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Multi-Stimuli Responsive FRET Processes of Dual-AIEgens in Amphiphilic Copolymer and Rotaxane Systems and Applications

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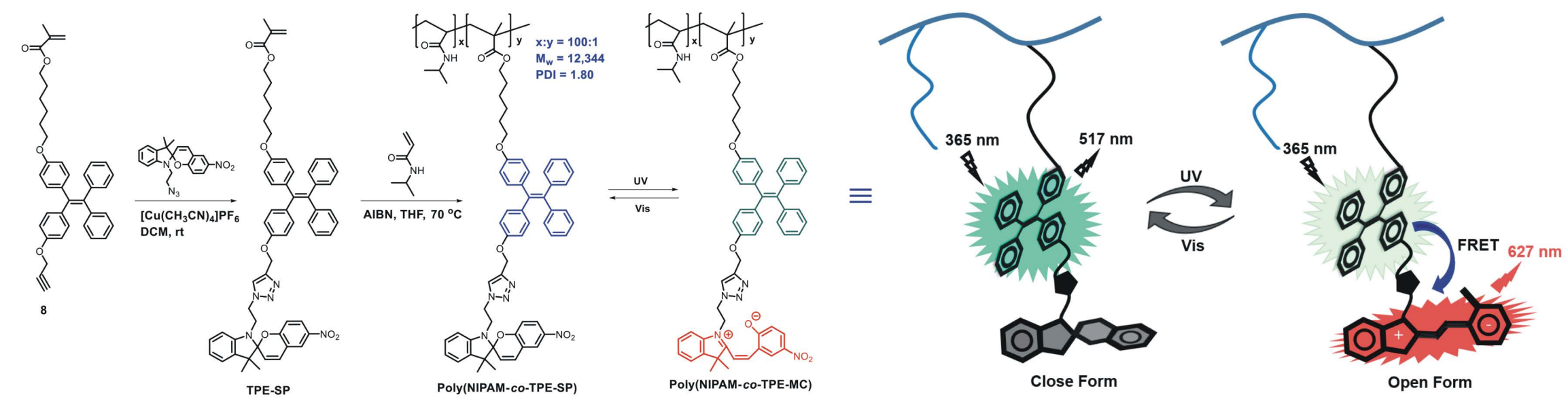


ABSTRACT

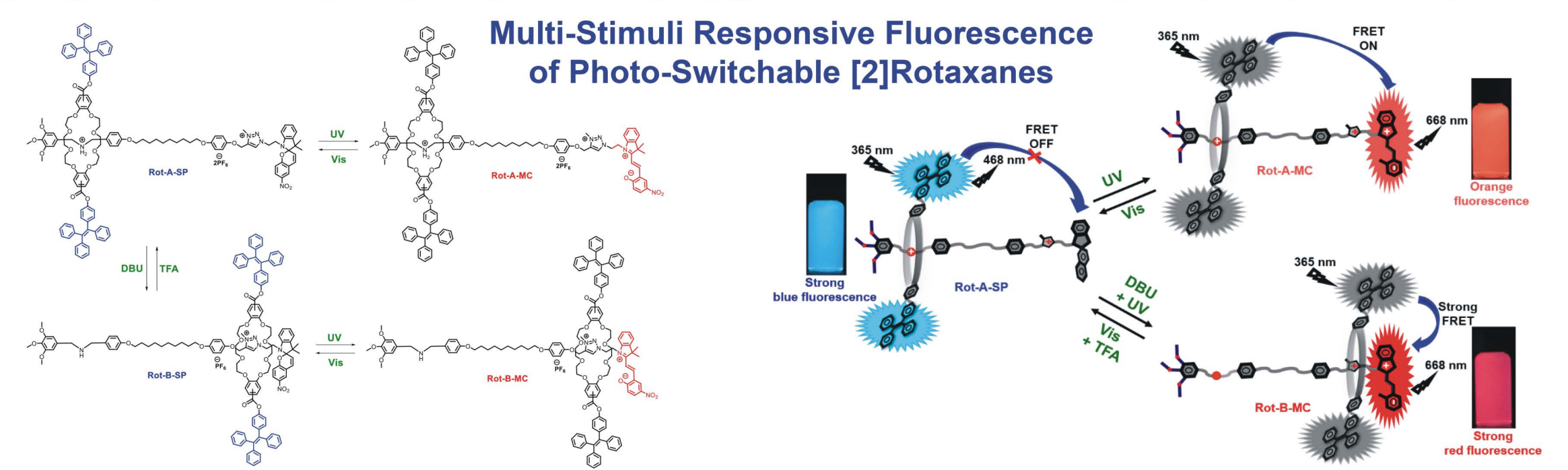
The novel multi-stimuli responsive FRET systems based on dual-AIEgens of tetraphenylethylene (TPE) and spiropyran/merocyanine (SP/MC) in amphiphilic aggregation-induced emission (AIE) copolymer, **poly(NIPAM-co-TPE-SP)/poly(NIPAM-co-TPE-MC)** and a series of photo-switchable [2]rotaxanes, **Rot-A-SP/Rot-A-MC**, **Rot-B-SP/Rot-B-MC** are designed and reported. Upon UV/Vis exposure, these AIE systems exhibit excellent reversible photo-switchable behaviors between the close form of non-emissive SP and the open form of emissive MC in semi- and aqueous solutions, leading to ratiometric fluorescence of TPE and MC emissions via Förster resonance energy transfer (FRET). Distinct FRET processes of these systems can be observed under various UV and visible light irradiations, acid-base conditions, thermal treatments, and cyanide ion interactions, which are also further confirmed by theoretical studies. Furthermore, the developed FRET sensor polymer **poly(NIPAM-co-TPE-MC)** shows a very high selectivity and sensitivity with a low detection limit towards the cyanide ion in water, which can be utilized for bio-imaging and cyanide detection in living cells. Owing to the interesting FRET phenomenon, **Rot-A-SP** displays excellent photochromic and fluorescence behaviors in a powder form and a solid film under UV/sunlight and Vis/heating processes, which have been successfully employed in distinct and reversible fluorescence photo-patterning applications.

MATERIALS AND METHODS

Synthesis of Monomer TPE-SP, Poly(NIPAM-co-TPE-SP), and Poly(NIPAM-co-TPE-MC)



Multi-Stimuli Responsive Fluorescence of Photo-Switchable [2]Rotaxanes



RESULTS AND DISCUSSION

Photo-Physical Studies, AIE Property, FRET Behaviors, and Applications of Copolymers

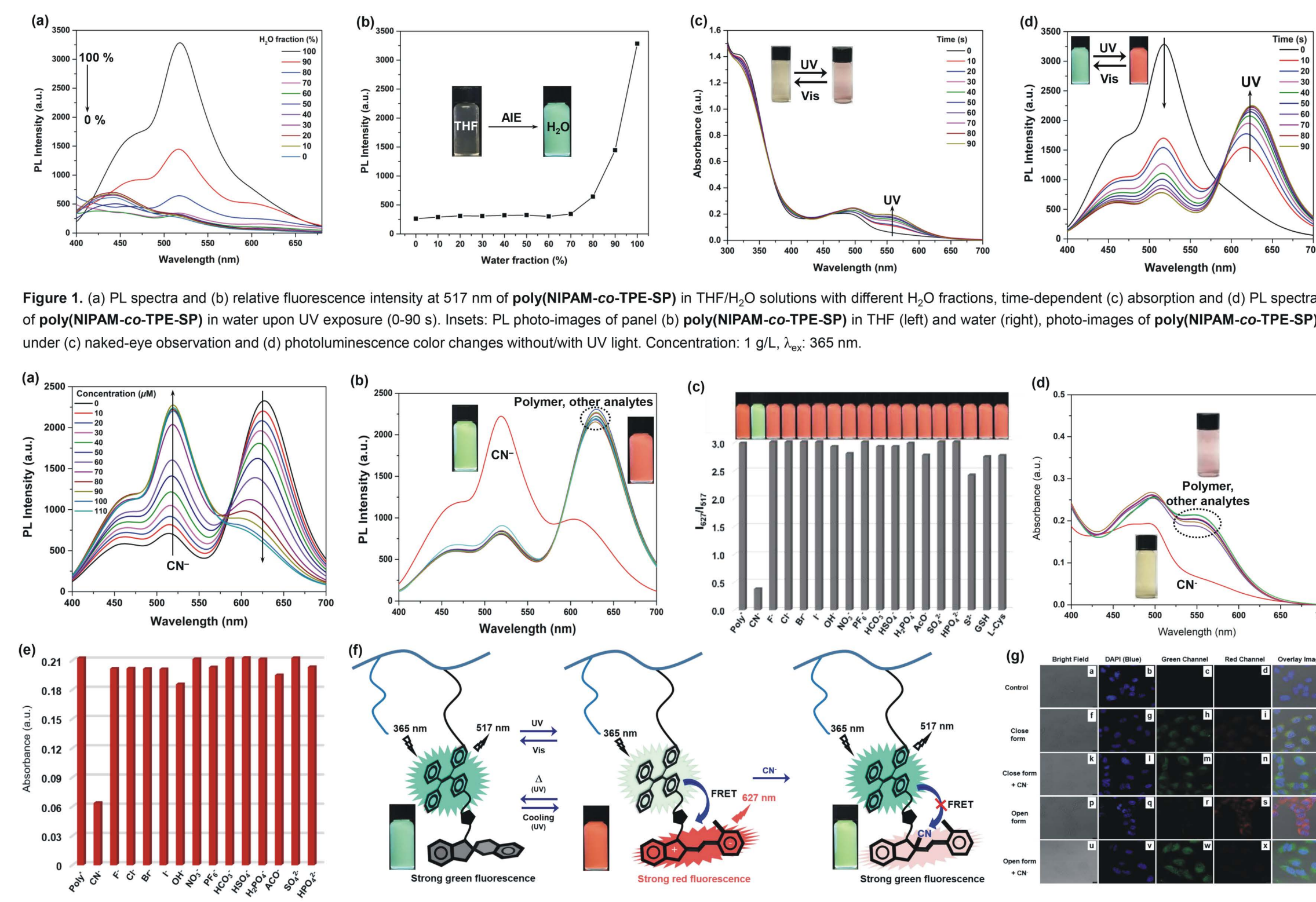


Figure 1. (a) PL spectra and (b) relative fluorescence intensity at 517 nm of poly(NIPAM-co-TPE-SP) in THF/H₂O solutions with different H₂O fractions, time-dependent (c) absorption and (d) PL spectra of poly(NIPAM-co-TPE-SP) in THF and water upon UV exposure (0-90 s). Inset: PL photo-images of panel (b) poly(NIPAM-co-TPE-SP) in THF (left) and water (right), photo-images of poly(NIPAM-co-TPE-SP) under (e) naked-eye observation and (f) photoluminescence color changes without/with UV light. Concentration: 1 g/L, λ_{exc} : 365 nm.

AIE Properties of [2]Rotaxanes

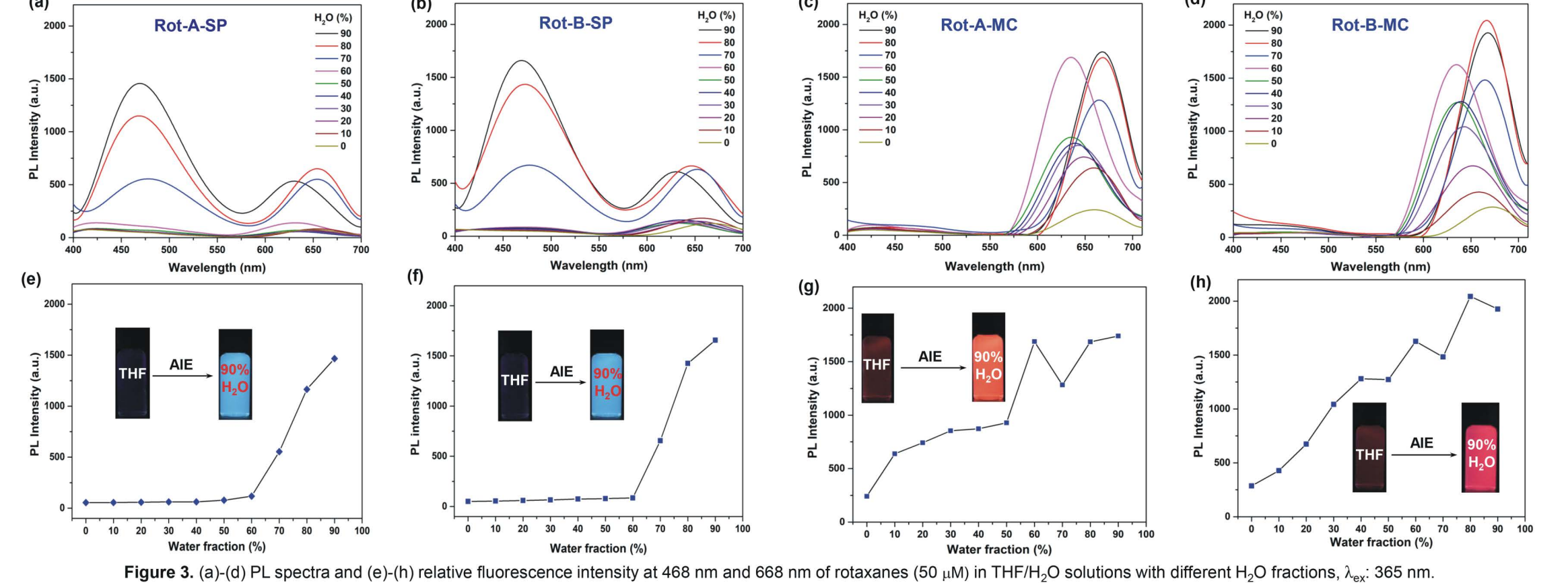


Figure 3. (a)-(d) PL spectra and (e)-(h) relative fluorescence intensity at 468 nm and 668 nm of rotaxanes (50 μ M) in THF/H₂O solutions with different H₂O fractions, λ_{exc} : 365 nm.

FRET Behaviors of [2]Rotaxanes

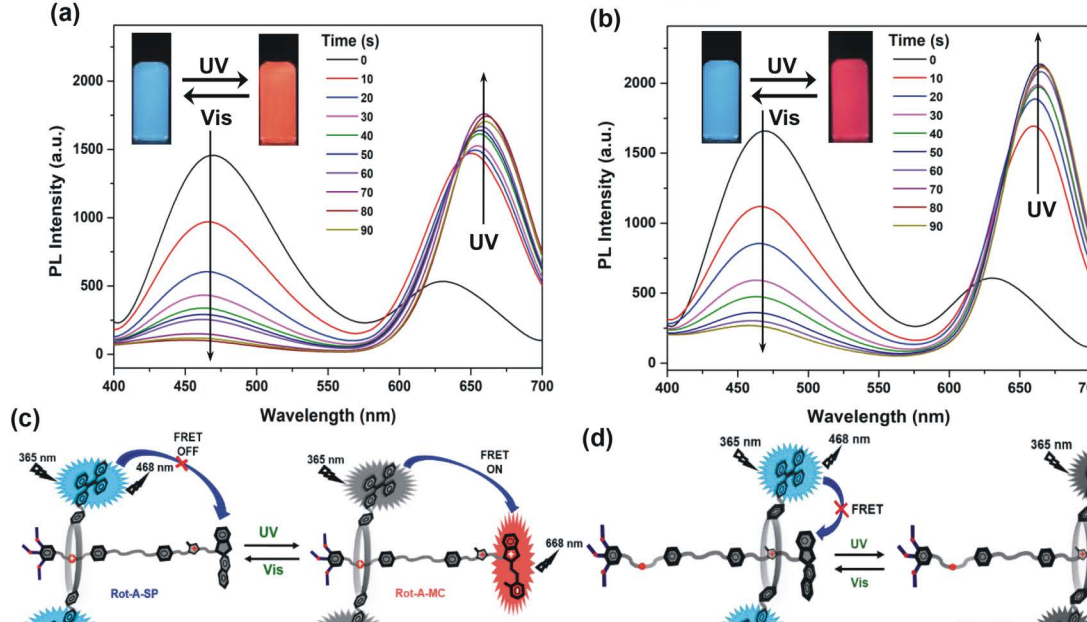


Figure 4. Time-dependent PL spectra of (a) Rot-A-SP, (b) Rot-B-SP (50 μ M) in H₂O/THF solvents (90% H₂O, v/v) upon UV exposure (0-90 s), (c) and (d) schematic illustrations of FRET processes, λ_{exc} : 365 nm.

Reversible Photo-Patterning Applications

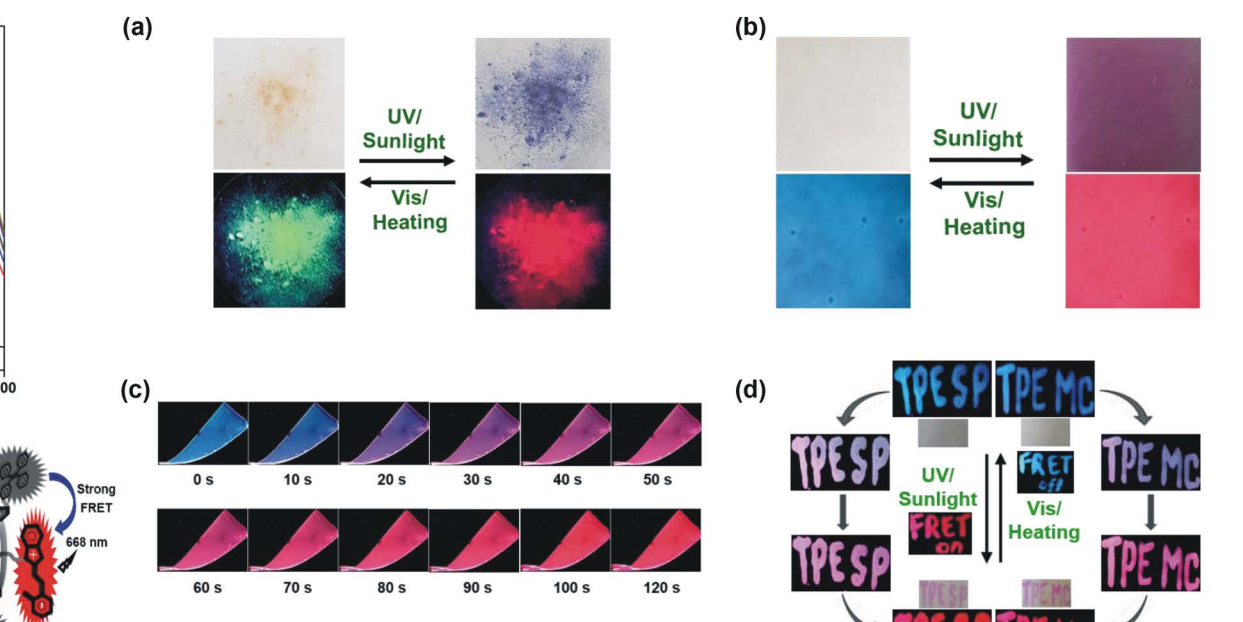


Figure 5. Photo-images of Rot-A-SP in (a) powder form, (b) coated cellulosic papers, (c) PMMA film, and (d) photo-patterning features of Rot-A-SP ink under various external treatments.

CONCLUSIONS

Novel photo-switchable FRET systems based on dual-AIEgens (TPE and MC) with multi-stimuli responsive fluorescence behaviors under external conditions, including UV and visible lights, pH control, thermal treatments, and CN⁻ interactions have been studied and reported. Owing to the useful FRET behavior, **poly(NIPAM-co-TPE-MC)** could be utilized for detecting CN⁻ by distinct ratio-metric fluorescence changes with very high selectivity and sensitivity in water as well as for cellular imaging and CN⁻ detection in living cells. Besides, a series of novel AIE [2]rotaxanes **Rot-A-SP**, **Rot-B-SP** and their photo-isomeric MC of bi-fluorophoric **Rot-A-MC**, **Rot-B-MC** display more efficient and stable FRET processes between TPE donor and MC acceptor moieties in the well-designed photo-switchable [2]rotaxanes under different extrinsic modulations. **Rot-A-SP** with interesting FRET phenomenon exhibits excellent AIE and photo-switchable properties in powder form and solid film, which are further utilized as photochromic and fluorescence inks on cellulosic papers for the applications of reversible photo-patterning. We believe that this report may contribute to facile and efficient FRET design of smart photo-switchable fluorescence materials for future potential applications.

SELECTED JOURNAL PUBLICATIONS

- Nhien, P. Q.; Chou, W.-L.; Cuc, T. T. K.; Khang, T. M.; Wu, C.-H.; Thirumalaivasan, N.; Hue, B. T. B.; Wu, J. I.; Wu, S.-P.; Lin, H.-C. Multi-Stimuli Responsive FRET Processes of Bifluorophoric AIEgens in an Amphiphilic Copolymer and Its Application to Cyanide Detection in Aqueous Media. *ACS Appl. Mater. Interfaces* 2020, 12, 10959-10972.
- Nhien, P. Q.; Cuc, T. T. K.; Khang, T. M.; Wu, C.-H.; Hue, B. T. B.; Wu, J. I.; Mansel, B. W.; Chen, H.-L.; Lin, H.-C. Highly Efficient Förster Resonance Energy Transfer Modulations of Dual-AIEgens between Tetraphenylethylene Donor and Merocyanine Acceptor in Photo-Switchable [2]Rotaxanes and Reversible Photo-Patterning Applications. *ACS Appl. Mater. Interfaces* 2020, 12, 47921-47938.
- Cuc, T. T. K.; Nhien, P. Q.; Khang, T. M.; Weng, C.-C.; Wu, C.-H.; Hue, B. T. B.; Li, Y.-K.; Wu, J. I.; Lin, H.-C. Optimization of FRET Behavior in Photo-Switchable [2]Rotaxanes Containing Bi-Fluorophoric Naphthalimide Donor and Merocyanine Acceptor with Sensor Approaches toward Sulfite Detection. *Chem. Mater.* 2020, 32, 9371-9389.



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