Chinese Chemical Letters 35 (2024) 110061

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Editorial

Reversible phosphorescence in pseudopolyrotaxane elastomer

Polyrotaxanes (PRs) constructed by macrocycle-threading polymers has been broadly developed for soft materials due to its unique supramolecular topological architecture, which can greatly improve the mechanical nature of materials [1,2]. Based on this, Choi and co-workers incorporated α-cyclodextrin (α-CD) based PR into a traditional polyacrylic acid adhesive, giving the polymer network unprecedented elasticity derived from the slip ring motion of the PR. This binder combination allows the pulverized silicon particles to remain agglomerated without disintegrating, allowing silicon particulate anodes to have stable cycle life at commercial levels of areal capacity [3]. Ito and co-workers exploited an optically transparent elastomer bearing high toughness and excellent extensibility utilizing a PR composed of α-CD and polyethylene glycol (PEG) as a cross-linking agent. The CD's pulley effect greatly dissipates the stress, achieving high stretchability and reciprocating performance [4]. Although PR has been applied to the construction of various soft materials, there have been no reports on mechanical force-responsive phosphorescent materials.

As an important signal in response to mechanical force, phosphorescence has the advantages of long luminescence lifetime, large Stokes shift, and involvement of triplet states [5]. Recently, Yong Chen, Yu Liu and co-workers from Nankai University synthesized a pseudopolyrotaxane (NPR) utilizing α-CD and naphthalene-derived polyethylene glycol (NPEG) (Fig. 1) [6]. The PEG chains, anchored at both ends of the naphthalene moiety, are threaded through the α-CD cavities, thereby forming the NPR. By combining NPR with waterborne polyurethane (WPU), they prepared supramolecular elastomers exhibiting reversible mechanically responsive room temperature phosphorescence (RTP) enhancement during the mechanical stretching process. The incorporation of CDs containing abundant hydroxyl groups not only facilitates the attainment of prolonged phosphorescence emission *via* the macrocyclic confinement effect but also augments mechanical properties through the establishment of hydrogen bonds with WPU chains. The resultant elastomer exhibits robust RTP characteristics, maintaining emission stability in aqueous solutions and diverse chemical environments. Notably, under a 200% strain, the phosphorescence intensity increases threefold owing to the further suppression of non-radiative transitions and NPR vibrations. Lastly, the developed RTP elastomer finds applications in information security and encryption.

The mechanical analysis revealed that the inclusion of NPR enhances both the strength and toughness of the WPU elastomer (Figs. 2a and b). Among various NPR masses investigated, the elastomer containing 5% NPR/WPU demonstrated the most favourable mechanical behaviour, exhibiting a fracture strain of 812%, fracture stress of 50.7 MPa, elastic modulus of 8.6 MPa, and toughness of 148 MJ/m^3. In comparison to the WPU elastomer alone, the 5% NPR/WPU composite displayed a notable enhancement in mechanical properties. Additionally, cyclic stretching measurements up to 200% strain indicated that the supramolecular elastomer containing 5% NPR/WPU exhibited excellent resilience.

Multiple intermolecular interactions serve as effective constraints on the mobility of phosphorescent chromophores, thereby impeding non-radiative decay processes. The network structure furnishes a rigid environment conducive to stabilizing the triplet state, avoiding the intrusion of quenchers and reducing RTP quenching. Therefore, the elastomer exhibited stretch-induced phosphorescence enhancement (Fig. 3a). Further experimentation demonstrated the elastomer's robust stability in various environments, including water, acids, bases, and organic solvents. Moreover, information patterns could be stored on a polydimethylsiloxane (PDMS) substrate (Fig. 3b). The PEG hydrogel, doped with NPEG, was fabricated for information storage purposes. Messages were inscribed using a saturated aqueous solution of CDs as ink (Fig. 3c). Authors also molded the NPEG/WPU elastomer into the letter "s" and the NPR/WPU elastomer into the letters "t, o, and p" (Fig. 3d). The hybrid elastomer displayed a message "stop" both in air and water. When turning off the UV light, "s" immediately vanished due to the absence of afterglow from NPEG/WPU, while the letters "top" remained visible, resulting in the correct information "top". These results demonstrated the application of elastomers with excellent RTP for information storage and encryption.

As a result, Chen, Liu and co-workers reported a novel supramolecular elastomer exhibiting reversible phosphorescence. Various interactions, including confinement induced by CD and interfacial hydrogen bonding within the elastomer, play a crucial role in stabilizing the triplet state. These interactions serve to curtail chromophore vibrations and facilitate sustained phosphorescent emission, particularly in specialized environmental conditions. Therefore, the resulting elastomer demonstrates excellent stability across diverse environments. Notably, the successful application of the elastomer with RTP for information storage and encryption under specific conditions underscores its versatility and practical utility.

In recent years, polyrotaxanes have garnered significant attention owing to their exceptional supramolecular topological structures, which have facilitated their extensive utilization across various soft material applications. Despite this, the exploration of PR for constructing phosphorescent materials *via* harnessing multiple interactions has been limited. In this context, Liu's research has pioneered the development of innovative supramolecular elas-

https://doi.org/10.1016/j.cclet.2024.110061

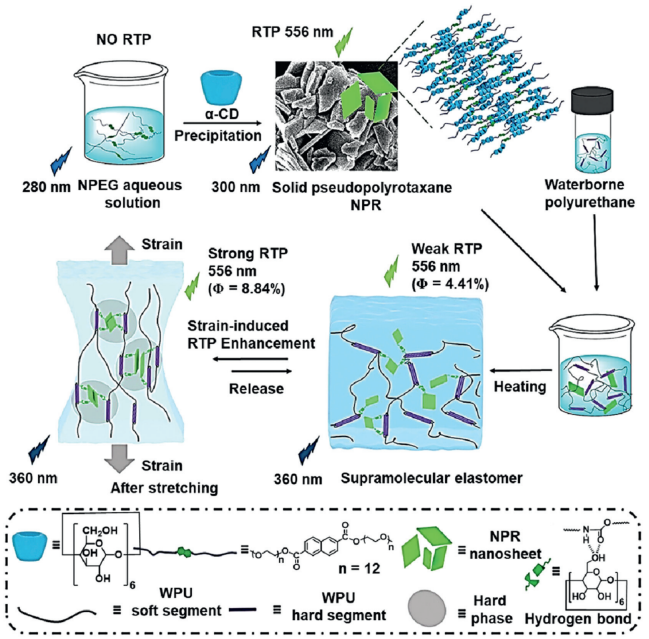

Fig. 1. Schematic illustration of mechanically stretched α-CD pseudopolyrotaxane elastomers with reversible phosphorescence behavior. Reproduced with permission [6]. Copyright 2024, Wiley Publishing Group.

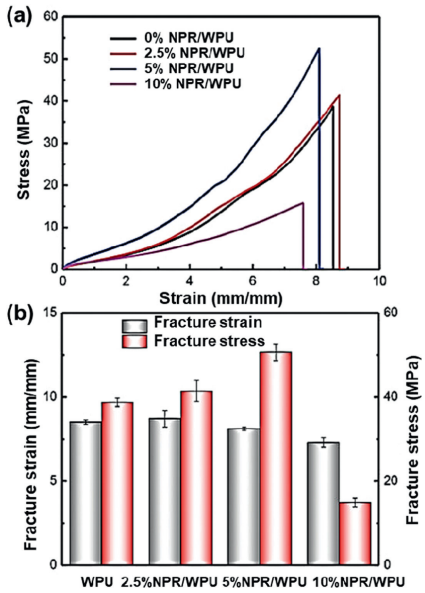

Fig. 2. Mechanical performances of supramolecular elastomers. (a) Tensile stress-strain curves. (b) The fracture stresses and fracture strains. Reproduced with permission [6]. Copyright 2024, Wiley Publishing Group.

tomers manifesting phosphorescent behavior, thereby constituting a notable progression in luminescent material science. This investigation not only diversifies the methodologies for fabricating supramolecular PR elastomers endowed with phosphorescent responsiveness but also serves as a wellspring of inspiration for the advancement of intelligent luminescent materials. It is envisaged that this PR-based phosphorescent material holds promise for multifarious applications spanning diverse domains, including displays, anti-counterfeiting measures, and information encryption within specialized environments. Furthermore, this study is poised to catalyze the creation of intelligent actuators endowed with responsive phosphorescence, thereby fostering innovative avenues in the realm of soft robotics and materials engineering.

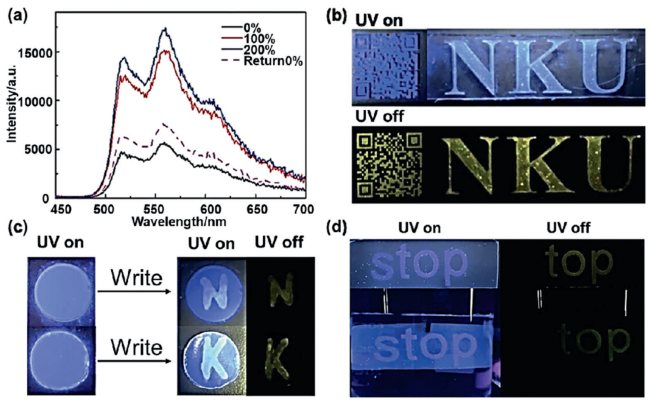

Fig. 3. (a) The phosphorescence emission spectrum (delay = 0.1 ms) of 5% NPR/WPU under different strain (λ_{ex} = 360 nm). (b) Pattern information storage performed by printing NPR/ink onto PMDS substrate. (c) Writable RTP hydrogel for information storage. (d) Data encryption process by fixing tailored luminescence elastomer in WPU elastomer in the atmospheric and water environment (pattern "s": NPEG/WPU samples; pattern "top": NPR/WPU samples). Reproduced with permission [6]. Copyright 2024, Wiley Publishing Group.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Fengyao Cui: Writing – original draft. **Qiaona Zhang:** Writing – original draft. **Tangxin Xiao:** Writing – review & editing, Writing – original draft, Validation, Supervision. **Zhouyu Wang:** Writing – original draft. **Leyong Wang:** Writing – review & editing, Supervision.

Fengyao Cui, Qiaona Zhang, Tangxin Xiao*
School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China

Zhouyu Wang
Department of Chemistry, Xihua University, Chengdu 610039, China

Leyong Wang*
Department of Chemistry, Xihua University, Chengdu 610039, China
Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

*Corresponding authors.
E-mail addresses: xiaotangxin@cczu.edu.cn (T. Xiao), lywang@nju.edu.cn (L. Wang).

Received 7 May 2024
Revised 24 May 2024
Accepted 27 May 2024
Available online 28 May 2024

References

[1] L. Chen, X. Sheng, G. Li, et al., Chem. Soc. Rev. 51 (2022) 7046–7065.
[2] T. Xiao, L. Zhou, X.Q. Sun, et al., Chin. Chem. Lett. 31 (2020) 1–9.
[3] S. Choi, T.W. Kwon, A. Coskun, et al., Science 357 (2017) 279–283.
[4] H. Gotoh, C. Liu, A.B. Imran, et al., Sci. Adv. 4 (2018) eaat7629.
[5] T. Wang, M. Liu, J. Mao, et al., Chin. Chem. Lett. 35 (2024) 108385.
[6] Y. Zhang, Y. Chen, J.Q. Li, et al., Adv. Sci. 11 (2024) 2307777.