A Stretchable Pillararene-Containing Supramolecular Polymeric Material with Self-Healing Property

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Abstract: Constructing polymeric materials with stretchable and self-healing properties arise increasing interest in the field of tissue engineering, wearable electronics and soft actuators. Herein, a new type of supramolecular cross-linker was constructed through host-guest interaction between pillar[5]arene functionalized acrylate and pyridinium functionalized acrylate, which could form supramolecular polymeric material via photo-polymerization of n-butyl acrylate (BA). Such material exhibited excellent tensile properties, with maximum tensile strength of 3.4 MPa and strain of 3000%, respectively. Moreover, this material can effectively dissipate energy with the energy absorption efficiency of 93%, which could be applied in the field of energy absorbing materials. In addition, the material showed self-healing property after cut and responded to competitive guest.

Keywords: pillararene; host-guest chemistry; supramolecular chemistry; supramolecular polymer

1. Introduction

Polymeric materials with stretchable property have got plenty of attention due to their widespread applications in the fields of tissue engineering, wearable electronics and soft actuators [1–7]. It is well known that there is always a trade-off between strength and toughness for the stretchable polymeric materials [8–10]. In general, strong interactions and rigid structures, such as covalent bonded gels, often provide higher tensile strength but with very low strain at break and slow self-healing, while weaker interactions lead to faster self-healing, but soft and viscoelastic materials [11–14]. For example, Huang reported a polymer gel based on the formation of acylhydrazone bonds [15]. The tensile breaking stress reached 1.2–2.7 MPa after solvent exchange from DMSO to water. However, the gel did not show self-healing behavior and the maximum strain at break was 40%, which limited their application. Therefore, it is still a challenge to explore a facile method to obtain polymeric materials with excellent strength and toughness as well as self-healing property.

Scientists have made great efforts to solve this problem by combining covalent bonded polymer with non-covalent interactions, including H-bond and coordination bond [16–18]. Among these various non-covalent interactions, host-guest chemistry, the central of supramolecular chemistry, has attracted tremendous attention, since it endows the system with reversible, tunable and dynamic properties [19–26]. For example, Suzuki and Takata reported the formation of tough films by evaporation of water from dispersions of elastomer microspheres crosslinked with rotaxane supramolecules, which contained crown ether [27]. Guo and colleagues prepared ultraductile, notch and stab resistant supramolecular hydrogels by copolymerization of acrylamide and adamantane monomer in the presence of cyclodextrin-functionalized polymer [28]. As the pioneer in this field, Harada and colleagues prepared flexible and tough elastomers with self-healing abili-
ties by using cyclodextrin derivatives [29]. Hence, host–guest interactions could make great contributions in preparation of polymeric materials with good mechanical and self-healing properties.

On the other hand, pillararenes, as a new fascinating family of macrocyclic host molecules, have attracted increasing attention due to their novel symmetric structures and extensive applications in the construction of novel supramolecular architectures [30–36]. For instance, Ogoshi succeeded in molecular weight fractionation by the confinement of single polymer chains of poly(ethylene oxide) in the one-dimensional channels of crystalline pillar[5]arene [37]. Huang constructed adaptive photosensitizers based on a host-guest complex containing a water-soluble pillar[5]arene and an AIEgen photosensitizer [38]. However, few supramolecular polymeric materials based on pillararene were reported [39–41], of which the mechanical performance was not good enough and need to be improved.

Herein, we successfully prepared a new type of supramolecular polymeric material with excellent stretchable and self-healing properties. Firstly, a bifunctional cross-linker of host-guest supramolecule (HGS) was constructed by mixing pillar[5]arene functionalized acrylate (AAP5A) with pyridinium functionalized acrylate (G) in acetone. Then, n-butyl acrylate (BA) was added and further transformed into a cross-linked supramolecular polymeric material (SP) by free radical polymerization under UV light (Scheme 1). Such material exhibited excellent tensile properties, with maximum tensile strength of 3.4 MPa and strain of 3000%, respectively. Moreover, this material can effectively dissipate energy with the energy absorption efficiency of 93%, which could be applied in the field of energy absorbing materials. In addition, the material showed self-healing property after cut and responded to competitive guest.

To construct the supramolecular crosslinker, pillar[5]arene functionalized acrylate (AAP5A) and pyridinium functionalized acrylate (G) were synthesized and characterized. (Scheme 2, Figures S1–S11, Supplementary Materials). The host-guest interaction between AAP5A and G was firstly studied by 1H-NMR (Figure 1). Curves a and d refer to the solution of G and AAP5A, respectively. The addition of AAP5A to G solution leads to remarkable changes (Figure 1, curve b), that is, the signals of protons $H_j$ from pyridinium group and $H_i$ from methylene group of G broadened severely and the signal of proton $H_k$ shifted upfield. According to the literature [42], the complexation induced upfield shift and broadening effect were remarkable when the carbon chain was long. On the other hand, the signal of proton $H_m$ shifted downfield, due to the shielding effect of the electron-rich cavities of pillararenes. All of these phenomena revealed that the pyridinium and methylene groups threaded into the cavity of pillararenes similar to the literatures.

![Scheme 1](image)
reported [42,43]. Furthermore, 2D NOESY spectrum showed the correlation peaks between $H_{j-k}$ and $H_m$ of G and $H_{10-11}$ of AAP5A (Figure S12), indicating that the guest molecule G successfully entered the cavity of AAP5A, which demonstrated the host-guest interaction between AAP5A and G. On the basis of $^1$H-NMR titration experiment (Figure S13) and the nonlinear curve fitting method (Figure S14), the binding constant of AAP5A with G was calculated to be $156 \pm 41$ mol·L$^{-1}$. According to the literature reported, the driving force of this supramolecular system can be attributed to the combination of hydrophobic and cation-π interaction between electron-lacking G and electron-rich P5A cavities [44].

![Scheme 2. Synthetic routes of AAP5A and G.](image)

**Figure 1.** $^1$H-NMR spectra (500 MHz, acetone-d$_6$, 298 K) of 4 mM G (a), 4 mM G + 8 mM AAP5A (b), 4 mM G + 8 mM AAP5A +20 mM G1(c) and 8 mM AAP5A (d).

Since the cavity of AAP5A can be threaded by the pyridinium and methylene groups of G, it is possible to construct a supramolecular cross-linker based on the pillararene-pyridinium group recognition motif. Next, polymerization of the monomer $n$-butyl acrylate (BA) was performed in acetone, using 2,4,6-trimethylbenzyldiphenylphosphine oxide (TPO) as the photo initiator and the host-guest supramolecule (HGS) as supramolecular crosslinker and a supramolecular polymeric material with optical transparency (Figure 2, inset) was obtained. Since the polymerizable groups were the same in BA, AAP5A and G, their reaction activities were similar, which made the component proportion in the
network facile to be adjusted by varying the feed ratio. As shown in Figure 2, the transmittance reached 96% in the wavelength range of 500–800 nm. Concerned the 3D network of supramolecular materials, FT-IR characterization was facile to take insight into this polymerization process. As shown in Figure S15 (Supplementary Materials), curves a and b referred to the signals of AAP5A and G, respectively. Mixing AAP5A with G lead to some changes. As shown in Figure S15, curve c, the stretching vibration peak of C-H (3037 cm\(^{-1}\)) and the aromatic group (1581 cm\(^{-1}\)) as well as the out-of-plane bending vibration absorption peak of trisubstituted C-H (894 cm\(^{-1}\)) from the pyridinium group of G disappeared, which was caused by the host-guest interaction between AAP5A and G. After polymerization, as shown in Figure S15, curve d, the out-of-plane bending vibration absorption peaks of benzene group (880, 853 cm\(^{-1}\)) on the pillararene did not move significantly, while the out-of-plane bending vibration absorption peak of C-H (810 cm\(^{-1}\)) from C=C disappeared, indicating that the raw material basically reacted completely in the process of photo polymerization. In addition, the stretching vibration absorption peak of the carbonyl group upshifted from 1718 to 1728 cm\(^{-1}\), due to the disappearance of the double bond, which destroyed the conjugated system of the double bond with the carbonyl group. All the phenomena revealed the successful polymerization of double bond and the formation of polymeric material.

Figure 2. UV-vis transmittance and the picture (inset) of the supramolecular material.

The density of crosslinker may have influence on the mechanical properties [45–47]. In order to investigate it further, three supramolecular polymeric materials (named SP-1, SP-2 and SP-3, respectively) with different content of host-guest supramolecule HGS (9, 7 and 5%) were prepared. The feed ratio was shown in Table S1 in detail. In the rheological test (Figure 3), the storage modulus \(G'\) of the two samples SP-1 and SP-2 were both greater than the corresponding loss modulus \(G''\) and there was no crossover within the experimental test range, indicating that these two samples were stable. As compared, the storage modulus \(G'\) and loss modulus \(G''\) of sample SP-3 crossed at the frequency of 1.00 Hz, showing its gelation ability becomes weak. In addition, the rheological test showed that the \(G'\) and \(G''\) of SP-1 hardly changed as the frequency varied and \(G' >> G''\) compared with the other two samples, revealing SP-1 is most stable among these samples. Therefore, with increasing of the content of HGS, the crosslinking density increased, leading to the enhancement of strength of these supramolecular polymeric materials. Previously, we reported a supramolecular gel with \(G'\) of only 2 kPa by mixing pillarene-containing copolymers with a bis(pyridinium) dication guest [40]. Interestingly, as compared, the \(G'\) of SP-1 was higher (1.5 \(\times\) 10\(^5\) Pa) by two orders of magnitude, indicating that mixing host-guest first and then doing the polymerization can effectively improve the mechanical stability of the supramolecular polymeric materials.
three samples were carried out. As shown in Figure S17, all these samples showed a characteristic peak at 2θ = 22.5°, which was attributed to the ordered accumulation of pillararenes arising from the π–π interaction and lead to the high tensile strength of the material. According to Bragg’s Law (λ = 2dsinθ), the corresponding spacing distance d was 0.395 nm. Compared with the regular structure formed by poly(ethylene glycol) (PEG) and α-cyclodextrin (2θ = 19.8°), the spacing distance of this pillararene-based regular structure was smaller, revealing that the supramolecular polymeric material was more transparent than those prepared from PEG and cyclodextrin, which is usually opaque [49].

![Figure 3. Rheology results of the supramolecular material at 4 °C. (SP-1 in black line, SP-2 in red line, SP-3 in blue line; storage modulus G’ (●), loss modulus G’’ (□), complex viscosity η (★)).](image-url)
Figure 4. The stress–strain curves of SP-1 (black curve), SP-2 (red curve) and SP-3 (blue curve).

The polymeric materials prepared in this way were very flexible as the elongations at break varied from 400 to 3000% and the toughness of the SP-2 could reach \(16.11 \text{ MJ}\cdot\text{m}^{-3}\) (Figure 5), which was much greater than the polybutyl acrylate (pBA) (1.71 \(\text{MJ}\cdot\text{m}^{-3}\)). Moreover, necking appeared in the latter stage of stretching, which was a typical ductile fracture behavior [50,51]. It was speculated that the butyl acrylate flexible group constituted the “soft segment” of the network, which effectively relieved the rigidity of pillararenes, acting as the “hard segment”. To demonstrate this speculation, differential scanning calorimetry (DSC) characterizations were conducted. As shown in Figure S18, the glass transition temperature (\(T_g\)) of the supramolecular material increased with the increasement of supramolecular crosslinker and the highest \(T_g\) was below the room temperature, indicating that the supramolecular crosslinked materials were flexible. Therefore, the rigid pillararenes and soft polybutyl acrylate chains, as well as the dynamic noncovalent bonds played important roles in enhancing the toughness of this supramolecular polymeric materials.

Figure 5. The toughness of SP-1 (black), SP-2 (red) and SP-3 (blue) and pBA (grey).

It is well known that the mechanical properties of materials usually involve a trade-off between modulus and elongation. In general, strong interactions often result in higher tensile strength with the loss of toughness, which makes the material brittle and hard. The reversible dynamic non-covalent bond can achieve higher toughness and self-healing properties of the material, as well as dissipate energy effectively, so it can be used as a candidate for energy-absorbing materials [52]. As shown in Figure 6, there was an obvious

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hysteresis appeared in the cyclic stress–strain test with a fixed applied strain of 100% and the energy absorption efficiency \( \omega \) was as high as 93\%, indicating that the reversible host–guest interaction led to effective dissipation of energy. When subjected to external forces, the flexible host–guest supramolecules with ability to move can effectively dissipate the external force, which could be used in the field of energy-absorbing materials.

![Figure 6. The energy absorbing properties of SP-1.](image)

The host-guest complexation is a reversible dynamic non-covalent bond, which may enable the polymeric materials with self-healing property. In order to study the self-healing behavior of this material, two samples of different colors (one sample was stained with rhodamine B for better observation) were cut into two pieces with the same size and then the different samples were put together to make the sections contacted. After 30 min, we found that the two samples were connected as a whole (Figure 7). In contrast, the covalent bond cross-linked samples could not form an integrity after being cut. Moreover, this reformed material could sustain a load of 333 g and still endure a large strain (Figures S19–S20, Supplementary Materials). These results indicated that we have successfully constructed a supramolecular polymeric material with self-healing property.

![Figure 7. The photos of the two cut samples (left) and re-formed one (right).](image)

This supramolecular polymeric material may be responsive to chemical stimulus owing to the dynamic non-covalent bond. According to the literature \[53\], the strong interaction between butanedinitrile (G1) and pillararene can push the pyridinium group out of the pillararene cavity. Therefore, we choose G1 to investigate the competitive process. First, the complexation behavior of AAP5A, G and G1 was studied by \(^1\)H-NMR (Figure 1,
After five times equivalent of G1 was added to the mixed solution of AAP5A and G, the signals of the protons H_j and H_i of G appeared again, the protons signal of H_k and H_m returned to the initial values, which proved that G1 and AAP5A formed a stronger complex in acetone and could destroy the structure of the supramolecular cross-linker formed by AAP5A and G. Therefore, with the addition of excessive amount of G1, the polymeric material turned to be a flowing sol state (Figure 8), showing the stimulus responsiveness to competitive guest molecules.

**Figure 8.** Reversible gel–sol transition of the supramolecular polymeric material.

### 3. Materials and Methods

1,4-Dibromobutane (99%), 1,6-Dibromohexane (98%), 4-methoxyphenol, acrylic acid, paraformaldehyde (99%) and boron trifluoride etherate (48%) were purchased from Shanghai Titan Scientific Co. (Shanghai, China) and used as received. 1,4-Dimethoxybenzene was purchased from Shanghai Excellent Chemical Co. Ltd. and used as received. TPO was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Pyridine was purchased from Aladdin Industrial Corporation (Shanghai, China). TPO was purchased from Shanghai Excellent Chemical Co. Ltd. All other solvents were obtained from commercial suppliers and were used directly without further purification. Ultrapure water was used in all relevant experiments.

^1H-NMR (500 MHz) and ^13C-NMR (126 MHz) spectra were recorded on a Bruker DPX500 spectrometer (Bruker BioSpin, Switzerland) using tetramethylsilane as an internal standard in CDCl\_3 or aceton-

\_d_6. MALDI-TOF mass spectrometry was performed on a Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan). FT-IR spectroscopy was obtained on a NEXUS 670 FTIR spectrometer (Thermo, USA). The rheological properties were studied by a MARS-3 (Thermo Haake Instruments, USA). Frequency sweeps from 0.01 to 100 Hz were performed at 0.1% strain under 4 °C on circular samples (20 mm diameter). Uniaxial tensile measurements were performed on a tensile testing machine HY-0508 (Shanghai Hengyi Test Instrument Co., Ltd., China) equipped with a 50 N load cell with a crosshead speed of 30 mm min\(^{-1}\) at room temperature. The testing rectangular samples were prepared with the length of 5 mm, width of 5 mm and thickness of 0.8–1 mm. As for the loading-unloading test and the successive loading-unloading tests, the crosshead velocity were both kept at 30 mm min\(^{-1}\). The toughness was calculated from the area of stress-strain curves [54]. The energy absorbing efficiency \(\omega\) were calculated according to the calculate equation in the literature [52]. Small angle and wide angle X-ray scattering were performed on a Smartlab SE (Bruker, Germany). All samples were prepared with thickness of <1 mm. DSC was performed on a Q2000 DSC (TA, USA) in nitrogen atmosphere. All the samples were first heated from 25 to 180 °C at a rate of 50 °C min\(^{-1}\) and held at this temperature for 3 min to eliminate the thermal history; then, they were cooled to −90 °C and heated again from −90 to 180 °C at a heating or cooling rate of 10 °C min\(^{-1}\).

### 4. Conclusions

In conclusion, we have successfully constructed a new type of host–guest supramolecular crosslinker based on pillar[5]arene functionalized acrylate and pyridinium functional-
ized acrylate, which can form a supramolecular polymeric material through photo polymerization of n-butyl acrylate. Such supramolecular polymeric material exhibited tunable stretchable property by varying the content of the supramolecular cross-linker. In addition, this material showed effective dissipation of energy, which could be applied in the field of energy absorbing materials. Moreover, this material exhibited self-healing property and stimulus response to competitive guest molecules, which were obviously different from covalent bond crosslinked network. This work provides an effective method for preparation of supramolecular polymeric materials with tunable stretchable, self-healing, chemical responsive and energy dissipative properties and offers a new paradigm for preparing multi-functional materials.

Supplementary Materials: The following are available online, Experimental details, Figures S1–S7: 1H-NMR, 13C-NMR spectra and MALDI-TOF of AAP5A; Figures S8–S11: 1H-NMR, 13C-NMR spectra of G; Figure S12: NOESY spectrum of a mixture of AAP5A and G; Figures S13–S14: 1H-NMR titration experiment and the nonlinear curve fitting method of AAP5A and G; Figure S15: FT-IR spectra of AAP5A, G, HGS, and SP-1; Figure S16: The picture of the covalent cross-linked polymeric material; Table S1: Feeding ratio of polymeric materials; Table S2: Summary of mechanical properties, Table S2: Summary of mechanical properties; Figure S17: Wide angle X-ray scattering of SP; Figure S18: DSC curves of SP; Figures S19–S20: Self-healing property of the supramolecular polymeric materials.

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Sample Availability: Samples of the compounds AAP5A and G are available from the authors.

References
1. Xia, D.; Wang, P.; Ji, X.; Khashab, N.M.; Sessler, J.L.; Huang, F. Functional supramolecular polymeric networks: The marriage of covalent polymers and macromolecule-based host-guest interactions. Chem. Rev. 2020, 120, 6070–6123. [CrossRef] [PubMed]
2. Morsali, M.; Khan, M.T.A.; Ashirov, R.; Hollo, G.; Baytekin, H.T.; Lagzi, I.; Baytekin, B. Mechanical control of periodic precipitation in stretchable gels to retrieve information on elastic deformation and for the complex patterning of matter. Adv. Mater. 2020, 32, 1905779. [CrossRef]
3. Li, W.; Gao, F.; Wang, X.; Zhang, N.; Ma, M. Strong and robust polyaniline-based supramolecular hydrogels for flexible supercapacitors. Angew. Chem. Int. Ed. Engl. 2016, 55, 9196–9201. [CrossRef] [PubMed]
4. Choudhury, S.; Saha, T.; Naskar, K.; Stamm, M.; Heinrich, G.; Das, A. A highly stretchable gel-polymer electrolyte for lithium-sulfur batteries. Polymer 2017, 112, 447–456. [CrossRef]
5. Le, X.; Lu, W.; Zheng, J.; Tong, D.; Zhao, N.; Ma, C.; Xiao, H.; Zhang, J.; Huang, Y.; Chen, T. Stretchable supramolecular hydrogels with triple shape memory effect. Chem. Sci. 2016, 7, 6715–6720. [CrossRef]
6. Zhao, Z.; Liu, Y.; Zhang, K.; Zhuo, S.; Fang, R.; Zhang, J.; Jiang, L.; Liu, M. Biphasic synergistic gel materials with switchable mechanics and self-healing capacity. Angew. Chem. Int. Ed. Engl. 2017, 56, 13464–13469. [CrossRef] [PubMed]
7. Xu, C.; Lee, W.; Dai, G.; Hong, Y. Highly elastic biodegradable single-network hydrogel for cell printing. ACS Appl. Mater. Inter. 2018, 10, 9969–9979. [CrossRef]
8. Lu, W.; Le, X.; Zhang, J.; Huang, Y.; Chen, T. Supramolecular shape memory hydrogels: A new bridge between stimuli-responsive polymers and supramolecular chemistry. Chem. Soc. Rev. 2017, 46, 1284–1294. [CrossRef]
9. Ye, D.; Yang, P.; Lei, X.; Zhang, D.; Li, L.; Chang, C.; Sun, P.; Zhang, L. Robust anisotropic cellulose hydrogels fabricated via strong self-aggregation forces for cardiomyocytes unidirectional growth. Chem. Mater. 2018, 30, 5175–5183. [CrossRef]
10. Zhao, B.; Xu, S.; Zheng, S. Synthesis, self-assembly and self-healing properties of organic–inorganic ABA triblock copolymers with poly(POSS acrylate) endblocks. Polym. Chem. 2019, 10, 2424–2435. [CrossRef]
11. Huang, J.; Liao, J.; Wang, T.; Sun, W.; Tong, Z. Super strong dopamine hydrogels with shape memory and bioinspired actuating behaviours modulated by solvent exchange. *Soft Matter.* 2018, 14, 2500–2507. [CrossRef] [PubMed]

12. Zhang, X.; Wang, J.; Jin, H.; Wang, S.; Song, W. Bioinspired supramolecular lubricating hydrogel induced by shear force. *J. Am. Chem. Soc.* 2018, 140, 3186–3189. [CrossRef] [PubMed]

13. Chen, Y.; Kushner, A.M.; Williams, G.A.; Guan, Z. Multiphase design of autonomic self-healing thermoplastic elastomers. *Nat. Chem.* 2012, 4, 467–472.

14. Liu, H.; Chung, H. Self-healing properties of lignin-containing nanocomposite: Synthesis of lignin-graft-poly(5-acetaminopentyl acrylate) via RAFT and click chemistry. *Macromolecules* 2016, 49, 7246–7256. [CrossRef]

15. Ju, H.; Zhu, F.; Xing, H.; Wu, Z.L.; Huang, F. Ultrasoft hydrogels prepared through Schiff’s base reaction of bis(p-formylphenyl) sebacate and pillar[5]arene appended with multiple hydrazides. *Macromol. Rapid. Commun.* 2017, 38, 1–6. [CrossRef]

16. Yan, X.; Liu, Z.; Zhang, Q.; Lopez, J.; Wang, H.; Wu, H.C.; Niu, S.; Yan, H.; Wang, S.; Lei, T.; et al. Quadruple H-bonding cross-linked supramolecular polymeric materials as substrates for stretchable, antitearing, and self-healable thin film electrodes. *J. Am. Chem. Soc.* 2018, 140, 5280–5289. [CrossRef]

17. Liu, Y.; Shi, B.; Wang, H.; Shangguan, L.; Li, Z.; Zhang, M.; Huang, F. Construction of metallacage-cored supramolecular gel by hierarchical self-assembly of metal coordination and pillar[5]arene-based host-guest recognition. *Macromol. Rapid. Commun.* 2018, 39, 1800655. [CrossRef]

18. Han, L.; Yan, L.; Wang, K.; Fang, L.; Zhang, H.; Tang, Y.; Ding, Y.; Weng, L.-T.; Xu, J.; Weng, J.; et al. Tough, self-healable and tissue-adhesive hydrogel with tunable multiphysical functionality. *NPG. Asia. Mater.* 2017, 9, 1–12. [CrossRef]

19. Wu, Y.; Li, H.; Yan, Y.; Shan, X.; Zhao, M.; Zhao, Q.; Liao, X.; Xie, M. Pillararene-containing polymers with tunable conductivity based on host–guest complexations. *ACS Macro. Lett.* 2019, 8, 1588–1593. [CrossRef]

20. Huang, F.H.; Gibson, H.W.; Bryant, W.S.; Nagyekar, D.S.; Frankoczek, F.R. First pseudorotaxane-like [3]complexes based on cryptands and parquat: Self-assembly and crystal structures. *J. Am. Chem. Soc.* 2003, 125, 9367–9371. [CrossRef] [PubMed]

21. Zhang, Y.-M.; Zhu, W.; Huang, X.-J.; Qu, W.-J.; He, J.-X.; Fang, H.; Yao, H.; Wei, J.-B.; Lin, Q. Supramolecular aggregation-induced emission gels based on pillar[5]arene for photoprotective detection and separation of multianalytes. *ACS Sustain. Chem. Eng.* 2018, 6, 16597–16606. [CrossRef]

22. Zafarnia, Y.; Kaizerman, D.; Hadar, M.; Bigan, N.; Granot, E.; Ghosh, M.; Adler-Abramovich, L.; Patolsky, F.; Cohen, Y. Pillararene-based two-component thixotropic supramolecular organogels: Complementarity and multivalency as prominent motifs. *Chem. Eur. J.* 2018, 24, 15750–15755. [CrossRef]

23. Jia, Y.-G.; Zhang, M.; Zhu, X.X. CO2-switchable self-healing host–guest hydrogels. *Macromolecules.* 2017, 50, 9696–9701. [CrossRef]

24. Sun, S.; Geng, M.; Huang, L.; Chen, Y.; Cen, M.; Lu, D.; Wang, A.; Wang, Y.; Shi, Y.; Yao, Y. A new amphiphilic pillar[5]arene: Synthesis and controllable self-assembly in water and application in white-light-emitting systems. *Chem. Commun.* 2018, 54, 13006–13009. [CrossRef]

25. Liu, X.Y.; Xu, H.; Zhang, L.Q.; Zhong, M.; Xie, X.M. Homogeneous and real super tough multi-bond network hydrogels created through a controllable metal ion permeation strategy. *ACS Appl. Mater. Inter.* 2019, 11, 42856–42864. [CrossRef]

26. Yang, L.; Tan, X.; Zhang, X. Supramolecular polymers: Historical development, preparation, characterization, and functions. *Chem. Rev.* 2015, 115, 7196–7239. [CrossRef] [PubMed]

27. Hiroshige, S.; Kureha, T.; Aoki, D.; Sawada, J.; Aoki, D.; Takata, T.; Suzukki, D. Formation of tough films by evaporation of water from dispersions of elastomer microspheres crosslinked with rotaxane supramolecules. *J. Am. Chem. Soc.* 2015, 137, 467–472. [CrossRef]

28. Ogoshi, T.; Fujinami, S.; Yamagishi, T.A.; Nakamoto, Y. para-Bridged symmetrical pillar[5]arenes: Their lewis acid catalyzed synthesis and host–guest property. *J. Am. Chem. Soc.* 2008, 130, 5022–5023. [CrossRef] [PubMed]

29. Chen, Y.; Liu, Z.; Zhang, Q.; Lopez, J.; Wang, H.; Wu, H.C.; Niu, S.; Yan, H.; Wang, S.; Lei, T.; et al. Quadruple H-bonding cross-linked supramolecular polymeric materials as substrates for stretchable, antitearing, and self-healable thin film electrodes. *J. Am. Chem. Soc.* 2018, 140, 5280–5289. [CrossRef]

30. Liu, X.Y.; Xu, H.; Zhang, L.Q.; Zhong, M.; Xie, X.M. Homogeneous and real super tough multi-bond network hydrogels created through a controllable metal ion permeation strategy. *ACS Appl. Mater. Inter.* 2019, 11, 42856–42864. [CrossRef]

31. Nomimura, S.; Osaka, M.; Park, J.; Ikura, R.; Takashima, Y.; Yamaguchi, H.; Harada, A. Self-healing alkyl acrylate-based supramolecular elastomers cross-linked via host–guest interactions. *Macromolecules* 2019, 52, 2659–2668. [CrossRef]

32. Ogoshi, T.; Fujinami, S.; Yamagishi, T.A.; Nakamoto, Y. para-Bridged symmetrical pillar[5]arenes: Their lewis acid catalyzed synthesis and host–guest property. *J. Am. Chem. Soc.* 2008, 130, 5022–5023. [CrossRef] [PubMed]

33. Lou, X.Y.; Li, Y.P.; Yang, Y.W. Gated materials: Installing macrometric arenes-based supramolecular nanovalves on porous nanomaterials for controlled cargo release. *Biotechnol. J.* 2019, 14, 1800354. [CrossRef] [PubMed]

34. Liu, X.Y.; Li, Y.P.; Yang, Y.W. Gated materials: Installing macrometric arenes-based supramolecular nanovalves on porous nanomaterials for controlled cargo release. *Biotechnol. J.* 2019, 14, 1800354. [CrossRef] [PubMed]

35. Ogoshi, T.; Takashima, S.; Yamagishi, T.A. Photocontrolled reversible guest uptake, storage, and release by azobenzene-modified microporous multilayer films of pillar[5]arenes. *J. Am. Chem. Soc.* 2018, 140, 1544–1548. [CrossRef]

36. Chen, Y.; Srikala, P.; Sun, B.; Qian, C.; Sun, G.; Cheng, M.; Lin, C.; Lu, X.; Jiang, J.; Wang, L. Stochiometry-controlled chirality induced by co-assembly of tetraphenylethylene derivative, γ-CD, and water-soluble pillar[5]arene. *ACS Appl. Bio. Mater.* 2020, 4, 2066–2072. [CrossRef]

37. Zhang, D.; Cheng, J.; Wei, L.; Song, W.; Wang, L.; Tang, H.; Cao, D. Host-guest complexion of monoanionic and dianionic guests with a polycationic pillararene host: Same two-step mechanism but striking difference in rate upon inclusion. *J. Phys. Chem. Lett.* 2020, 11, 2021–2026. [CrossRef] [PubMed]

38. Chen, J.-F.; Lin, Q.; Yao, H.; Zhang, Y.-M.; Wei, T.-B. Pillar[5]arene-based multifunctional supramolecular hydrogel: Multistimuli responsiveness, self-healing, fluorescence sensing, and conductivity. *Mater. Chem. Front.* 2018, 2, 999–1003. [CrossRef]

39. Old, X.Y.; Song, N.; Yang, Y.W. Fluorescence resonance energy transfer systems in supramolecular macrocyclic chemistry. *Molecules* 2017, 22, 1640. [CrossRef]
37. Ogoshi, T.; Suto, R.; Yagyu, M.; Kojima, R.; Kakuta, T.; Yamagishi, T.; Doitomi, K.; Tummanapelli, A.K. Molecular weight fractionation by confinement of polymer in one-dimensional pillar[5]arene channels. Nat. Commun. 2019, 10, 479. [CrossRef]

38. Shao, L.; Pan, Y.T.; Hua, B.; Xu, S.D.; Yu, G.C.; Wand, M.B.; Liu, B.; Huang, F.H. Constructing adaptive photosensitizers via supramolecular modification based on pillararene host-guest interactions. Angew. Chem. Int. Ed. 2020, 59, 11779–11783. [CrossRef]

39. Xia, W.; Ni, M.; Yao, C.; Wang, Y.; Chen, D.; Lin, C.; Hu, X-Y.; Wang, L. Responsive gel-like supramolecular network based on pillar[6]arene–ferrocenium recognition motifs in polymeric matrix. Macromolecules 2015, 48, 4403–4409. [CrossRef]

40. Chang, J.; Zhao, Q.; Kang, L.; Li, H.; Xie, M.; Liao, X. Multiresponsive supramolecular gel based on pillararene-containing polymers. Macromolecules 2016, 49, 2814–2820. [CrossRef]

41. Chen, J-F.; Chen, P. Pillar[5]arene-based resilient supramolecular gel with dual-stimuli responses and self-healing properties. ACS Appl. Polym. Mater. 2019, 1, 2224–2229. [CrossRef]

42. Li, C.; Xu, Q.; Li, J.; Yao, F.; Jia, X. Complex interactions of pillar[5]arene with paraquats and bis(pyridinium) derivatives. Org. Biomol. Chem. 2010, 8, 1568–1576. [CrossRef]

43. Park, J.; Choi, Y.; Lee, S.S.; Jung, J.H. Critical role of achiral guest molecules in planar chirality inversion of alanine-appended pillar[5]arenes. Org. Lett. 2021, 21, 1232–1236. [CrossRef] [PubMed]

44. Chi, X.D.; Yu, G.C.; Ji, X.F.; Li, Y.; Tang, G.P.; Huang, F. Redox-responsive amphiphilic macromolecular [2]pseudorotaxane constructed from a water-soluble pillar[5]arene and a paraquat-containing homopolymer. ACS Macro. Lett. 2015, 4, 996–999. [CrossRef]

45. Sun, Y.; Gao, G.; Du, G.; Cheng, Y.; Fu, J. Super tough, ultrastretchable, and thermoresponsive hydrogels with functionalized triblock copolymer micelles as macro-cross-linkers. ACS Macro. Lett. 2014, 3, 496–500. [CrossRef]

46. Sawada, J.; Aoki, D.; Kuzume, M.; Nakazono, K.; Otsuka, H.; Takata, T. A vinylic rotaxane cross-linker for toughened network polymers from the radical polymerization of vinyl monomers. Poly. Chem. 2017, 8, 1878–1881. [CrossRef]

47. Baddi, S.; Palanisamy, A. Thermoreversible gelation of poly(urethane acyl-semicarbazides) carrying cycloaliphatic moieties and studies on selective adsorption of dyes from wastewater. Eur. Pol. J. 2018, 99, 90–101. [CrossRef]

48. Guo, M.; Pitet, L.M.; Wyss, H.M.; Vos, M.; Dankers, P.Y.; Meijer, E.W. Tough stimuli-responsive supramolecular hydrogels with hydrogen-bonding network junctions. J. Am. Chem. Soc. 2014, 136, 6969–6977. [CrossRef] [PubMed]

49. Li, J.; Li, X.; Zhou, Z.; Ni, X.; Kam, W.L. Formation of supramolecular hydrogels induced by inclusion complexation between pluronic and r-cyclodextrin. Macromolecules 2001, 34, 7236–7237. [CrossRef]

50. Zhang, T.; Guo, Q. Continuous preparation of polyHIPE monoliths from ionomer-stabilized high internal phase emulsions (HIPEs) for efficient recovery of spilled oils. Chem. Eng. J. 2017, 307, 812–819. [CrossRef]

51. Guan, X.; Jiang, H.; Ngai, T. Pickering high internal phase emulsions templated super-hydrophobic–oleophilic elastic foams for highly efficient oil/water separation. ACS Appl. Polym. Mater. 2020, 2, 5664–5673. [CrossRef]

52. Lai, J.C.; Jia, X.Y.; Wang, D.P.; Deng, Y.B.; Zheng, P.; Li, C.H.; Zuo, J.L.; Bao, Z. Thermodynamically stable whilst kinetically labile coordination bonds lead to strong and tough self-healing polymers. Nat. Commun. 2019, 10, 1–6. [CrossRef] [PubMed]

53. Li, Z.-Y.; Zhang, Y.; Zhang, C.-W.; Chen, L.-J.; Wang, C.; Tan, H.; Yu, Y.; Li, X.; Yang, H.-B. Cross-linked supramolecular polymer gels constructed from discrete multi-pillar[5]arene metallacycles and their multiple stimuli-responsive behavior. J. Am. Chem. Soc. 2014, 136, 8577–8589. [CrossRef] [PubMed]

54. Liu, Y.J.; Cao, W.T.; Ma, M.G.; Wan, P. Ultrasonically wearable soft strain sensors of conductive, self-healing, and elastic hydrogels with synergistic “soft and hard” hybrid networks. ACS Appl. Mater. Inter. 2017, 9, 25559–25570.