*-PAA matrix with TOA-TOAOH buffer system



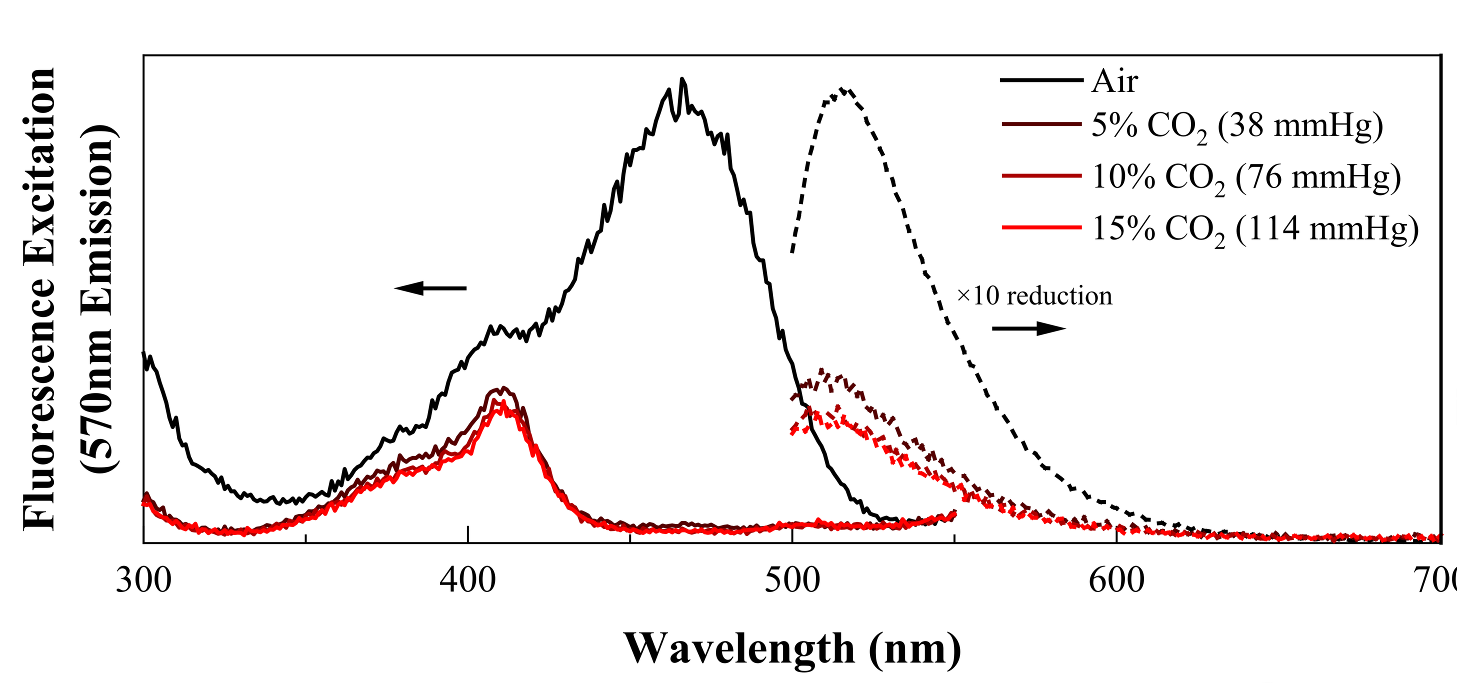


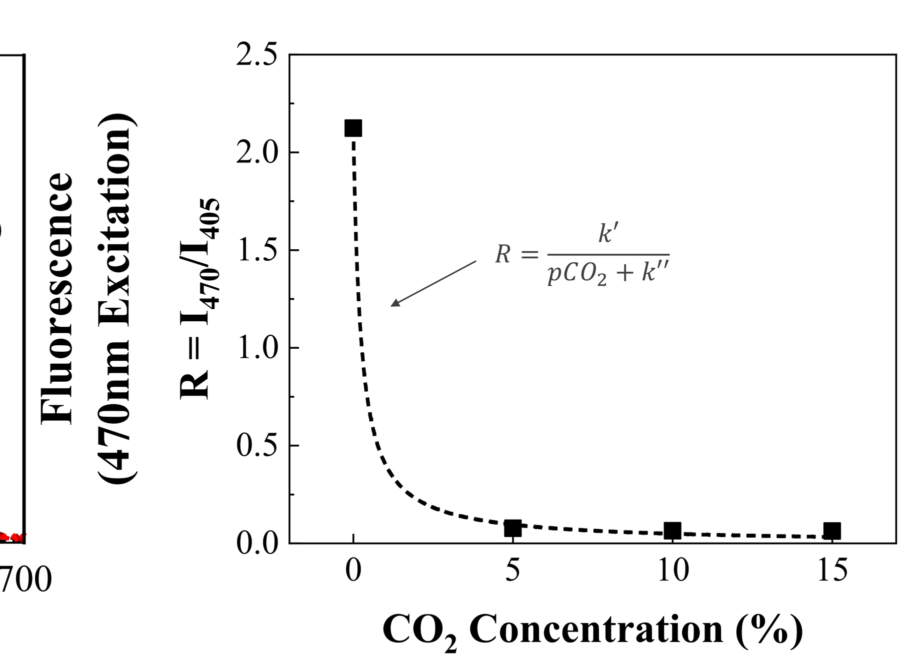


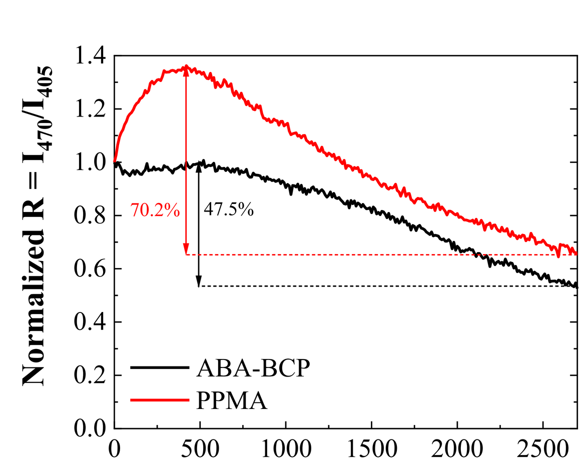
Photostability (Stretched exponential model)		
Wavelength	405 nm	470 nm
PDMS-*b*-PAA	1540 min	34.1 min
PPMA	39.4 min	28.6 min

- Sensors with sensitivity within 0 - 15% pCO_2 were fabricated
- Isosbestic point @405nm could be used as the reference peak
- R = I_{470}/I_{405} followed the model derived in the theoretical section The sensors retained their pCO_2 sensing capability after 100 times stretching of at least 200% strain
- Compared to PPMA, the new block copolymer displayed substantially reduced photobleaching

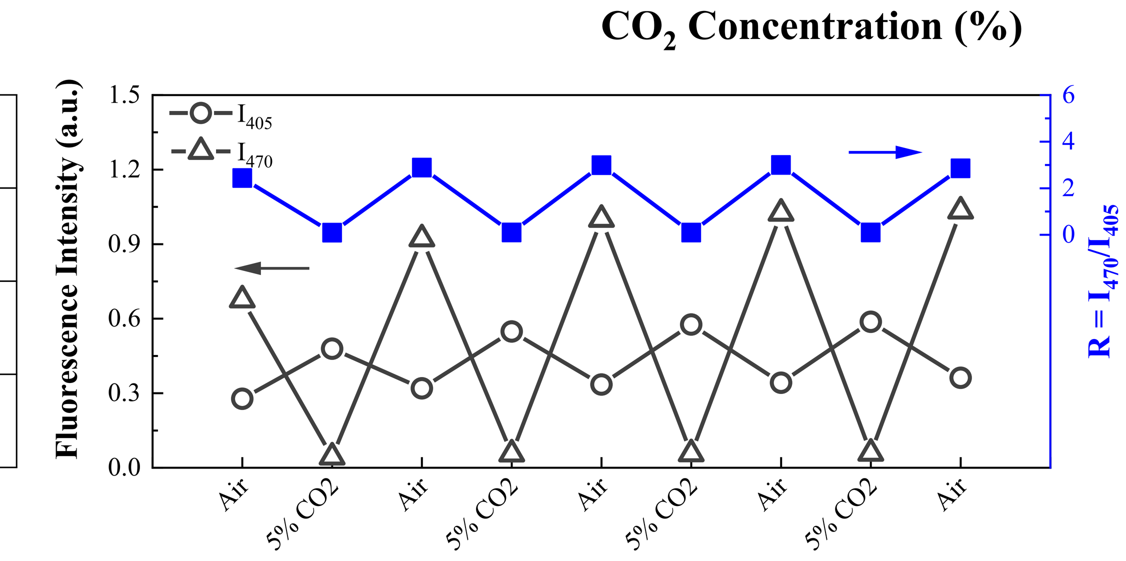
ABA-BCP matrix with TOA-TOAOH buffer system







Photostability (Stretched exponential model)		
Wavelength	405 nm	470 nm
ABA-BCP	301 min	49.1 min
PPMA	39.4 min	28.6 min



- Sensitivity within the physiological pCO_2 window ($R_{air}/R_{5\%\ CO2}$) was greatly improved by 13.1 times to 27.5 from 2.1 of the PDMS-*b*-PAA matrix
- ABA-BCP further mitigated the photobleaching of HPTS, which resulted in extraordinarily stable photophysical properties over 10 min
- Sensors made of the ABA-BCP showed excellent reversibility over 5 times (> 90 min), during which R = I_{470}/I_{405} remained within ± 2.5% error
- Stretchable films retained their pCO_2 sensing capability after 100 times of stretching with 200% strain
- The sensors made out of ABA-BCP quantitatively showed excellent pCO_2 sensing capability in the physiological range under the mock extracorporeal membrane oxygenation (ECMO) system