

## REVIEW

View Article Online  
View Journal | View IssueCite this: *Mater. Chem. Front.*,  
2026, **10**, 1352Received 12th February 2026,  
Accepted 12th April 2026

DOI: 10.1039/d6qm00118a

rsc.li/frontiers-materials

# Photoisomerizable molecule-grafted nanofluidic channels: strategies, mechanisms and applications

Xiaolu Li,<sup>a</sup> Shengjie Fan,<sup>a</sup> Rongchi Zhang,<sup>a</sup> Guodong Hu,<sup>a</sup> Jia Liu,<sup>a</sup> Xingjie Wang,<sup>a</sup>  
Linfeng Chen \*<sup>ab</sup> and Fan Xia \*<sup>a</sup>

The pursuit of artificial systems that emulate the precision and adaptability of biological nanochannels has culminated in the development of photoresponsive ionic nanofluidics. Incorporating photoisomerizable molecular switches (*e.g.*, azobenzene, spiropyran, diarylethene) enables precise molecular-level control, enabling multi-dimensional regulation of pore size, surface charge, and wettability, offering unique advantages for smart ion-transport regulation. Despite substantial progress, the field still lacks a systematic framework connecting molecular modification strategies, transport regulatory mechanisms, and applications, which restricts the rational design of high-performance nanofluidic systems. This review addresses this critical gap by establishing a comprehensive, hierarchical molecule-strategy-mechanism-application framework based on recent developments. We systematically categorize and critically analyze three core modification approaches (*i.e.*, direct grafting, mediator-assisted tethering, and host-guest embedding), elucidate the hierarchical regulatory mechanism from single-property modulation to multi-dimensional synergistic control, and map these fundamental principles to advanced applications in energy conversion, ionic gating, and biomimetic devices. By integrating these principles and outlining a forward-looking research roadmap, this review provides a foundational blueprint for the rational design of next-generation, high-performance photonic nanofluidic channel devices with great potential across energy, environmental, and biomedical sectors.

## 1. Introduction

The exquisite regulatory functions of biological ion channels—which precisely control the transport of ions and molecules with spatiotemporal precision in response to stimuli—represent a pinnacle of evolutionary engineering.<sup>1,2</sup> Inspired by this, the field of intelligent nanofluidics has emerged at the intersection of materials science,

<sup>a</sup> State Key Laboratory of Geomicrobiology and Environmental Changes, Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan 430074, China. E-mail: chenlinfeng@cug.edu.cn, xiafan@cug.edu.cn

<sup>b</sup> Shenzhen Research Institute of China, University of Geosciences, Shenzhen 518057, P. R. China



Xiaolu Li

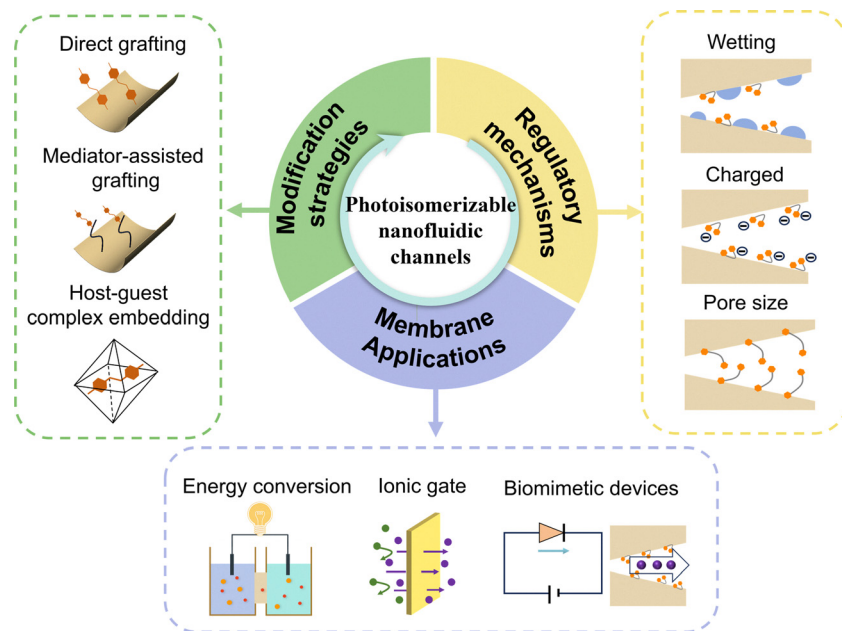
Xiaolu Li is currently a PhD candidate in the Faculty of Materials Science and Chemistry, China University of Geosciences (Wuhan). Her research interests focus on biomimetic iontransporting nanochannels and their applications in smart nanofluidic membranes.



Shengjie Fan

Shengjie Fan received his BSc degree from Qingdao University of Technology in 2019. He is currently a PhD Student at the Faculty of Material Science and Chemistry, China University of Geosciences (Wuhan). His research interests focus on nanoconfined ion transport.





**Fig. 1** Schematic illustration of the hierarchical framework for photoisomerizable ionic nanofluidic channels. The framework integrates molecular design, strategic modification, hierarchical regulatory mechanisms, and advanced applications, providing a roadmap for rational device development.

nanotechnology, and bioengineering, creating artificial nanochannels responsive to pH,<sup>3,4</sup> temperature,<sup>5,6</sup> light,<sup>7,8</sup> voltage,<sup>9,10</sup> and ligand binding.<sup>11,12</sup> These systems have demonstrated remarkable potential in energy harvesting, sensing and detection, and controlled ion transport.<sup>13–16</sup>

Among various external stimuli, light has emerged as an exceptional control modality due to its unique advantages of non-contact manipulation, spatiotemporal precision, minimal sample invasion, and remote controllability. Light-gated nanochannels engineered with photoisomerizable molecules constitute the most intensively studied and promising direction in this field, owing to their distinctive molecular-level regulatory

properties. Typical photoisomerizable molecules, including azobenzene, spiropyran and diarylethene, undergo reversible conformational transitions upon specific wavelength light irradiation, accompanied by pronounced changes in molecular geometry, polarity, charge state, or hydrophilicity. These reversible structural changes enable versatile multi-modal coordinated control over ion translocation through concurrent modulation of channel aperture, surface charge density, and interfacial wettability, establishing photoisomerizable molecules as optimal molecular switches for constructing high-performance light-responsive nanofluidic channels.<sup>17,18</sup>



**Linfeng Chen**

*Linfeng Chen received his BE degree from Huazhong University of Science and Technology (HUST) in 2008 and obtained his PhD degree from the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) with Prof. Yanlin Song in 2014. Later, he worked as a postdoctoral researcher in Technion-Israel Institute of Technology and National University of Singapore. He is currently a professor of the Faculty of Materials Science and Chemistry, China University of Geosciences (Wuhan). His research interests include bioinspired interfacial wetting materials, nano-confined ion transport and biosensors.*



**Fan Xia**

*Fan Xia obtained his PhD degree from the Institute of Chemistry, Chinese Academy of Sciences in 2008, under the direction of Prof. Lei Jiang. He then worked as a postdoctoral fellow in Prof. Alan J. Heeger's group in the University of California, Santa Barbara. In 2012, he joined Huazhong University of Science and Technology (HUST) as a professor. Currently, he is a professor and vice president of China University of Geosciences (Wuhan). His research interest is focused on bioanalytical chemistry.*



Despite substantial progress and evolution of diverse modification strategies and regulatory paradigms in light-responsive nanofluidic channel research in recent years, the field remains fragmented. Research remains largely empirical, typically correlating a specific molecule modification with an observed output (*e.g.*, ionic current change) without establishing a unified hierarchical framework linking molecular structure, strategic integration method, physicochemical transition, and the resulting transport behavior and application performance. This deficiency results in disjointed understanding of how molecular isomerization governs ion translocation mechanisms and impedes the rational, predictive design of functional nanochannel devices. Consequently, performance optimization often relies on empirical trial-and-error rather than principled design rules.

This review addresses this deficiency by introducing a systematic, hierarchical framework that bridges molecular design, modification strategy, regulatory mechanism, and application development of photoisomerizable nanochannel. We first classify and critically analyze three dominant modification strategies for photoisomerizable molecules in nanochannels—direct grafting, mediator-assisted grafting, and host-guest embedding—providing clear guidelines for strategy selection based on target performance parameters. We then establish a systematic mechanistic classification that progresses from single-property modulation (wettability, electrostatics, or sterics) to dual-property synergistic control and ultimately multi-dimensional coupled regulation, explicitly linking photoisomerization-induced physicochemical transitions to ion transport behaviors. Finally, we explicitly map these fundamental principles to frontier applications in energy conversion, ionic gate and biomimetic devices, while outlining key challenges and research directions. This integrated framework

provides both a theoretical foundation and practical roadmap to accelerate the development of next-generation high-performance light-controlled ionic nanofluidics (Fig. 1).

## 2. Photoisomerizable molecules

Photoisomerizable molecules serve as the core functional units for constructing photoresponsive intelligent nanochannels. Their photophysical properties, isomerization kinetics and associated physicochemical transitions directly dictate the channels' light-responsive performance, regulatory precision, and operational stability.<sup>19–21</sup> A comprehensive understanding of these molecular switches is therefore a prerequisite to rational channel design. The most widely utilized molecules are azobenzene, spiropyran, and diarylethene, each with distinct characteristics tailored to channel functionality (Fig. 2 and Table 1). Azobenzene and their derivatives undergo efficient, reversible *trans-cis* isomerization upon light stimulation (Fig. 2a). The *trans* isomer is planar and hydrophobic, while the *cis* isomer is bent and more hydrophilic, with a significant length change ( $\sim 0.9$  nm) and an increase in dipole moments.<sup>22–25</sup> This makes azobenzene ideal for steric gating and wettability switching. The planar *trans* form also facilitates  $\pi$ - $\pi$  stacking, enabling light-controlled assembly/disassembly of supramolecular structures. Spiropyran exhibits remarkable multifunctional switching, reversibly transforming between a closed, neutral, hydrophobic spirocyclic form (SP) and an open, zwitterionic, hydrophilic merocyanine form (MC) upon light irradiation (Fig. 2b). This transition involves a dramatic dipole moment increase ( $\sim 5$  D to 16 D) and charge generation, making spiropyran exceptionally effective for electrostatic gating and wettability switching.<sup>26</sup> Its additional responsiveness to pH, temperature, and mechanical stress enables multi-stimuli-

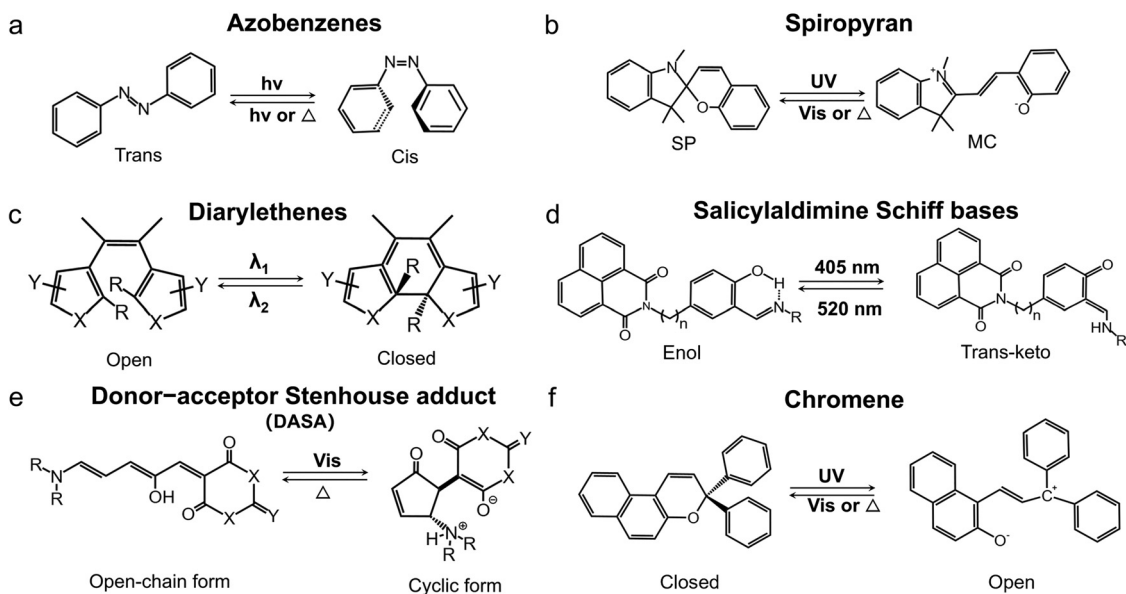


Fig. 2 Photoisomerization of representative light-responsive molecules. (a) Azobenzenes. (b) Spiropyran. (c) Diarylethenes. (d) Salicylaldehyde Schiff bases. (e) Donor-acceptor Stenhouse adduct. (f) Chromene.



**Table 1** Structural and performance characteristics of typical photoisomerizable molecules for photoresponsive nanochannels

Molecule	Isomerization	Key property changes	Strengths	Limitations	Ref.
Azobenzene	<i>Trans</i> (vis) ↔ <i>cis</i> (UV)	Length ( $\Delta \sim 0.9$ nm), dipole ( $\Delta \sim 3$ D), hydrophilicity	Fast kinetics, robust cycling, versatile functionalization	UV light required for <i>cis</i> , possible photodegradation	22 and 23
Spiropyran	SP (vis) ↔ MC (UV)	Charge (neutral ↔ zwitterion), dipole ( $\Delta \sim 11$ D), hydrophilicity	Large dipole/charge change, multi-stimuli responsive	Thermal relaxation of MC, moderate fatigue resistance	26 and 27
Diarylethene	Open (vis) ↔ closed (UV)	Conformation, polarity (tunable), $\pi$ -system	Exceptional thermal stability & fatigue resistance	Often smaller change in polarity/charge	30 and 31

responsive channels.<sup>27–29</sup> Diarylethene derivatives are photochemically reversible (P-type) switches with exceptional thermal stability of both isomers and outstanding fatigue resistance (Fig. 2c).<sup>30–32</sup> These characteristics are critical for long-term channel operation. While property changes are primarily optical, judicious molecular design can introduce complementary changes in polarity or conformation.

In addition to traditional photochromic molecules, several emerging candidates including salicylaldehyde Schiff bases, donor-acceptor Stenhouse adduct (DASA) and chromenes (Fig. 2d–f), show distinctive advantages. Salicylaldehyde Schiff bases undergo photoisomerization through a synergistic process involving excited-state intramolecular proton transfer and C=N *cis-trans* isomerization.<sup>33,34</sup> This process proceeds without covalent bond cleavage or large-scale conformational rearrangement, endowing the molecules with low reaction barriers and excellent fatigue resistance. In contrast to UV-activated conventional photochromes, DASA isomerizes efficiently under visible light, avoiding photodamage.<sup>35,36</sup> They undergo reversible photoisomerization from the linear conjugated triene (open-chain form) to the cyclopentenone (cyclic form) and recover thermally in the dark. This isomerization follows a synergistic pathway of *Z/E* isomerization and conrotatory  $4\pi$ -electrocyclization, accompanied by significant molecular contraction, charge redistribution, and wettability modulation. Chromenes are classical benzopyran-based photochromic molecules whose photoisomerization involves reversible pyran C–O bond cleavage, enabling efficient ring-opening/closing switching.<sup>37,38</sup> Owing to their structural flexibility, chromenes show high modifiability and promising multifunctional integration potential. Although their integration into nanochannel systems remains relatively underexplored, these desirable properties render them highly promising for the construction of high-performance next-generation photoresponsive ionic nanochannels.

The selection of photoisomerizable molecule is a fundamental design choice that dictates achievable regulatory mechanisms, operational wavelengths, and long-term performance. A brief summary of the dominant photoisomerizable molecules is shown in Table 1.

### 3. Strategic modification of integrating photo-switches with nanochannels

The integration of photoisomerizable molecules with nanochannels substrate is critical for constructing photoresponsive

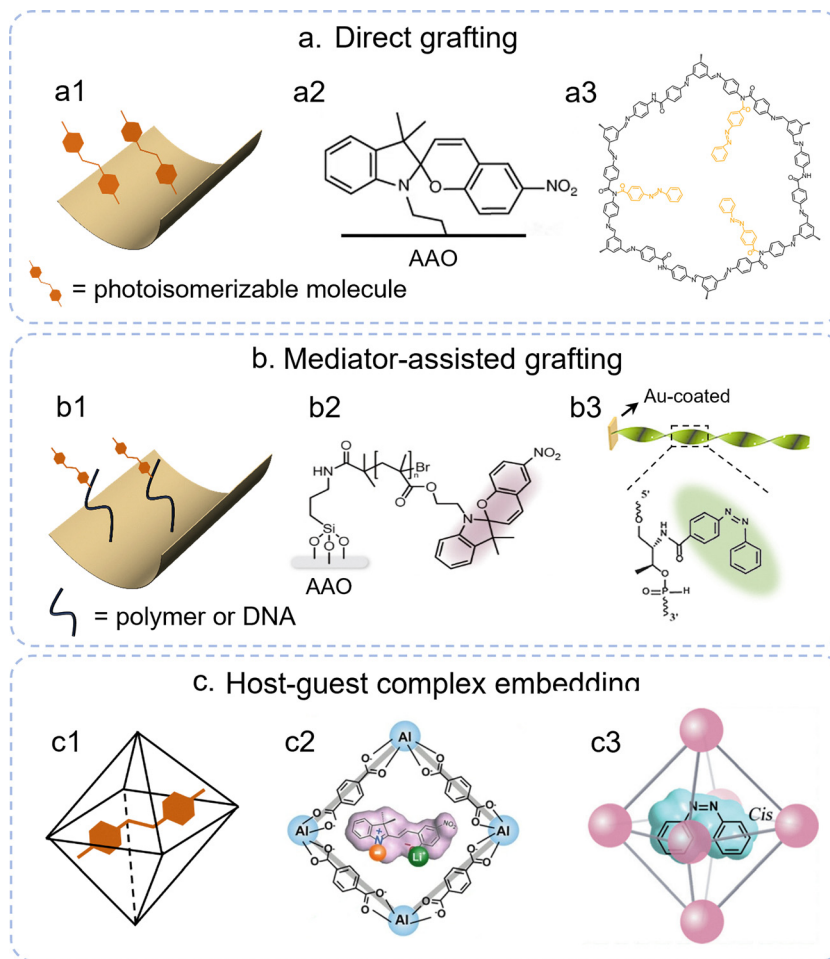
nanofluidic channels. The modification strategy directly governs functional group density, molecular orientation, isomerization freedom, and operational stability—all paramount to the performance of photoresponsive nanofluidic channels. This section systematically analyzes three fundamental strategies, providing a critical comparative analysis to guide selection.

#### 3.1 Direct grafting

Direct grafting is one of the most commonly used strategies for the functionalization of nanochannels with photoisomeric molecules. It anchors photoisomerizable molecules directly onto channel surfaces through covalent bonds, creating a well-defined, stable interface (Fig. 3a1).<sup>39–42</sup> This approach offers advantages of simple preparation, robust bonding and fast response. For instance, Zhang *et al.* covalently grafted spiropyran molecules onto the inner walls of anodic aluminum oxide (AAO) nanochannels *via* an amide coupling reaction.<sup>40</sup> This functionalization could be completed in only two steps at room temperature. The resulting modified surface exhibited both robust interfacial bonding and reliable reversible photo-switching performance (Fig. 3a2). Xiao *et al.* employed a covalent coupling strategy to precisely graft amino-functionalized azobenzene onto the pore-wall bottom of polyethylene terephthalate (PET) conical nanochannels.<sup>41</sup> This strategy enabled site-specific modification of photoresponsive units while fully preserving the pristine channel structure. Owing to the general applicability of this strategy, the methodology can be further extended to pore functionalization design of novel crystalline organic framework materials. Wang *et al.* covalently grafted azobenzene molecules onto the pore wall surfaces of covalent organic framework (COF) nanochannels *via* a post-synthetic amidation reaction.<sup>42</sup> This strategy achieved precise molecular anchoring and favorable channel regularity, and synergistically combined fast photoresponse with reliable structural controllability (Fig. 3a3).

Direct grafting can ensure high stability, fast response and efficient signal transmission between photoisomeric molecules and the substrate. However, increasing grafting density to improve surface coverage tends to intensify molecular crowding, which in turn restricts isomerization freedom and weakens property changes. To address such trade-offs, controlled polymerization and post-synthetic grafting have improved modification uniformity and tunability. In addition, precise regulation of grafting density remains difficult, while molecular detachment during long-term cycling and strong substrate dependence jointly restrict its scalable applications.





**Fig. 3** Schematic illustration of three primary strategies for integrating photoisomerizable molecules into nanochannels. (a) Direct grafting. (a1) Schematic representation of photoisomerizable molecules covalently anchored onto the inner walls of nanochannels. (a2) Direct grafting of spiropyran onto the AAO nanochannel wall, demonstrating successful surface functionalization. Adapted under a CC BY license.<sup>40</sup> Copyright 2023 by the authors. (a3) Direct grafting of azobenzene onto the COF framework, exemplifying the generality of this direct grafting strategy. Reproduced with permission.<sup>42</sup> (b) Mediator-assisted grafting. (b1) Schematic depiction of photoisomerizable molecules attached to nanochannel surfaces *via* polymeric or biomolecular (e.g., DNA) mediators. (b2) Chemical structure of a silane-based mediator grafted with spiropyran. Reproduced under a CC BY license.<sup>45</sup> Copyright 2025 by the authors. (b3) Example of DNA-mediated azobenzene functionalized on channel wall. Adapted with permission.<sup>46</sup> Copyright 2021, American Chemical Society. (c) Host-guest complex embedding. (c1) Schematic of photoresponsive molecules physically embedded within porous framework materials (e.g., MOFs). (c2) Spiropyran molecules encapsulated within the MIL-53 framework, illustrating host-guest confinement. Reproduced with permission.<sup>49</sup> Copyright 2025 Elsevier. (c3) Azobenzene embedded in the UiO-66 framework, demonstrating the generality of the host-guest encapsulation strategy. Reproduced with permission.<sup>51</sup> Copyright 2020, John Wiley and Sons.

### 3.2 Mediator-assisted grafting

This strategy employs molecular or biological linkers (e.g., polymer tethers or DNA) to bridge photoisomerizable molecules and the substrates,<sup>43–46</sup> endowing it with prominent merits of flexible design, functional synergy, and precise regulation (Fig. 3b1). For example, Chen *et al.* employed a polymer mediator-assisted modification strategy to *in situ* graft spiropyran onto the pore walls of AAO nanochannels.<sup>45</sup> This strategy endowed the system with a broader ion-transport regulation window, and achieved a maximum impedance reduction of 40.2% within 7 min of UV irradiation (Fig. 3b2). Chen and co-workers utilized DNA as a bridging mediator to covalently anchor azobenzene-functionalized ATP aptamers onto gold-coated conical glass nanopipettes.<sup>46</sup> The azobenzene moiety

underwent reversible photoisomerization, allowing precise regulation of the conformation of ATP-specific DNA aptamers. This conformational change further mediated gated ion transport through the confined nanochannel. Such light-responsive ion transport behavior further allowed reliable, reversible monitoring of intracellular ATP gradients at the single-cell level (Fig. 3b3).

The complexity of mediator systems introduces both opportunities and challenges. Biological mediators, such as DNA, offer exquisite recognition capabilities but suffer from environmental sensitivity (e.g., temperature, pH). Synthetic polymer tethers provide greater robustness but may reduce response speed due to chain dynamics. A key advantage is the ability to spatially organize switching units, creating cooperative effects that enhance regulatory magnitude. Nevertheless, poor



Table 2 Summary of typical modification strategies for constructing photoresponsive nanochannels

Modification strategies	Bonding mode to channel surface	Advantages	Disadvantages	Ref.
Direct grafting	Direct covalent bonding	Simple preparation/fast response	Restricted isomerization freedom/limited material combinations	40 and 41
Mediator-assisted grafting	Mediator-mediated covalent bonding	Flexible function design/spatial organization	Environment sensitivity/reduced response speed	44 and 45
Host-guest complex embedding	Non-covalent (spatial confinement-dependent)	High isomerization freedom/precise spatial confinement	Prone to molecular leakage/poor dispersion uniformity	50 and 51

batch-to-batch reproducibility represents a major bottleneck, often arising from ill-defined mediator structures and heterogeneous surface anchoring. Meanwhile, insufficient long-term stability of mediators under continuous operation further limits reliability in realistic settings, highlighting the need for more robust design principles toward scalable device fabrication.

### 3.3 Host-guest complex embedding

This approach physically encapsulates photoisomerizable molecules within porous matrices (*e.g.*, metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), polymers) without covalent attachment (Fig. 3c1). The core advantages of this strategy for fabricating photoresponsive nanochannels reside in its precisely controllable molecular dispersibility, exceptional framework-molecule compatibility, and maximized isomerization freedom.<sup>47–51</sup> For example, Garg *et al.* demonstrated the precise dispersion capability of this method by embedding nitro-substituted spiropyran into UiO-67.<sup>48</sup> Specifically, 7.5 spiropyran molecules were accurately encapsulated per unit cell with an intermolecular distance of 1.37 nm, enabling homogeneous dispersion without noticeable aggregation. Yu *et al.* achieved the direct encapsulation of spiropyran into MIL-53 through a one-step *in situ* strategy,<sup>49</sup> thereby avoiding the prerequisite modification of the MOF framework or photoresponsive molecules (Fig. 3c2). X-ray diffraction characterization confirmed the preservation of MIL-53's crystalline integrity post-encapsulation, underscoring the method's excellent compatibility. Heidi A. Reichl *et al.* confined diarylethene molecules into the pores of MOFs *via* noncovalent encapsulation, and realized the stable distribution of photoresponsive units by means of spatial confinement effect, endowing them with controllable photoisomerization behavior and anti-fatigue properties.<sup>50</sup> Qian *et al.* confined azobenzene within UiO-66 sub-nanochannels, enabling unconstrained molecular isomerization with a high on-off ratio of 17.8.<sup>51</sup> This value was substantially higher than that of traditional direct grafted channels (1.3–1.5), thus highlighting the inherent superiority of the host-guest embedding method in isomerization regulation (Fig. 3c3).

Embedding strategies exhibit excellent photoresponsive cyclic stability, and the reported systems can endure up to 100 reversible switches without significant performance degradation. However, they face challenges in controlling molecular distribution and preventing leakage. To address this issue,

strategies including enhanced host-guest interactions, hierarchical confinement, and cavity steric hindrance are employed to mitigate leakage. In MOF systems, precise control over crystallization and loading to ensure effective confinement of photoisomerizable molecules without damage is crucial but technically demanding. For polymer matrices, achieving uniform dispersion while maintaining adequate loading for significant property changes requires careful optimization of processing parameters. Such demanding processing conditions impede large-scale fabrication and limit the scalability of embedding strategies for practical applications.

The above mentioned modification strategies are summarized in Table 2. Each of the three photoisomeric molecule modification strategies possesses distinct characteristics and can be selectively used in different material systems and application scenarios. Direct grafting is applicable to substrates with well-defined surface chemical properties, offering rapid response but requiring improvement in long-term stability; mediator-assisted grafting excels in functional integration and signal amplification, yet system complexity and environmental stability need further optimization; host-guest embedding demonstrates outstanding cyclic stability and dynamic regulation capabilities, but imposes stringent requirements on preparation technology and structural control. With the continuous development of interface chemistry, nanomanufacturing, and material design technologies, the modification strategies for light-responsive intelligent channels will continue to evolve toward higher precision, enhanced stability, and superior functional integration.

## 4. Hierarchical mechanisms of ion transport regulation

Understanding how photoisomerization translates to ion transport modulation requires analyzing the fundamental mechanisms. We establish a hierarchical framework based on the physical principles governing ion permeation: (1) wettability, (2) electrostatic interaction (charge), (3) steric exclusion (size). These principles can operate individually or synergistically, creating progressively sophisticated regulatory paradigms. In this review, the classification of different systems is primarily based on the regulatory factors explicitly mentioned in the original literature.



#### 4.1 Single-parameter regulation

The single-parameter regulation mechanism refers to the scenario where photoisomerization reactions mainly alter only one core physicochemical property of nanochannels (*e.g.*, wettability, charge polarity, or geometric pore size). This mechanism features a clear cause-effect relationship, facilitating theoretical modeling and performance prediction.

**4.1.1 Wettability regulation.** Transport in nanoconfined spaces is highly sensitive to interfacial wettability. Biological systems efficiently control the ion transport by regulating the channel wettability.<sup>45,52,53</sup> Photoisomerizable molecules with large polarity changes, like spiropyran and some azobenzene derivatives, enable dynamic control over this fundamental parameter. Modifying spiropyran-containing polymers on the surface of porous materials successfully regulated ion transport by virtue of the wettability changes of spiropyran under different light irradiation. Alternatively, Xie *et al.* demonstrated pure wettability gating using azobenzene-modified nanochannels.<sup>52</sup> In the *cis* state (UV light irradiation), channels remained hydrophobic, maintaining a gas/liquid interface that hindered ion transport (OFF state). Visible light-induced transition to the *trans*-azobenzene enabled cyclodextrin inclusion complex formation, rendering channels hydrophilic and enabling ion flow (ON state) (Fig. 4a1).

**4.1.2 Electrostatic interaction regulation.** Surface charge density influences ion transport *via* Coulombic interactions. Photoisomerizable molecules that undergo charge generation or significant dipole moment changes enable the electrostatic interactions regulation of ion transport. For example, Wang *et al.*'s AAO-Cu<sub>x</sub>S/Spiro heterogeneous nanochannels exemplified electrostatic gating.<sup>54</sup> Under visible light, neutral SP forms allowed ions to pass through the channels smoothly (ON state). Upon 365 nm UV light irradiation, spiropyran underwent a ring-opening reaction to form a zwitterionic structure, creating high local charge density that electrostatically trapped counterions and hindered ion migration through charge screening effects (OFF state) (Fig. 4a2).

Recently, Li *et al.* constructed a visible-light-responsive bionic nanochannel modified with retinal inspired by plant chloroplast, which provided a novel application paradigm for photoisomerization molecule-mediated electrostatic regulation of ion transport.<sup>55</sup> Retinal was modified onto the surface of PET-based conical nanochannels *via* a Schiff base reaction, and the photo-induced isomerization property of retinal was utilized to realize precisely controlled release of the bactericide methylene blue (MB). Under visible light irradiation, retinal underwent conformational transition, resulting in enhanced negative potential on the inner surface of the channels (charge density increased from  $-1.05 \times 10^{-3} e^- \text{ nm}^{-2}$  to  $-1.37 \times 10^{-3} e^- \text{ nm}^{-2}$ ). This promoted the release of positively charged MB through electrostatic interactions, with a release flux of  $8.78 \mu\text{mol m}^{-2} \text{ h}^{-1}$ , which was four times that in the dark state.

**4.1.3 Steric hindrance regulation.** Photoisomerization can physically change the effective pore size of nanochannels, thereby enabling precise modulation of ion transport. Azobenzene, with its significant length change, is prototypical.<sup>56,57</sup> Li

*et al.* reported azobenzene-tethered DNA (Azo-DNA)-modified nanochannels. These systems realized pure steric gating through indirect structural regulation driven by macromolecular conformational folding.<sup>57</sup> Under 450 nm visible light irradiation, Azo-DNA folding from a relaxed single-strand state to a compact hairpin structure increased the effective pore size of the channels and enhanced ion transport. After 365 nm UV light irradiation, DNA strands returned to a relaxed state, reducing the channel pore size and blocking ion transport. Such a current ON/OFF ratio ( $\sim 3.2$ ) originated from the steric hindrance triggered by conformational changes of the photoisomerizable units (Fig. 4a3). In contrast to this indirect regulation *via* DNA conformational switching, Yin *et al.* designed an azobenzene-modified photoresponsive COF material,<sup>42</sup> where steric gating was directly achieved by the geometric isomerization of azobenzene itself. Specifically, under 365 nm UV light irradiation, *cis*-azobenzene exhibited a curved shape, the effective pore size of the channels was approximately 1.39 nm, allowing Al<sup>3+</sup> to pass through; under dark conditions or 450 nm visible light irradiation, *trans*-azobenzene exhibited a straight structure, the effective pore size of the channels was reduced to approximately 1.12 nm, producing significant steric hindrance to ions with larger hydrated radii, the Al<sup>3+</sup> flux decreased significantly, and the K<sup>+</sup>/Al<sup>3+</sup> selectivity ratio reached more than 6000.

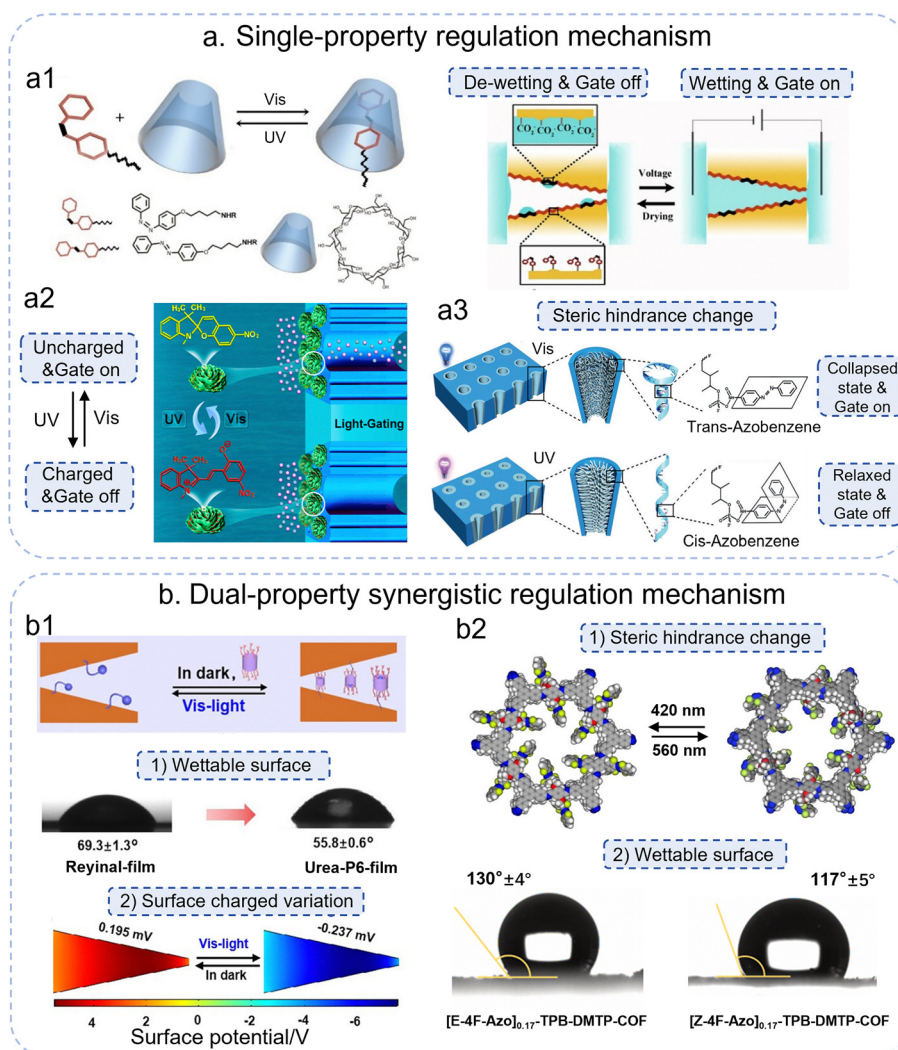
The single-property regulation mechanism features a clear structure-activity relationship and straightforward attribution of experimental results. Accordingly, it facilitates the establishment of accurate theoretical models and the prediction of system performance. For example, in wettability regulation experiments, when it is confirmed that the pore size is much larger than the size of solute molecules, the change in transport rate can be clearly attributed to the change in wettability. This simplicity also makes material design and synthesis relatively straightforward, and laboratory-scale preparation and verification are easier to achieve. However, single-dimensional regulation exhibits notable limitations. First, it struggles to satisfy complex or variable ion-transport demands, including precise discrimination of ions with different valences or sizes and selective transport in complicated solution environments. Second, its function is relatively simple with limited regulation sensitivity and range. Thus, it cannot realize the sophisticated and precise gating behavior of biological ion channels, which restricts the expansion of its application scenarios.

#### 4.2 Dual-property synergistic regulation

Dual-property regulation leverages simultaneous changes in two fundamental physicochemical properties of nanochannels (*e.g.*, the combination of wettability and charge, or that of pore size and charge), creating cooperative effects where the combined impact exceeds the sum of individual contributions. This approach enables the enhanced system's sensitivity and selectivity.<sup>58,59</sup>

The synergistic modulation of wettability and electrostatic interactions represents a powerful strategy for creating high-performance photogating systems in nanochannels, as these





**Fig. 4** Single and dual-parameter regulation mechanisms. (a) Single property regulation. (a1) Wettability regulation. Azobenzene molecules are grafted onto channels; visible-UV light stimulation induces their configuration transition, regulating the surface wettability of the channels. Reproduced with permission.<sup>52</sup> Copyright 2018, American Chemical Society. (a2) Charge regulation. Spiropyran molecules are modified *via* spin-coating; light isomerization enables dynamic regulation of the surface charge of the channels. Reproduced with permission.<sup>54</sup> Copyright 2016, American Chemical Society. (a3) Steric regulation. visible/UV light triggers *trans*-*cis* isomerization of azobenzene, dynamically regulating the dimensional structure of the channels. Reproduced with permission.<sup>57</sup> Copyright 2016, John Wiley and Sons. (b) Dual-property regulation. (b1) Synergistic regulation of surface wettability and charge: retinal-modified channels assemble into urea-functionalized films, which switch surface wettability (contact angle:  $68.3^\circ$  to  $55.8^\circ$ ) and surface charge (potential:  $0.198$  mV to  $-0.237$  mV) under dark/visible light conditions. Reproduced with permission.<sup>60</sup> Copyright 2020, John Wiley and Sons. (b2) Synergistic regulation of steric hindrance and wettability: *E/Z*-azobenzene-functionalized COFs achieve reversible pore size switching (*via*  $420/560$  nm light) and surface wettability adjustment (contact angle:  $130^\circ$  to  $117^\circ$ ) through *cis*-*trans* isomerization potential distribution *via* light-induced *cis*-*trans* isomerization. Reproduced with permission.<sup>61</sup> Copyright 2024, American Chemical Society.

factors often exhibit mutually reinforcing effects under nanoconfinement. As a notable example, Quan *et al.* developed a retinal-functionalized pillar[6]arene system that achieved “wettability + charge” dual-regulation through retinal’s simultaneous hydrophilicity and charge changes upon isomerization.<sup>60</sup> This design enabled dual (wettability and electrostatic) regulation by first covalently tethering retinal to *L*-lysine on the PET channel surface, followed by the host-guest inclusion of ethylurea-modified pillar[6]arene (urea-P6). The key mechanism lay in the light-induced retinal isomerization, which reversibly controlled the assembly and disassembly of

the urea-P6 complex. This process directly toggled the channel surface from a hydrophilic (urea-P6-present) to a hydrophobic (retinal-exposed) state, while concurrently altering the surface charge landscape for controlled ion transport (Fig. 4b1). Benefiting from the synergistic enhancement effect of wettability and electrostatic interactions, the relatively hydrophilic and positively charged ethylurea groups on Urea-P6 could efficiently capture and transport chloride ions at a rate of  $5.578$  nmol  $\text{cm}^{-2}$   $\text{h}^{-1}$ . Owing to this performance advantage, the system exhibited greater application potential than those regulated by a single parameter.



In contrast, an alternative approach focuses on the cooperative regulation of steric hindrance and electrostatic microenvironment to achieve photogated ion transport. Wang *et al.* engineered a self-assembled ion channel through the allosteric incorporation of an azobenzene photoswitch.<sup>61</sup> Reversible isomerization under 365/450 nm irradiation concurrently modified the molecular conformation and dipole moment of the azobenzene units. This process synergistically modulated steric hindrance *via* the disruption of  $\pi$ - $\pi$  stacking and self-assembly. Meanwhile, the accompanying changes in the electrostatic environment enabled dynamic and reversible photocontrol of chloride ion transport. These works demonstrate a biomimetic strategy for designing light-gated ion channels *via* dual-property synergistic regulation, which overcomes the limitations of single-regulation mechanisms and provides new insights for achieving more precise and efficient control over ion transport (Fig. 4b2).

The core merit of the dual-property synergistic regulation mechanism resides in its synergistic enhancement effect, which enables performance substantially outperforming that of single-dimensional regulation. Synchronous modulation of charge and pore size synergistically elevates ion transport efficiency by an order of magnitude, endowing the system with high sensitivity and selectivity, as well as considerable application potential in chiral separation and specific ion detection. Notwithstanding, this mechanism entails non-negligible challenges: the high difficulty of synergistic matching requires

in-depth comprehension of photoresponsive molecular structures, isomerization behaviors, and their interactions with nanochannel materials. In addition, the increased number of variables complicates both system design optimization and theoretical modeling.

### 4.3 Multi-dimensional coupled regulation

Multi-property regulation represents the most advanced paradigm, simultaneously modulating three or more physicochemical properties (*e.g.*, wettability, charge and pore size) of nanochannels triggered by photoisomerization to achieve biological-level complexity and adaptability. These systems typically employ photoisomerizable molecules in responsive matrices (*e.g.*, MOFs, COFs, smart polymers) where molecular changes trigger cascading structural reorganizations.

For example, Ren *et al.* demonstrated an azobenzene-COF system that exhibited three coupled changes.<sup>62</sup> Under visible light irradiation, the sulfonic acid groups ( $-\text{SO}_3\text{H}$ ) of *trans*-azobenzene were fully ionized (surface charge), increasing the inner surface negative density of the nanochannel (Fig. 5). This negatively charged surface adsorbed a large number of water molecules *via* strong hydrogen bonding interactions, reducing the effective pore size to 7.4 Å (pore size). In contrast, upon irradiation with 365 nm UV light, azobenzene underwent isomerization to the *cis* conformation. The bent molecular structure exposed the relatively hydrophobic  $-\text{N}=\text{N}-$  groups, leading to reduced pore hydrophilicity and an increase in the

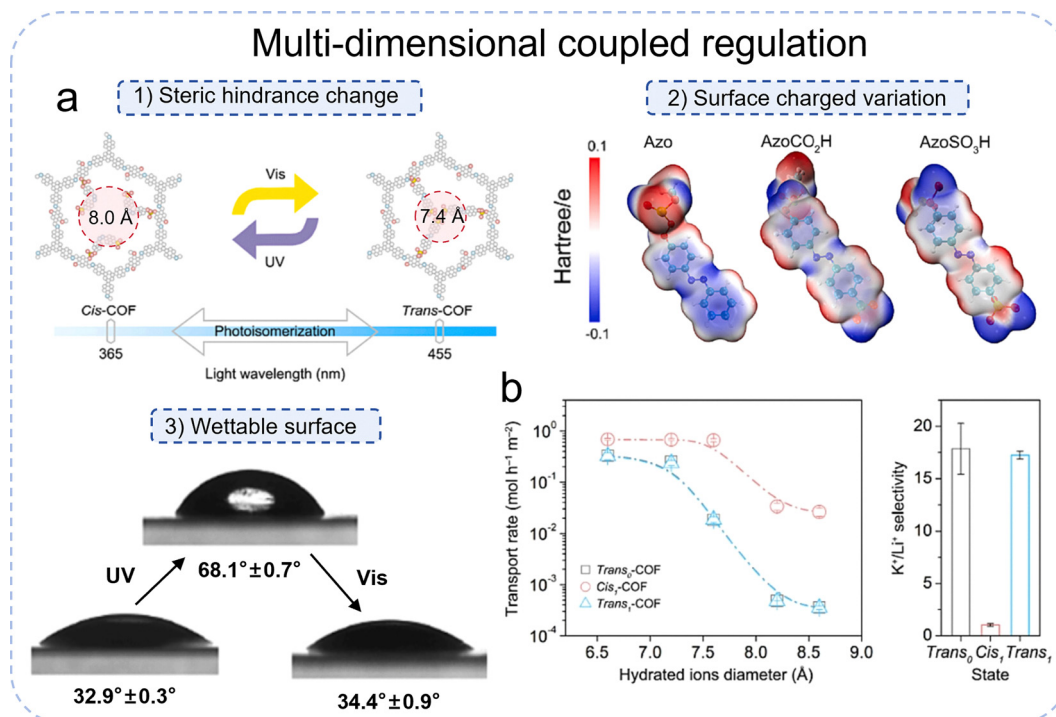


Fig. 5 Multi-dimensional coupled regulation mechanism. (a) Azobenzene-functionalized COFs undergo *cis*-*trans* isomerization under 365 nm UV/455 nm visible light, synchronously regulating three key parameters: (1) steric hindrance (effective pore size: 8.0 Å (*cis*) vs. 7.4 Å (*trans*)); (2) surface charge (tunable *via* azobenzene derivatives); (3) surface wettability (contact angle: 32.9° (UV) vs. 34.4° (Vis)). (b) Ion transport rate (left) of *trans*-COF, *cis*-COF, and -COOH-grafted Azo-COF as a function of hydrated ion diameter; K<sup>+</sup>/Li<sup>+</sup> selectivity (right) of the system in *trans/cis* photoresponsive states. Reproduced with permission.<sup>62</sup> Copyright 2024, Elsevier.



**Table 3** Photoisomerizable molecules for smart nanochannels: modification strategies, mechanisms, and performance metrics

Molecules	Modification strategies	Regulation mechanisms	Regulation coupling mode	Typical performance metrics	Ref.
Azobenzene	Direct grafting/mediator-assisted grafting/host-guest complex embedding	Steric hindrance/wettability/electrostatic	Single/dual/multi-factor coupling (system-dependent)	Maximum gating ratio $\sim 10^2$ / fastest response time: 15 s	42 and 51
Spiropyran	Direct grafting/mediator-assisted grafting/host-guest complex embedding	Steric hindrance/wettability/electrostatic	Single/dual/multi-factor coupling (system-dependent)	Maximum gating ratio $\sim 10^4$ / fastest response time: 10 s	52 and 54
Diarylethene	Direct grafting/host-guest complex embedding	Steric hindrance/electrostatic	Single/dual factor coupling (system-dependent)	Maximum gating ratio $\sim 10^2$ / thermal stability	32 and 50

effective pore size to  $\sim 8.0$  Å. In addition, the planar structure of *trans*-azobenzene facilitated intermolecular  $\pi$ - $\pi$  stacking interactions. This triple-coupled regulation, which integrates surface charge, pore size, and wettability, breaks through the limitations of single- or dual-parameter regulation and enables more precise and comprehensive dynamic manipulation of the nanochannel microenvironment.

Similarly, Zhang *et al.* reported a spiropyran-MIL-53 system which exhibited three-way coupling through SP-MC isomerization within a flexible MOF.<sup>63</sup> In the dark, the closed-loop SP form was electrically neutral and hydrophobic. This resulted in a small effective pore size within the channel, blocking ion transport (OFF state)—with the ionic current only reaching 9.1  $\mu$ A. Upon 365 nm UV light irradiation, the molecules isomerized to the open-loop hydrophilic MC form, exhibiting increased polarity and negative charge. Consequently, the effective pore size increased ( $\sim 3.8$  Å to 4.7 Å) and surface charge change (from positive to negative) significantly decreased the  $K^+$  ion migration barrier from 3.43 eV to 1.07 eV, leading to a drastic surge in ionic current to 113.9  $\mu$ A and an ON/OFF ratio of 16.2. By synchronously modulating multiple physicochemical properties *via* photoresponsive effects, this system exhibits a complex responsive capability far exceeding that of single-dimensional regulation, offering a new paradigm for the construction of highly biomimetic and high-precision intelligent ion-transport systems. Endowed with angstrom-scale tunable effective pore size and the synergistic regulation of charge and wettability, this system achieves excellent ion sieving performance. Specifically, the ideal selectivity of  $K^+/Li^+$  reaches 17.9 in single-salt systems, and the stable separation efficiency is maintained in mixed-salt systems after multiple photoswitching cycles, providing core support for scenarios such as efficient lithium extraction.

While multi-dimensional systems offer unprecedented functionality, their complexity presents challenges. The intertwined variables pose great challenges to mechanism elucidation, and the precise assembly of functional molecules at the nanoscale imposes extremely high requirements on fabrication processes. Additionally, the system stability, cyclic lifespan, and performance in real-world environments require further in-depth evaluation.

After systematically reviewing the structural properties of representative photoisomerizable molecules, modification

strategies for nanochannels, and regulatory mechanisms of light-controlled transport, we have summarized the above content into Table 3 for intuitive comparison of the design concepts and performance boundaries of different photoresponsive systems. This table not only serves as a highly concise recapitulation of the preceding discussion, but also explicitly reveals the advantages and limitations of various photoisomeric systems through quantitative metrics (*e.g.*, gating ratio, response time), thereby providing direct guidance for the design and optimization of novel light-controlled nanofluidic channel devices in future research.

In summary, research on photoisomerization-regulated ion transport in nanochannels has evolved from the modulation of a single physicochemical parameter to sophisticated dual-dimensional cooperative regulation and even multi-dimensional coupled regulation systems. Although multi-property coupled regulation faces challenges such as complex and elusive mechanisms and extremely high requirements for fabrication processes, it can mimic the high complexity and adaptability of ion channels in biological systems. This provides broad prospects and development directions for the future development of next-generation intelligent separation membranes, biomimetic sensors, and energy conversion devices.

## 5. Applications of photoresponsive ionic nanochannels

The unique capabilities of photoisomerizable molecule-functionalized nanochannels have demonstrated promising applications in multiple cutting-edge fields, including energy harvesting, ionic gate, and biomimetic devices. This section maps the hierarchical mechanisms to frontier application areas, highlighting, evaluating their progress and challenges.

### 5.1 Energy conversion

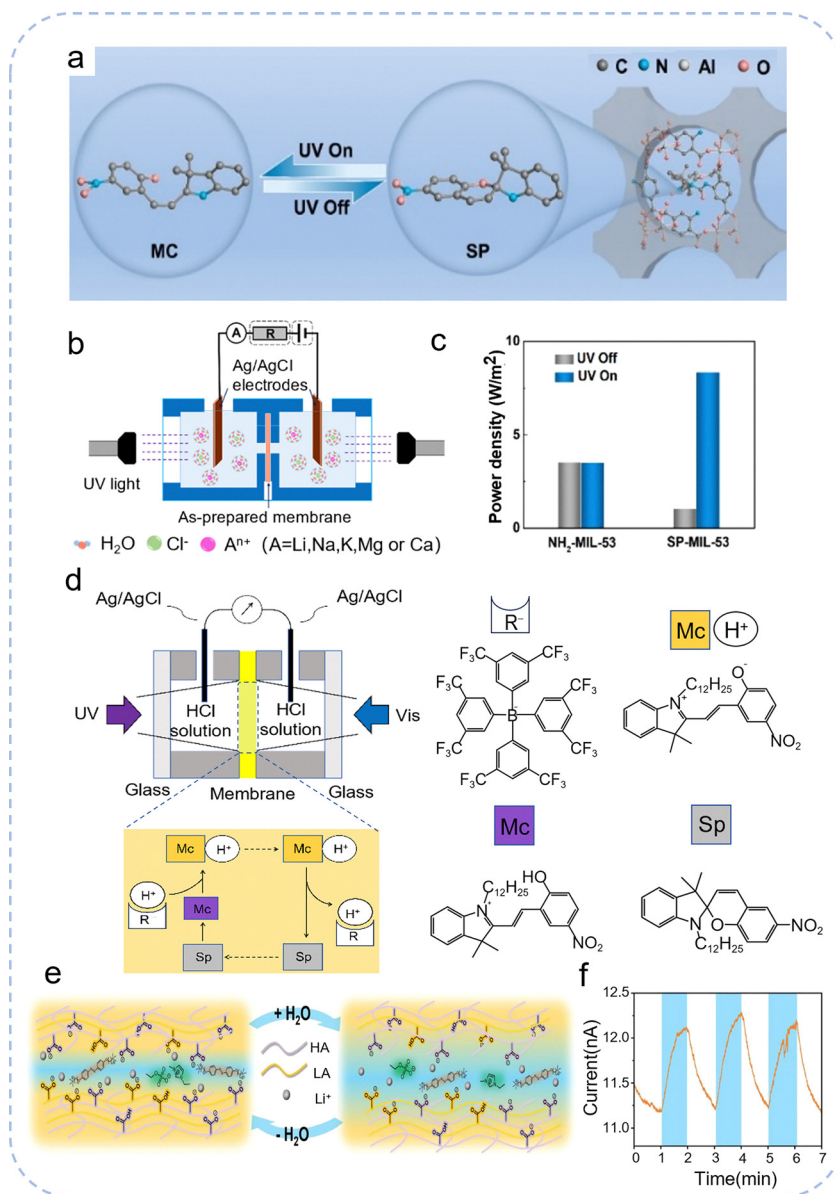
The pursuit of green energy technologies has positioned photoresponsive nanofluidic channels as a promising platform for light-regulated power generation, leveraging their unique advantage of light-enhanced directional ion transport and efficient energy conversion. Early systems focused on passive, gated osmotic energy conversion. For instance, Zhang *et al.*



fabricated spiropyran-modified MIL-53 MOF sub-nano-channels,<sup>64</sup> where UV-induced ring-opening to the hydrophilic MC form increased surface charge density and hydrophilicity, while relieving the steric hindrance caused by the closed spiropyran form within the channels (Fig. 6a–c). The light-triggered switch in interfacial properties and steric hindrance allowed precise control over ion selectivity and flux, generating

a high osmotic power density of  $8.3 \text{ W m}^{-2}$  under a 50-fold KCl concentration gradient.

A significant leap forward involves systems that actively convert light into an ionic gradient, emulating biological proton pumps. Recently, Xie *et al.* reported such a system by designing a spiropyran-doped liquid pore membrane.<sup>65</sup> Its innovative mechanism hinges on electrostatic modulation



**Fig. 6** Applications of photoresponsive nanofluidic channels in energy conversion. (a) Schematic illustration of the *in situ* fabrication process for the spiropyran-modified MIL-53 composite film, using anodic aluminum oxide membrane as both the aluminum source and substrate in the presence of spiropyran; (b) schematic diagram of the osmotic energy conversion test device constructed with the composite film; (c) comparison of light-driven power density performance among different membrane materials. Reproduced with permission.<sup>64</sup> Copyright 2022, American Chemical Society. (d) Artificial light-harvesting system based on spiropyran-modified porous polymer membranes. Under UV/visible/thermal stimulation, SP isomerizes with MC, synchronously regulating transmembrane proton ( $\text{H}^+$ ) transport to enable light-controlled switching of ionic current. Reproduced with permission.<sup>65</sup> Copyright 2014, Springer Nature. (e) A two-dimensional supramolecular nanofluidic channel is constructed using photoresponsive azobenzene derivatives as functional motifs, combined with hyaluronic acid (HA) and alkaline dispersion of lipoic acid (LA), and this membrane enables moisture-driven spontaneous electricity generation. (f) Results of *in situ* photoresponsive current output signal detection. Reproduced with permission.<sup>63</sup> Copyright 2025, John Wiley and Sons.



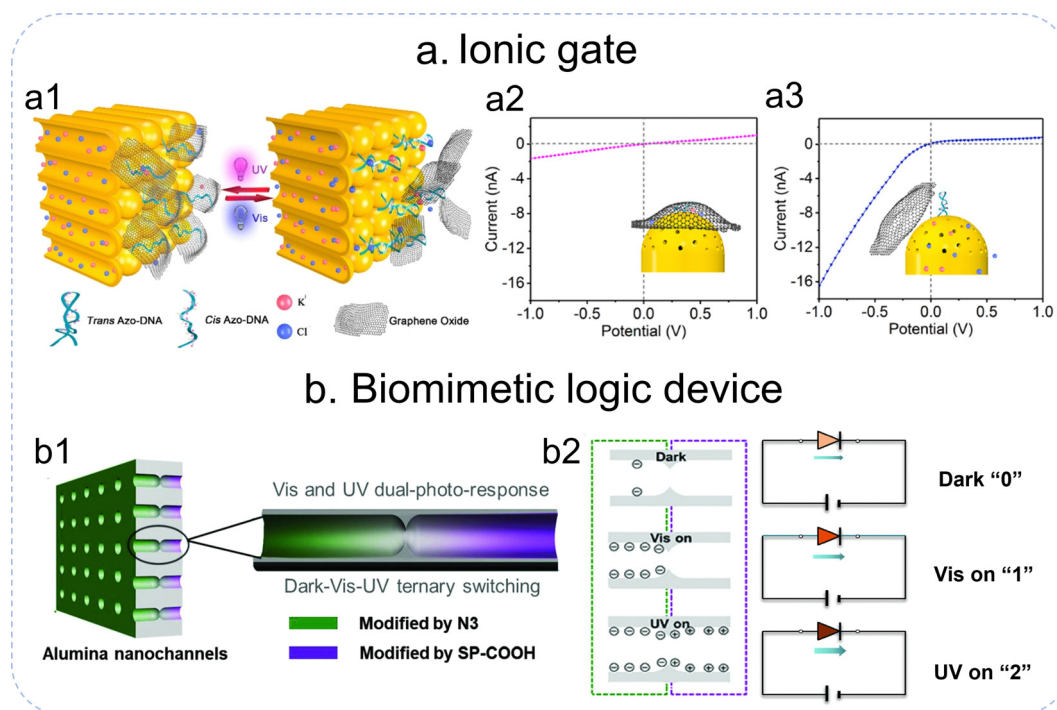
induced by SP/MC isomerization. UV light triggered the ring-opening of SP to form MC, which carries a charged zwitterionic structure and strong electrostatic affinity for  $H^+$ . Meanwhile, visible light-drove reverse isomerization back to the neutral SP form, which exhibited weak proton binding. Such reversible electrostatic switching further enabled directional transmembrane transport of  $H^+$  and the establishment of a proton gradient (Fig. 6d). This active nanofluidic channel generated an open-circuit voltage of 210 mV and an energy conversion efficiency of approximately 0.12%. It demonstrates a shift from passive gating to active photochemical energy conversion, a more complex mechanism requiring precise kinetic control of isomerization, electrostatic proton binding and transport coupling.

Advancing from functional realization to green sustainability, Zhang *et al.* prepared azobenzene-doped supramolecular polyelectrolyte films with layered nanochannels and light-regulated capability.<sup>63</sup> Photoisomerization of azobenzene modulated both steric hindrance and wettability, enhancing water uptake and membrane hygroscopicity. The elevated water content promoted ion dissociation and increases mobile charge carriers, thereby raising ionic flux and strengthening the spontaneous ionic current (Fig. 6e). Upon 365 nm UV light irradiation, the spontaneous current of the composite film increased from  $\sim 11.2$  nA to  $\sim 12.2$  nA; after terminating the irradiation

for 1 minute, the current reverted to  $\sim 11.2$  nA. This photoresponsive current switching process was reproducible for at least three cycles with no apparent fatigue behavior (Fig. 6f). Notably, the material exhibits excellent recyclability, maintaining stable performance after dissolution-re-evaporation cycles, thus providing a sustainable energy solution for wearable devices and similar applications.

## 5.2 Ionic gate

Photoresponsive nanochannels constructed from photoisomeric molecules, endowed with reversible structural transformation capabilities, serve as distinctive molecular platforms for the precise modulation of ion transport.<sup>66–68</sup> These advanced nanoarchitectures exhibit highly promising application prospects in pivotal fields including ion gating transport and water purification, owing to their unique light-triggered tunability over ion flux and selectivity. Shi *et al.* demonstrated such a light-regulated nanochannel ionic I gate *via* a graphene oxide (GO)/azobenzene-DNA modified porous AAO nanochannel.<sup>66</sup> The *trans/cis* isomerization of azobenzene modulated DNA conformation, thereby regulating the  $\pi$ - $\pi$  stacking interaction between GO and DNA. Such a structural conversion amplified the steric hindrance effect and enables reversible physical coverage or exposure of the underlying nanochannel. Under alternating visible/UV light irradiation, the system realized



**Fig. 7** Applications of photoresponsive nanofluidic channels in ionic gate and biomimetic logic device (a) ionic gate. (a1) Photoresponse mechanism of azobenzene-DNA modified graphene oxide-based channels: *trans/cis* azobenzene isomerization drives the transmembrane transport of  $K^+$  and  $Cl^-$ . (a2)  $I-V$  curve under UV light: GO adsorption onto single-stranded Azo-DNA blocks ion transport. (a3)  $I-V$  curve under visible light: GO desorption due to Azo-DNA hairpin formation restores ion. Reproduced with permission.<sup>66</sup> Copyright 2019, American Chemical Society. (b) Biomimetic logic device. (b1) Photoresponsive alumina nanochannels modified with N3/spirocyclohexane. (b2) Visible/UV dual stimulation enables "OFF-ON" ion transport switching, and combined with dark-state regulation, it achieves dark-UV-visible ternary conductance switching and logical functions. Reproduced with permission.<sup>70</sup> Copyright 2018, John Wiley and Sons.



“ON-OFF” switching of ion transport with a current ratio of 4.2. Meanwhile, it exhibited outstanding steric hindrance regulation and excellent reversible switching stability (Fig. 7a1–a3).

To address global water scarcity, Ou *et al.* developed a sunlight-responsive poly spiropyran modified-MIL-53 material, offering an innovative solution for sustainable water desalination.<sup>68</sup> Constructed by confining poly (spiropyran acrylate) molecules within the pores of MIL-53, this material leverages the photoisomerization property of spiropyran to achieve controllable adsorption and desorption of salt ions. The structural transformation of spiropyran enabled simultaneous regulation of electrostatic interactions and surface wettability, which further governed the ion capture and release behavior. Under dark or UV light conditions, SP isomerized into zwitterionic MC with enhanced hydrophilicity and paired positive/negative binding sites, allowing efficient adsorption of cations and anions and reaching equilibrium within 30 minutes. Upon sunlight irradiation, the hydrophobic neutral SP form was recovered, weakening electrostatic interactions and triggering rapid ion release to finish regeneration in only 4 minutes. It exhibited a maximum NaCl adsorption capacity of 2.88 mmol g<sup>-1</sup>, and when treating 2233 ppm synthetic brackish water, it achieved a freshwater yield of 139.5 L kg<sup>-1</sup> d<sup>-1</sup> with an energy consumption of only 0.11 Wh L<sup>-1</sup>, along with excellent cycling stability. This work opens up a new pathway for the design of low-energy desalination materials.

### 5.3 Biomimetic devices

The high level of application involves designing systems that mimic the integrated intelligence of biology. Initial efforts replicate adaptive environmental response. Zhang *et al.* developed a light/pH dual-responsive nanochannel membrane that emulated the multi-signal response and synergistic regulation mechanism of biological membranes.<sup>69</sup> In this system, azobenzene moieties enabled direct modulation of surface wettability *via* photoisomerization-driven conformational changes. In parallel, tertiary amine groups served as the pH-responsive units to control the surface charge state. By synergistically tuning wettability and charge *via* light and pH, the material achieved efficient and controllable oil–water separation. This represents a dual-stimuli synergistic mechanism for creating environmentally adaptive interfaces. Moving beyond such basic functional emulation, Zhang *et al.* achieved high-level intelligent regulation by constructing hourglass-shaped nanochannels modified with N3/spiropyran,<sup>70</sup> which precisely mimicked the multi-level signal transduction mechanism inherent to biological ion channels. The electron transition of N3 dye under UV/visible light simulated the generation of biological electrical signals. Meanwhile, spiropyran underwent selective isomerization only under UV irradiation. The resulting photoinduced conformational transition altered the surface charge state within the nanochannels, thereby enabling electrostatic regulation of ion transport. Their synergy realized “0-1-2” three-level ion conductance switching with a response current difference of 500 nA. Endowed with diode-like transport behaviors, the channel

successfully reproduced the signal coding function of biological neural networks. It enabled stable sequential logical switching (*e.g.*, “0-1-2-0” and “0-1-2-1-0”), providing a paradigmatic model for biomimetic logic devices (Fig. 7b1 and b2).

These two works represent a progressive advancement from emulating basic biological transport and environmental adaptation to replicating complex neural signal regulation, which not only highlights the versatile potential of photoresponsive nanochannels in constructing high-performance intelligent biomimetic devices but also pushes the boundary of bio-inspired nanofluidics toward practical applications in smart separation, logical computing, and beyond.

## 6. Summary

This review has established a unified, hierarchical framework that connects the molecular features of photoisomerizable switches to the macroscopic performance of intelligent nanofluidic channel devices. We have demonstrated that: (1) the molecular choice (azobenzene, spiropyran, or diarylethene) predetermines the primary regulatory axis (steric, electrostatic/wettability, or durable switching); (2) the modification strategy (direct, mediator-assisted, and host–guest embedding) dictate critical performance parameters such as stability, responsivity, and functional density; and (3) the engineered regulatory mechanism evolves from single-parameter control to synergistic and multi-dimensional coupled regulation, with increasing complexity enabling richer, more biomimetic functionalities. This framework provides a rational blueprint for designing devices tailored to specific applications, whether energy conversion, precision delivery, or adaptive biomimetics.

Despite remarkable progress, several critical challenges remain, and focused efforts are needed in several key areas. (1) Advanced *in situ* characterization and modeling. Moving beyond indirect measurements is crucial. The development and application of *in situ* spectroscopic techniques (*e.g.*, surface-enhanced Raman scattering, X-ray absorption, and nanoscale charge and wettability characterization) within operational nanochannels are needed to directly confirm molecular states and conformational changes. Coupled with multi-scale computational models, this will allow for the definitive deconvolution of synergistic and coupled mechanisms and the creation of true structure–property relationships. This integrated strategy may also help quantify the contribution of each property change to ion transport, thereby offering more rational guidance for materials design. (2) Next-generation material and molecular innovation. This includes designing switches with red-shifted activation for biological compatibility, developing robust, cooperative matrices (*e.g.*, mechanically stable COFs, 2D material laminates) that amplify responses, and creating orthogonal multi-switch systems for independent control of multiple ionic pathways. (3) Device integration and engineering. Laboratory-scale proof-of-concept must evolve into functional, integrated devices, and performance study under realistic operating conditions. For example, for energy devices, long-term testing



under relevant concentration gradients and fouling conditions is essential.

The field of photoresponsive ionic nanofluidics stands at an exciting inflection point. The foundational knowledge is now sufficiently mature to support a strategic shift from exploratory synthesis to purpose-driven, framework-guided design. By embracing this integrated perspective and tackling the interdisciplinary challenges ahead, researchers can accelerate the development of a new class of intelligent fluidic systems. These systems promise not only to mimic biology but to create functional technologies for sustainable energy, personalized medicine, and adaptive soft robotics, ultimately establishing photonics ionics as a cornerstone of next-generation nanotechnology.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

All data included in this mini-review are available from the original publications cited in the reference list. No new experimental data were generated in this study.

## Acknowledgements

This work was supported by the National Key R&D Program of China (2021YFA1200403), the National Natural Science Foundation of China (22275171, 22090050 and U24A20502), Guangdong Basic and Applied Basic Research Foundation (2024A1515012749), and the Natural Science Foundation of Shenzhen (JCYJ20220530162406014).

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