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ARTICLE

## Photochromic sensors: a versatile approach for recognition and discrimination

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Photochromic sensors are widely used in detecting and monitoring analytes. Due to the photoswitchable properties, photochromic sensors show advantages on providing more recognition states and sensing information, and thus better sensitivity to external stimulations. Via reasonable design of photochromic sensors with various ionophores, dyes, platforms and metallic complexations, it is promising to achieve visual, sensitive and high-throughput detection. In this review, we summarized the applications of photochromic sensors in the areas of specific recognition and multi-analyte discrimination, based on their isomerization to light, as well as pH, temperature, solvent, *etc.* Specially, the multi-analyte determination was introduced, which has aroused extensive interests in recent years.

### 1 Introduction

Photochromic molecules can undergo photoinduced reversible conversion between different states. Generally, two isomers are involved, and they perform the inter-transformation under UV, visible or IR irradiation. By modulation of light, reaction occurs between opening and closing, *trans*- and *cis*-isomerizations, *etc.* In recent years, numbers of photochromic derivatives have been synthesized such as crown ethers or calixarenes conjugated compounds, in which the ionophore can combine with kinds of molecules, thus becoming efficient receptors.<sup>1</sup> Also, based on the photoswitchable molecules, novel materials and devices, like photocontrollable gels,<sup>2</sup> nanoparticles,<sup>3</sup> membranes<sup>4</sup> and porous frameworks,<sup>5</sup> have been extensively fabricated. With the photoisomerization, some properties of the molecules change, such as absorption spectra,<sup>6</sup> emissive behaviours,<sup>7</sup> refractive index,<sup>8</sup> electronic properties,<sup>9</sup> magnetic responses,<sup>10</sup> *etc.* These phenomena endow the applications of photochromic materials in various fields such as logic gates and communication networks,<sup>11</sup> molecular switches and unit,<sup>12</sup> data recording and storage,<sup>13</sup> ions and molecules detection,<sup>14</sup> drugs delivery,<sup>15</sup> *etc.*

Typical photochromic molecules including azobenzene, dithienylethene, spiropyran and spirooxazine, and their photoisomerization are shown in Scheme 1. Attributed to the unique photoswitchable property, photochromic materials play a versatile role in chemical sensing, usually by colorimetric and fluorometric analysis. Different from the sensors with a

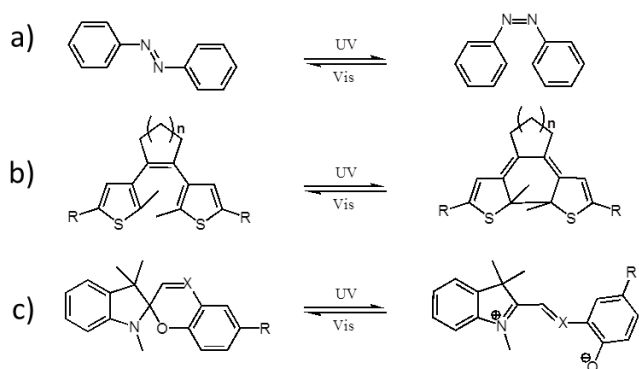
single state, photochromic sensors own several advantages as below. 1) The recognition forms of photochromic sensors can be changed by different stimulated lights, resulting in multiple signal outputs and more sensing information for analysis. 2) Photoinduced process can generate isomers with several recognition units, which is able to bind with different analytes. For example, UV irradiation can trigger a spiropyran molecule from ring-closed form to ring-opened structure that possesses an electron-rich phenolate to recognize cations and a positively charged indolium for anions detection (Scheme 1c). Thus, the sensors are promising for multi-analyte detection. 3) The isomerization of the photochromic sensors can be tuned not only by the lights, but also by temperature,<sup>16</sup> pH values,<sup>17</sup> ion species,<sup>18</sup> electric fields,<sup>19</sup> *etc.* With analysis for the changes of signal outputs, multiple external stimulations can be monitored and detected.

In this article, we focus on the applications of photochromic sensors in different areas, *i.e.* for specific recognition (metal ions, anions, biomolecules, gas and vapour, pH and temperature), and multi-analyte discrimination. Besides the stimulation of light, other conditions like pH and solvent are also included. Progress of photochromic sensors and mechanisms for sensing are summarized. Specially, discrimination of multi-analyte is introduced and emphasized, which has aroused extensive interests in recent years.<sup>20, 21</sup>

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**Scheme 1** Photoisomerization of (a) azobenzene, (b) dithienylethene, (c) spiroopyrane (X refers to carbon atom) and spirooxazine (X refers to nitrogen atom).

## 2 Photochromic sensors for specific recognition

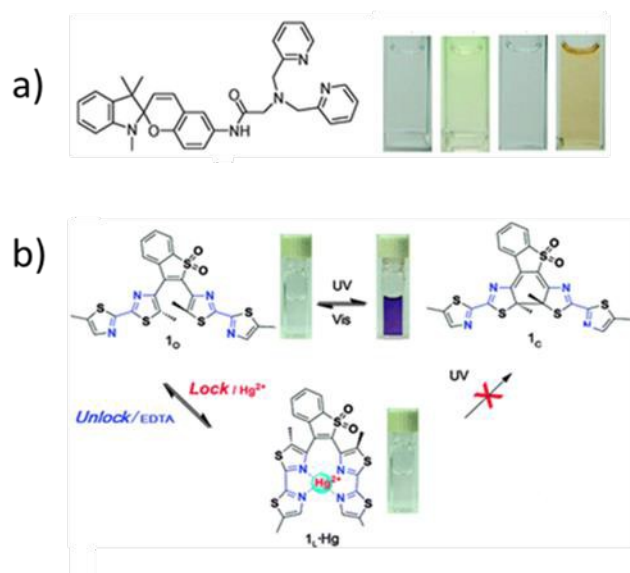
### 2.1 Photochromic sensors for metal ions

Large numbers of work have contributed the development of metal ions recognition. Various photochromic compounds were synthesized, with ionophores that could bind metal ions. These sensors usually contain electron-rich moieties such as N or O or S included functional groups, or receptors with caves such as crown ethers and calixarenes. By tuning the light, sensing signals (absorption, fluorescence, potentiometric response, etc.) can be obtained.

Inouye *et al.* synthesized a series of crown spiroopyrane and spirooxazine derivatives (SPs) in the 1990s. With absorption and  $^1\text{H}$  NMR analysis, they found the molecules could selectively uptake and release alkali and alkaline-earth metal ions by manipulation of light, thus could acting as photoswitchable sensors.<sup>14, 22-24</sup> Recognition of transition metal ions has been largely developed. By attaching a methyl pyridinyl group to the spirochromene indolic nitrogen and a methoxy group to the phenolate moiety, Giordani *et al.* designed a SP sensor for  $\text{Zn}^{2+}$ .<sup>25</sup> Changing the functional group jointed to the indolic nitrogen, they also developed a class of SP colorimetric sensors for  $\text{Cu}^{2+}$ .<sup>26</sup> Shiraishi *et al.* reported a spiroopyran-amide-dipicolylamine linkage for  $\text{Co}^{2+}$  recognition (Fig. 1a).<sup>27</sup> The solution was colorless in the dark or under UV irradiation. However, it turned yellow after adding  $\text{Co}^{2+}$  under UV irradiation. This was due to the ring opening of SP (*i.e.* a MC form). Strong coordination of  $\text{Co}^{2+}$  with amide O promoted the isomerization, and no other cations investigated could result in the coloration, which suggested the molecule acting as a selective sensor for  $\text{Co}^{2+}$ . Utilizing the thermal isomerization, they also designed a SP molecule for  $\text{Cu}^{2+}$  sensing.<sup>28</sup> When the solution was treated with  $\text{Cu}^{2+}$  at  $60^\circ\text{C}$ , a strong absorption appeared at 450-650 nm. In addition to the colorimetric strategies, fluorometric approaches were reported by the groups of Yang and Chan. They used SP mixed with zinc meso-tetraphenylporphyrin solution<sup>29</sup> or covalently attached with a morpholine functionality,<sup>30</sup> based on the inner filter effect or dual fluorescence response respectively, to realize selective  $\text{Cu}^{2+}$  fluorescent sensing. The specificity

remained in mixtures, which promoted recognition in biological system like human serum.

Dithienylethene derivatives (DTEs) are a class of promising photochromic compounds due to their excellent thermal-stability and fatigue-resistance.<sup>31</sup> With the extensive studies of DTEs as molecular switches, DTE sensors for metal ions are rapidly developed. Tian *et al.* contributed a series of work to investigate the interaction between DTEs and metal ions.<sup>32-34</sup> They reported the photochromism of a symmetrical pyridine-tethered DTE by  $\text{Zn}^{2+}$  which could combine with the pyridinic nitrogen.<sup>35, 36</sup> With addition of  $\text{Zn}^{2+}$ , the transformation of DTE ring-opening to closing form was enhanced almost 3 times under UV irradiation. Other metal ions including  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  could not induce the enhancement, suggesting the DTE as a selective sensor to  $\text{Zn}^{2+}$ . Unsymmetrical DTEs with recognition units for  $\text{Hg}^{2+}$  were designed.<sup>37, 38</sup> Upon addition of  $\text{Hg}^{2+}$ , fluorescence was quenched, while other metal ions could not induce the obvious spectral response. Also based on the fluorescence turn-off, Yi and co-workers designed a terpyridine functionalized DTE and found the fluorescence selectively decreased by  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ .<sup>39</sup> They introduced the phenomena to visualize the process of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  uptake by cells. The group of Yin and Liu synthesized an imidazole-based DTE to detect  $\text{Fe}^{3+}$ , by means of the selectively quenching fluorescence.<sup>40</sup> Utilizing metal-locked strategies, Li *et al.* designed gated photoswitches for selectively  $\text{Hg}^{2+}$  recognition.<sup>41</sup> As shown in Fig. 1b, the bis(dithiazole)ethene could undergo conversion from colorless ring-opening form  $1_0$  to purple ring-closing  $1_c$  under UV irradiation. However, with addition of  $\text{Hg}^{2+}$ , the route was locked. Photochromism was prevented, and other common metal ions could not act as the lock: only  $\text{Hg}^{2+}$  was appropriate for the square planar coordination pocket provided by the rigid dithiazoles. Thus a sensor for  $\text{Hg}^{2+}$  was obtained. A similar approach for  $\text{Cu}^{2+}$  recognition was reported by Pu *et al.*<sup>42</sup> The different principle of their sensor was that the DTE was firstly exposed to UV irradiation, causing transformation of a colorless opened to a purple closed structure. Then addition of  $\text{Cu}^{2+}$  resulted in a bleaching process, meanwhile prevented the re-coloration by UV irradiation. They also reported a series of DTE based fluorescent probes for sensing metal ions. By changing substituent groups of DTE, they designed fluorescent turn-on or shifted sensors for  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$ .<sup>43-45</sup> In addition, with investigations of metal ions effect on DTE fluorescence in different solvents, they demonstrated a selective photochromic sensor for  $\text{Al}^{3+}$  in acetonitrile and  $\text{Cu}^{2+}$  in acetonitrile/water binary solvent, respectively.<sup>46</sup> Similarly, a DTE sensor for  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  in acetonitrile, and  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$  in acetonitrile/water binary solvent was designed.<sup>47</sup> Zeng *et al.* synthesized a DTE with a crown ether as ionophore.<sup>48</sup> The compound could be used as a sensor: UV irradiation induced ring-opening to ring-closing coloration was prevented by  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ , while  $\text{Cu}^{2+}$  impressively enhanced the fluorescence.



**Fig. 1** (a) Structure of spiropyran-amide-dipicolylamine and the responses to different conditions (from left to right: dark, UV irradiation and with  $\text{Co}^{2+}$  in the dark and under UV irradiation, respectively). Reproduced by permission of The Royal Society of Chemistry.<sup>27</sup> (b) Gated bis(dithiazole)ethene photoswitches modulated selectively by  $\text{Hg}^{2+}$ . Reproduced by permission of The Royal Society of Chemistry.<sup>41</sup>

## 2.2 Photochromic sensors for anions

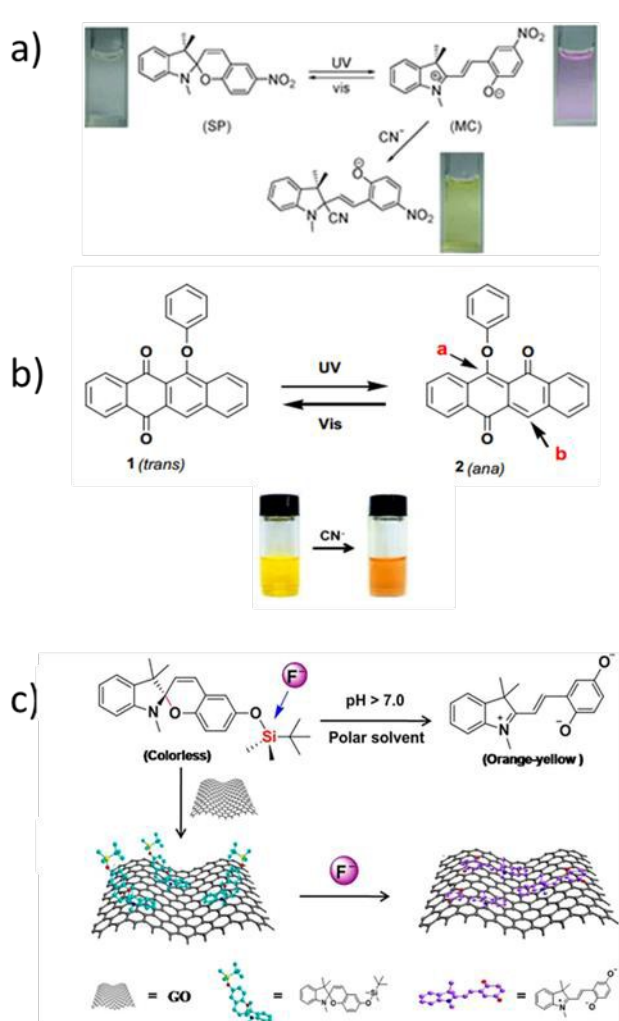
Anions play an important role in environmental and biological areas. People have paid increasing attention to the toxicity of cyanide anion ( $\text{CN}^-$ ), the physiological requirements for halide (*i.e.*  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) and phosphate ions as well as the safe dosage. So far, lots of strategies for anions sensing have been developed; photochromic sensors have shown the capability of efficient recognition.

Shiraishi and co-workers presented a series of SPs to realize  $\text{CN}^-$  sensing. As shown in Fig. 2a, the *N*-methylated SP could selectively combine with  $\text{CN}^-$  via a nucleophilic interaction to form a complex in a 1:1 stoichiometry.<sup>49</sup> Quantitative analysis was carried out. Processed in a water/MeCN solution, the sensor could detect  $\text{CN}^-$  in the range of 1.7–300  $\mu\text{M}$ . With attachment of an extra  $-\text{NO}_2$  unit to the meta-position of the original  $-\text{NO}_2$  functional group, they obtained a SP sensor in aqueous media, which could recognize  $\text{CN}^-$  in a level of 0.8  $\mu\text{M}$ .<sup>50</sup> Also, by replacing the  $-\text{NO}_2$  functional group with a fluorescein moiety, they synthesized a SP that performed ratiometric quantification of  $\text{CN}^-$  in longer wavelength absorption.<sup>51</sup> Not only the colorimetric approaches but also fluorescent sensors were designed based on the simple SP.<sup>52, 53</sup> The coumarin contained SP could realize  $\text{CN}^-$  sensing with detection limit of 0.5  $\mu\text{M}$  by fluorescence analysis. Apart from SPs, Tian *et al.* developed two near-infrared (NIR) DTEs, which contained electron donating and accepting units.<sup>54</sup> UV irradiation induced the ring-opening to ring-closing isomerization, resulting in a new absorption peak at 734 nm. With addition of  $\text{CN}^-$ , nucleophilic reaction occurred and interrupted the intramolecular charge transfer (ICT) between electron donor and acceptor. Thus the NIR absorption

decreased and fluorescence of ring-opening form increased a lot, showing sensing information to  $\text{CN}^-$ . A phenoxyquinone derivative was designed for  $\text{CN}^-$  recognition by Kim and co-workers.<sup>55</sup> The photochromism was based on rearrangement between *trans*- and *ana*- forms induced by UV or Vis irradiation (referred to the isomerization between 1 and 2 in Fig. 2b). Addition of  $\text{CN}^-$  into UV irradiated sensor solution caused the colour changing from yellow to pale brown.

Halide ions including  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  have also been recognized by photochromic sensors. Bakker *et al.* fabricated a reversible photodynamic bulk optode sensor for  $\text{Cl}^-$  based on SP.<sup>56</sup> The optical sensor could provide both spectral and electric responses for  $\text{Cl}^-$ . Yang *et al.* designed a composite consisting of a SP based silylated sensor (SPS) and graphene oxide (GO) sensing platform to selectively detect  $\text{F}^-$  (Fig. 2c).<sup>57</sup> Nucleophilic reaction between SPS and  $\text{F}^-$  promoted the ring-open process, thus leading to increased absorption and colour changing from colorless to orange-yellow. On the other hand, GO could shorten the response time of SPS to 1/6 and lower the detection limit more than 1 order of magnitude, attributed to the large specific surface area and hydrophilic groups on the surface. DTEs are largely introduced into halides sensing. The group of Li and Huang synthesized symmetrical<sup>58</sup> or unsymmetrical<sup>59</sup> organoboron-based DTEs to investigate the photochromism by  $\text{F}^-$ . Since the boron atom was a Lewis acid, and  $\text{F}^-$  was a strong Lewis base, the reaction between them caused obvious absorption changes of the DTEs, which could not occur with other anions addition. Yam *et al.* also designed an organoboron-based DTE and showed the similar results for  $\text{F}^-$ .<sup>60</sup> The group of Yin and Liu presented a series of DTEs that could bind with halide anions through hydrogen bond.<sup>61, 62</sup> Fluorescence quenching caused by  $\text{I}^-$  and coloration caused by  $\text{F}^-$  enabled the DTEs as selective anion sensors.

Considering the importance of pyrophosphate ion ( $\text{PP}_i$ ) in biological system, Yang *et al.* designed a SP with a bis(2-pyridylmethyl)amine (Dpa) unit.<sup>63</sup> The SP could coordinate with  $\text{Zn}^{2+}$ , leading to fluorescence intensity increased at 620 nm and decreased at 560 nm. The SP- $\text{Zn}^{2+}$  could subsequently combine with  $\text{PP}_i$ , resulting in a bridged dimer complex and decreased fluorescence intensity at 620 nm whereas increase at 560 nm. Thus, with the assistance of  $\text{Zn}^{2+}$ , a SP sensor for  $\text{PP}_i$  was realized.



**Fig. 2** (a) Structure of *N*-methylated SP and the response to CN<sup>-</sup>. Reproduced by permission of The Royal Society of Chemistry.<sup>52</sup> (b) Photoisomerization of phenoxyquinone derivative and response to CN<sup>-</sup>. Reproduced by permission of Elsevier Ltd.<sup>55</sup> (c) Response of SPS-GO composite to F<sup>-</sup>. Reproduced by permission of American Chemical Society.<sup>57</sup>

### 2.3 Photochromic sensors for biomolecules

Application of photochromic compounds in the biological area has developed for several decades, while it is still booming recently.<sup>64-72</sup> Searching for more rapid, economic, convenient and sensitive sensors has always been the focus of biomolecules recognition, which is of importance either *in vitro* or *in vivo*. Attributed to the multi-stimulation induced isomerization and excellent colorimetric or fluorescent properties, photochromic materials are a class of promising sensors. Here, we overview their applications in the sensing of amino acids and peptides, enzyme and coenzyme, and DNA, which are the most researched bio-analytes for photochromic sensors.

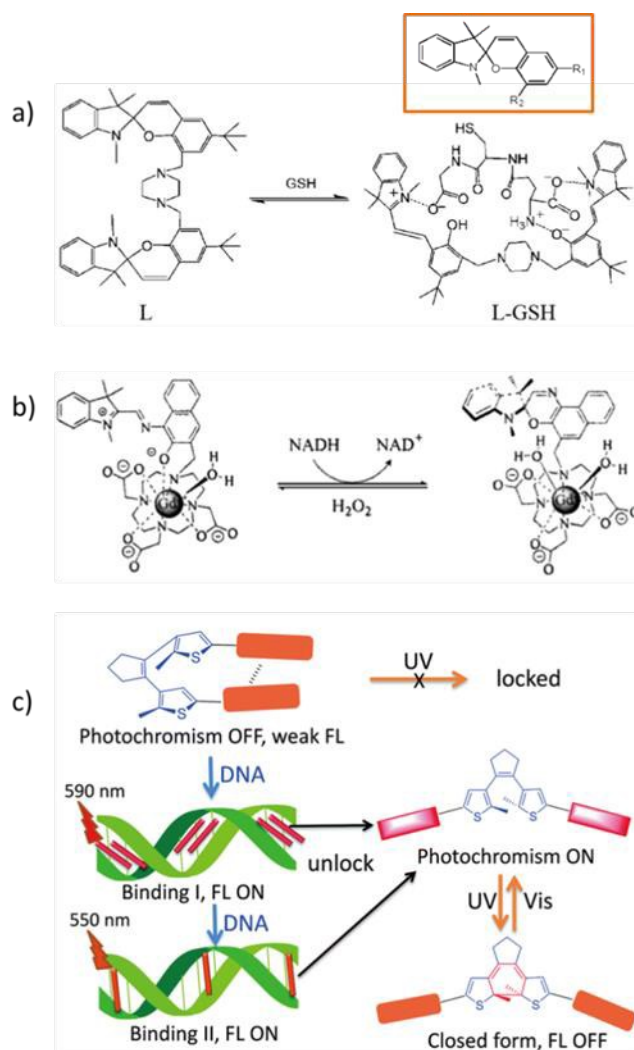
As described above, SP can form an open-structure (MC) upon UV irradiation (Scheme 1c). MC is zwitterionic (positive charge on the indolic N and negative charge on the phenolate O), which provides sites for electrostatic interaction with

complementary charged analytes.<sup>73,74</sup> Based on this principle, lots of work on amino acids and peptides sensing have emerged. Yang and co-workers designed a series of SP sensors (inset in Fig. 3a) for thiol-containing amino acids and peptides (e.g. cysteine, homocysteine, glutathione). When R<sub>1</sub> and R<sub>2</sub> were tert-butyl and *N,N*-dimethylaminomethyl respectively, a bis-SP sensor L could be obtained.<sup>75,76</sup> As shown in Fig. 3a, the open-structure of L had two sites for electrostatic interaction. Compared with mono-SP, L showed higher affinity for analytes and directional electrostatic interaction, which enabled L selectively combined with glutathione (GSH). GSH binding with L induced a conformational rigidity and thus reduction in ICT between phenolate O and electron-deficient quaternary N. Upon addition of GSH, L displayed a strong absorption enhancement at 446 nm and increased fluorescence at 643 nm; similar structured molecules, such as cysteine (Cys) and homocysteine (Hcy), could not significantly affect the fluorescence output, indicating L as a highly selective GSH sensor. Because of the moderately high hydrophobicity, L was cell-permeable and could be introduced to image GSH *in vivo*. The authors also designed a SP with nitro groups R<sub>1</sub> and R<sub>2</sub>.<sup>77</sup> By combination of simultaneous nucleophilic substituted reaction and complementary electrostatic interaction, the SP could realize more sensitive recognition for thiol-containing amino acids and peptides. Using GSH as a model analyte, the colorimetric SP sensor could detect GSH with a detection limit of  $1.0 \times 10^{-8}$  M. Since there exist enantiomers of amino acids, chirality sensing is essential. Fuji and co-workers reported chiral binaphthyl SPs to recognize chiral amino acids.<sup>78</sup> They firstly exposed the SPs solutions to UV irradiation, generating MC forms. After complexation of amino acids and subsequently removal of UV irradiation, the solutions started to fade. By comparison of the half-lives for decoloration, it was found that SP of (*R*)-configuration interacted with D-amino acids more strongly and (*S*)-configuration preferred to L-amino acids.

SPs are also employed in sensing of enzyme and coenzyme.<sup>9</sup> Qu and co-workers designed SP modified multi-walled carbon nanotubes (MWNTs) and sequent colorimetric assay for lysozyme recognition.<sup>79</sup> After UV irradiation, the MWNT-SP was isomerized to MWNT-MC, which was characterized by increased absorption at 545 nm. MWNT-MC could bind with horseradish peroxidase (HRP) and enhance its catalytic activity (indicated as increased absorption at 652 nm), while MWNT-SP had no this effect. Based on this phenomenon, a colorimetric assay for lysozyme could be obtained, with assistance of an anti-lysozyme DNA aptamer. When the DNA aptamer was added into the solution of MWNT-MC and HRP, DNA molecules could absorb on the surface of MWNT-MC and thus block the interaction between HRP and MWNT-MC. As a result, HRP activity was lowered, with decreased absorption at 652 nm. However, addition of lysozyme could restore the HRP activity, due to its specific binding with the DNA aptamer. By monitoring the HRP activity, the authors could recognize lysozyme with the detection limit of 30 nM. For coenzyme, Louie and co-workers reported a magnetic resonance imaging (MRI) approach to detect nicotinamide adenine dinucleotide

(NADH) levels, based on a MC-Gd complex (Fig. 3b).<sup>80</sup> NADH could react with MC-Gd via redox, resulting in ring-closing form SP-Gd. The isomerization was evidence by decreased absorption of MC-Gd at 440 nm and fluorescence at 539 nm. Based on this redox induced isomerization, MRI method was then employed to realize NADH detection.

Photochromic sensors for DNA have been developed. Andréasson and co-workers investigated the DNA binding with SP.<sup>81, 82</sup> Only the ring-opening form MC could combine with DNA, causing the absorption band blue-shifted from 512 nm to 420 nm. This characteristic change of absorption could be used to detect DNA. Yi and co-workers designed a DTE based approach to recognize DNA.<sup>83</sup> As shown in Fig. 3c, a thiazole orange (TO) modified DTE was prevented to undergo photoswitchable process in aqueous medium. Because the strong hydrophobic interaction and  $\pi$ - $\pi$  stacking made TO easily self-aggregated, the TO-DTE was restricted to a parallel configuration and could not perform photoisomerization. Upon addition of DNA, the interaction between the TO-DTE and DNA unlocked the isomerization, resulting in a change of absorption and fluorescence. There were two binding modes of TO-DTE and DNA. When the molar ratio of base pairs and TO-DTE ( $R$ ) was low ( $R < 1.6$ ), the mode binding I occurred, with increased absorption at 492 nm and enhanced fluorescence blue-shifted from 620 nm to 590 nm; when  $R$  value was in the range of 1.6-10 ( $1.6 < R < 10$ ), the mode was binding II, with decreased absorption at 492 nm and a new absorption band at 514 nm, and fluorescence further shifted to 550 nm. This DNA induced binding modes switching and corresponding changes on absorption and fluorescence could be utilized to monitor DNA.



**Fig. 3** (a) Bis-SP sensor for GSH. The inset is the structure of mono-SPs sensors for thiol-containing amino acids and peptides. Reproduced by permission of American Chemical Society.<sup>76</sup> (b) Redox reaction between NADH and MC-Gd complex, inducing ring-opening MC-Gd to ring-closed SP-Gd. Reproduced by permission of Wiley-VCH.<sup>80</sup> (c) Binding of TO-DTE with DNA, unlocking the photoisomerization. Reproduced by permission of The Royal Society of Chemistry.<sup>83</sup>

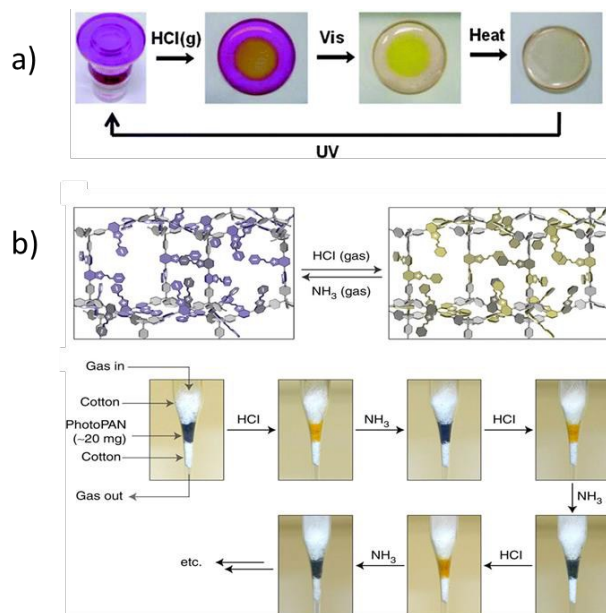
#### 2.4 Photochromic sensors for gas and vapour

For gas and vapour sensing, porous materials show their advantages due to the excellent sorption and penetrability of gaseous analytes. Networks of polymers and organic-inorganic frameworks are good candidates as the sensing platforms or scaffolds. By combination of photochromic compounds and porous materials, efficient photoswitchable gas and vapour sensors can be obtained.

Kim and co-workers developed a SP-embedded PDMS for HCl vapour detection.<sup>84</sup> As shown in Fig. 4a, the porous and flexible SP-PDMS membrane turned to purple after UV irradiation, suggesting the formation of ring-opening MC-PDMS composite. With treatment of HCl vapour, the exposed area became yellow immediately. Visible light irradiation triggered the switch of unexposed MC-PDMS to colorless SP-

PDMS, while the HCl vapour treated area remained yellow; heat treatment could induce the decolorization. The phenomena indicated that HCl led to the transformation of MC to protonated MCH state, which was evidenced by the new absorption band at 430 nm. The SP-PDMS membrane could recognize HCl vapour with the detection limit of 18ppb. Other acidic gases such as HCOOH, AcOH, TFA and HNO<sub>3</sub> could not induce the significant purple to yellow change, suggesting the membrane selective for HCl vapour sensing. Based on the interest of researches on phenoxyquinone derivatives,<sup>55</sup> the authors also designed a phenoxyquinone-embedded PDMS membrane to recognize the vapour of primary aliphatic amines (R-NH<sub>2</sub>).<sup>85</sup> The UV irradiation induced *ana*- configured phenoxyquinone could react with R-NH<sub>2</sub>, with colour changing from yellow to pale purple. This membrane could realize the colorimetric detection of R-NH<sub>2</sub>, since secondary and tertiary amines showed no obvious effects on the composite.

Klajn and co-workers designed a photoresponsive porous aromatic network (PhotoPAN) by introducing SP to construct the nanoporous materials.<sup>86</sup> As shown in Fig. 4b, the solid-state PhotoPAN was in a MC state (deep blue) because the desolvation process resulted in the contraction of the network, bringing the SP moieties in close proximity and thus stabilizing the MC form. The PhotoPAN could absorb HCl gas, leading to colour change from deep blue to bright yellow, corresponding to the formation of protonated MCH. Then treatment of NH<sub>3</sub> gas reversed the colour change, indicating the conversion of MCH to MC. The process could be repeated many times, suggesting the use of PhotoPAN to perform gaseous HCl/NH<sub>3</sub> monitoring.



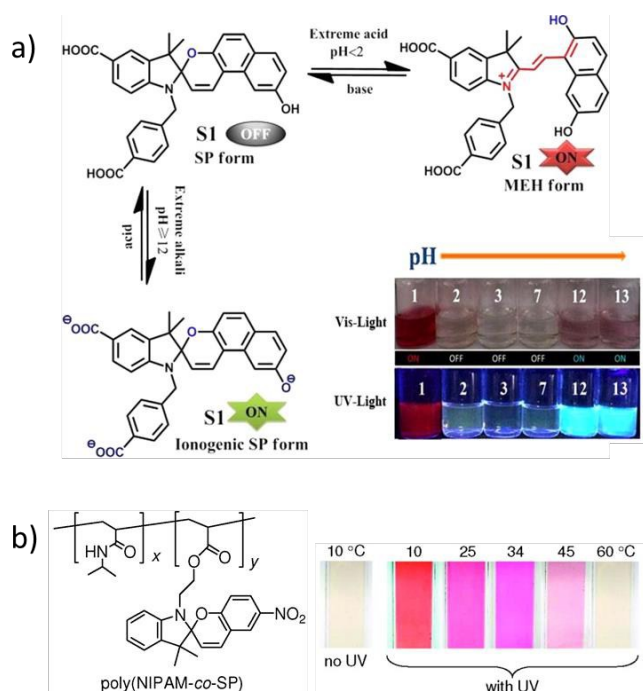
**Fig. 4** (a) Responses of SP-PDMS membrane to gaseous HCl and subsequent photo- and heat-treatments. Reproduced by permission of The Royal Society of Chemistry.<sup>84</sup> (b) Monitoring of PhotoPAN to gaseous HCl and NH<sub>3</sub>. Reproduced by permission of Macmillan Publishers Limited.<sup>86</sup>

## 2.5 Photochromic sensors for pH and temperature

As mentioned above, the isomerization of photochromic materials is influenced by the environment, thus they can be used in the monitoring of external stimulations. Specially, SPs are a class of multi-responsive compounds; they are sensitive to pH and temperature.<sup>87, 88</sup> Based on SPs, photochromic sensors for pH and temperature can be designed.

Yin and co-workers synthesized an “on-off-on” switchable SP (S1) for pH sensing (Fig. 5a).<sup>89</sup> S1 was colorless and non-fluorescent in the pH range of 3.0–11.0, exhibiting a “turn-off” state. Under extreme pH conditions, S1 “turned on”, displaying fluorescent red color in extreme acid range (pH < 2.0) and blue green in extreme alkaline range (pH ≥ 12.0). The bulky benzoic acid attached to the indole N and electron-withdrawing carboxyl to the indole 6-position stabilized the ring-closed SP form of S1, thus the ring-opening process occurred only in extreme acid range. On the other hand, in extreme alkaline range, the ionogens (benzoic acid, carboxylic acid and hydroxyl) ionized, resulting in another “turn-on” state. Utilizing the pH-dependant fluorescence, bacterial cells imaging under extreme pH conditions could be realized. Also based on the pH induced interconversion of SP among protonated ring-opening MCH, ring-opening MC, ring-closed SP forms, Tian and co-workers demonstrated a bis-SP functionalized peptide for pH monitoring and subsequent lysosomal imaging.<sup>90</sup> Below pH 2, the peptide showed a sharp absorption band at 410 nm and relatively weak fluorescence at 623 nm, corresponding to the MCH state; increase of pH induced absorption red shift to 514 nm and higher fluorescence intensity at 623 nm, characterized as MC form; when pH ≥ 10, absorption and fluorescence could not be observed, suggesting the dominance of SP state. Acid lysosomes of live cells could be stained by the peptide, with red luminescence.

The ring-closed SP has a lower ground state energy comparative to the MC form, therefore the MC form can thermally revert to the more stable SP form.<sup>91</sup> Based on this thermally-dependant transformation, SP temperature indicator can be obtained. Shiraishi and co-workers designed a copolymer, poly(NIPAM-co-SP), to realize colorimetric thermometer.<sup>92</sup> As shown in Fig. 5b, the copolymer consisted of poly-*N*-isopropylacrylamide (NIPAM) and SP units. Without UV irradiation, the solution of poly(NIPAM-co-SP) exhibited no absorption at > 450 nm. UV treatment resulted in a ring-opening isomerization, showing absorption  $\lambda_{\max}$  at 519 nm when the temperature was 10 °C. Increase of temperature led to a red shift of  $\lambda_{\max}$ , and the color changed from orange (10 °C) to pink and then to purple (34 °C,  $\lambda_{\max}$  = 546 nm). The bathochromic shift was corresponded to the quinoidal form of MC, which was induced by the coil-to-globule phase transition of polyNIPAM. With increasing temperature, the polymer aggregated and formed a less polar domain, leading to conversion of MC from zwitterionic to quinoidal form. When temperature was higher than 34 °C, the color faded due to the thermal reversion of MC to SP. Thus the poly(NIPAM-co-SP) could be used as temperature indicator at a range of 10–34 °C.



**Fig. 5** (a) Switchable S1 for pH sensing. Extreme acid and alkaline induce turn-on fluorescence. Reproduced by permission of American Chemical Society.<sup>89</sup> (b) Temperature colorimetric sensing by poly(NIPAM-co-SP). Reproduced by permission of American Chemical Society.<sup>92</sup>

### 3 Photochromic sensors for multi-analyte discrimination

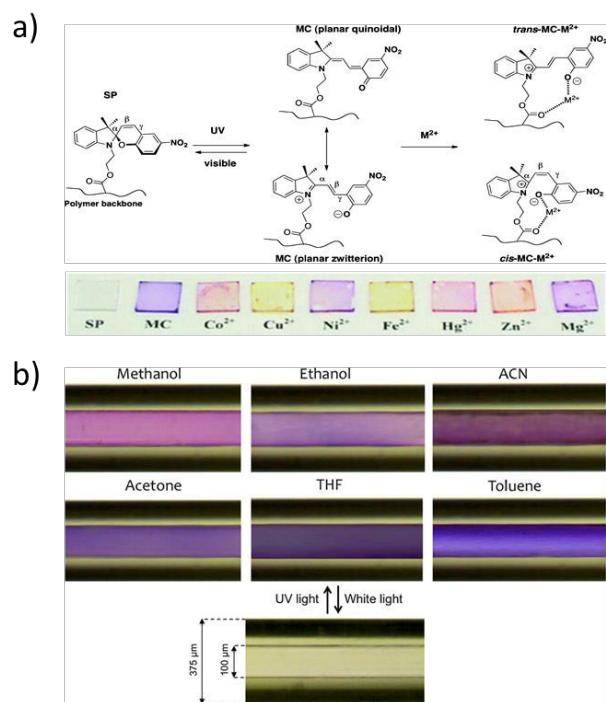
Multi-analyte sensing has been developed rapidly in recent years. In contrast to specific targeting, multi-analyte sensing aims to perform discrimination among multiple structures- or properties-similar analytes, with detectable and differential signal outputs. Inspired by the olfactory system of human beings, conceptually chemical nose was created to realize multi-analyte sensing.<sup>93</sup> The chemical nose consists of sensor arrays, in which a series of responsive and non-specific sensing molecules are invested. Via comprehensive analysis of the multiple sensing signals, discrimination among analytes can be conducted with kinds of analysis methods, including principle component analysis (PCA), linear discriminant analysis (LDA), hierarchical clustering analysis (HCA), *etc.*<sup>94</sup>

Usually, the arrays need numbers of compounds as sensors, which involves complicated chemical synthesis or low-efficient high-throughput screening.<sup>95</sup> A key point to the research of sensor arrays is to reduce the sensing molecules and minimize the arrays. Attributed to the isomerization and consequently multiple signal outputs, a single photochromic material has the potential to serve as several sensors when external stimulations change. Therefore, reduced sensor arrays can be achieved.

SPs have shown an excellent example as efficient sensors for multi-analyte discrimination. Locklin and co-workers designed a copolymer poly(MMA<sub>90</sub>-co-SPMA<sub>10</sub>) consisting of 10

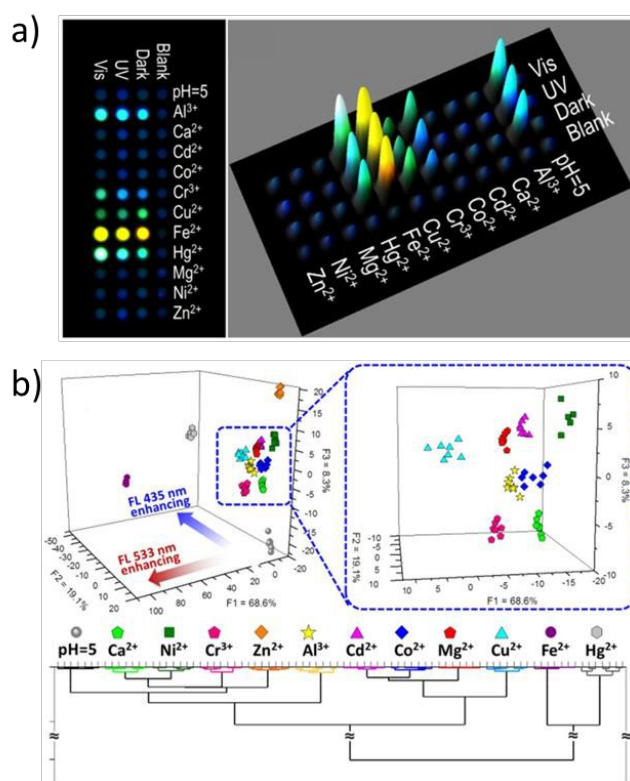
mol% spiropyran methacrylate derivative (SPMA) and 90 mol% methyl methacrylate (MMA), to investigate its responses to divalent metal ions.<sup>96,97</sup> As shown in Fig. 6a, the SPMA unit exhibited a quinoidal or a zwitterionic MC state with UV irradiation.<sup>98</sup> Upon complexation with metal ions ( $M^{2+}$ ), *trans*-MC- $M^{2+}$  or *cis*-MC- $M^{2+}$  formed, depending on the species of metal ions. Metal ions such as  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  complexation led to blue shift of absorbance maxima, suggesting *trans*-MC- $M^{2+}$  forms;  $Fe^{2+}$  and  $Cu^{2+}$  complexation resulted in two absorption peaks, which was due to the formation of *cis*-MC- $M^{2+}$ . Each metal ion gave a distinct color to the MC state poly(MMA<sub>90</sub>-co-SPMA<sub>10</sub>) film, thus providing recognition of the 7 divalent metal ions by naked-eyes. Quantitative analysis could be carried out in the concentration range of 1  $\mu$ M to 100 mM. Furthermore, by comparison of binding affinities between SPMA and various metal ions, the authors realized identification of mixtures that contained different concentrations of metal ions.<sup>99</sup> Based on the solvatochromism of SP, Benito-Lopez and co-workers designed fused silica microcapillaries in which the inner walls were functionalized with SP polymeric brushes, to identify multiple solvents with different polarities.<sup>100</sup> With UV irradiation, the SP monomer displayed different colors and absorption spectra in various solvents; increase of polarity induced blue shift of the absorption and color change from blue to red. The solvent-dependant color of SP monomer enabled the detecting capability of the SP polymeric brushes coated capillaries. As shown in Fig. 6b, when the solvents were passed through the capillaries under UV irradiation, hypsochromic shift of colors were observed from highly polar solvents (like methanol) to highly nonpolar solvents (like toluene). White light irradiation recovered the colorless SP polymer coating, providing the potential for fabrication of reusable miniaturized sensing platforms.





**Fig. 6** (a) Photoisomerization of poly(MMA<sub>90</sub>-co-SPMA<sub>10</sub>) and complexation with divalent metal ions. Reproduced by permission of American Chemical Society.<sup>98</sup> The bottom displays photographs of poly(MMA<sub>90</sub>-co-SPMA<sub>10</sub>) films in the presence of different metal ions. Reproduced by permission of The Royal Society of Chemistry.<sup>96</sup> (b) Responses of SP polymeric brushes coated capillaries to different polarized solutions passing through. Reproduced by permission of American Chemical Society.<sup>100</sup>

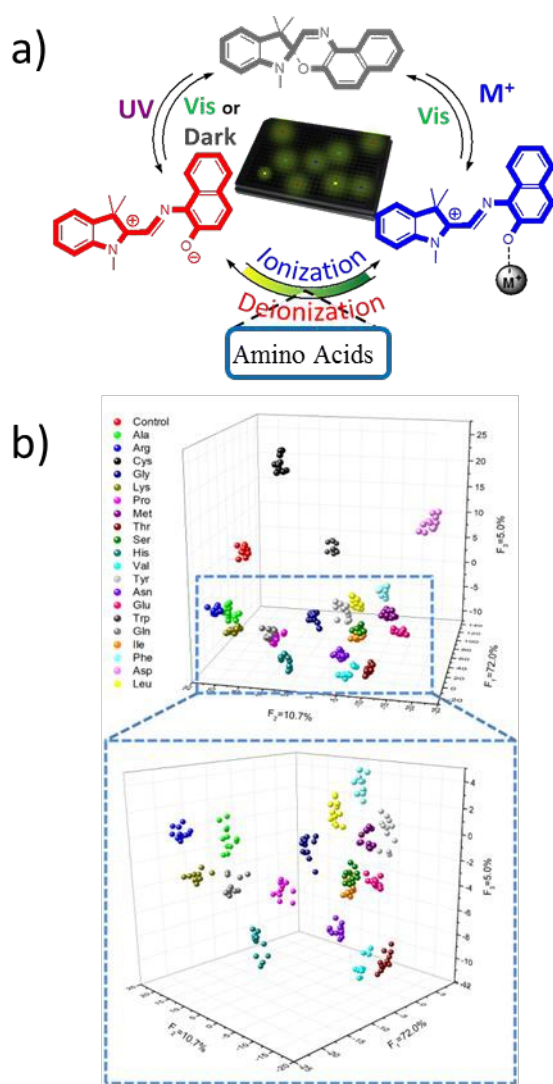
Based on the interest of our group on the exploration of minimized sensor array,<sup>20</sup> we designed a photochromic sensor microchip for multiple metal ions detection with only one sensing compound.<sup>101</sup> Via simply pipetting small amounts of metal ions into the solution of a commercial SP molecule, followed by gathering and analyzing of the fluorescent signals under dark, UV and visible light conditions, we successfully detected 11 metal ions at one time. The sensor microchip is shown in Fig. 7a. The complexations and binding affinities between SP and various metal ions were different, which fundamentally enabled the sensing ability of SP. As SP underwent interconversion among different states with changed light stimulations, the complexation with metal ions varied as well, leading to different fluorescent signals. The multiple signals showed more chemical sensing information, which contributed to the detection. The results of multi-detection were performed by LDA, which was used to evaluate similarities between different groups. As shown in Fig. 7b, 11 metal ions and 1 blank control sample were clearly discriminated (7 trials for each), with 100% correct classification. In the 3D graph of LDA results, clusters of metal ions arranged according to the responsive fluorescence at 435 nm and 533 nm, corresponding to the results of HCA which was used to investigate the resemblances among the analytes.



**Fig. 7** (a) Fluorescent responses of photochromic SP microchip to multiple metal ions. (b) LDA score plots (upper) and HCA graph (bottom) of photochromic SP microchip response to 11 metal ions and 1 blank control sample. Reproduced by permission of Macmillan Publishers Limited.<sup>101</sup>

Based on the successful detection of multiple metal ions, we applied the sensor microchip to real-world samples. 16 kinds of natural mineral water from various countries were detected, showing 100% correct classification as well.

In consideration of the important roles that amino acids play in human beings, we designed a photochromic SP-metallic sensor chip for identification of 20 natural amino acids.<sup>102</sup> Using the commercial SP molecule combined with several metal ions, we simply realized the recognition of the 20 highly similar analytes. As shown in Fig. 8a, the sensor chip processed transformation among different states under dark, UV and visible light conditions, respectively. Different fluorescent emissions of the isomers suggested the potential of the sensor chip for convenient multi-detection. Amino acids could bind to the SP-metallic complexes, consequently perturbed the balance of the multi-state. As the 20 natural amino acids had different binding affinities to the SP-metallic complexes, the balance perturbations varied for each amino acid, thus resulting in different fluorescent signals. 10 SP-metallic complexes were utilized to constitute the sensor chip. Each amino acid owned distinct fluorescent fingerprint pattern to the 10 SP-metallic complexes; the sensor chip displayed different fluorescent emissions under dark, UV and visible light conditions. By gathering and comprehensive analysis of the



**Fig. 8** (a) Scheme of 20 natural amino acids identification by photochromic sensor chip composed of TNSP-metallic complexes. (b) LDA score plots of photochromic sensor chip response to 20 natural amino acids and 1 control sample. Reproduced by permission of American Chemical Society.<sup>102</sup>

fluorescent fingerprint patterns, we achieved the identification of the 20 natural amino acids. As shown in Fig. 8b, clusters of the 20 amino acids and 1 control sample were clearly separated, with 100% correct classification. Furthermore, the sensor chip could realize recognition of amino acid mixtures, as well as identification in complicated environments such as human serum.

## Conclusions

In this article, we introduced the photochromic materials and summarized the applications of photochromic sensors in the areas of specific recognition for metal ions, anions, biomolecules, gas and vapour, pH and temperature. Specially, photochromic sensors applied in multi-analyte discrimination were emphasized. Currently, chemical sensing and analysis of

photochromic sensors are focused on complex analyte testing, high-throughput multi-analyte recognition and vivo biosensing. Different from other chemical sensors, photochromic sensors can offer various molecular configurations or molecular states with abundant optical information, contributing dynamic and multi-state analysis methods. The most commonly used photochromic sensors are DTEs and SPs. DTEs can perform the optically manipulated DNA or protein stain, or metallic chelation with coordination group modification. The lock/unlock manner provides a unique strategy for analyte detection. SPs possess inherent binding sites (indolic N and phenolate O), which can be served as recognition as well as modification units. Their multi-stimulation responses, obvious colorimetric and fluorometric signal outputs endow the applications in a large area of sensing. Via rational design of photochromic sensors with various ionophores, dyes, platforms and metallic complexations, it is promising to achieve visual, sensitive and high-throughput detection. Since chemical sensing is required to process against interferent components, it is still a great challenge to design non-interferential but cross-reactive photochromic sensors. Meanwhile, the limit of detection remains to be improved. For multi-analyte discrimination, the multiple states of photochromic sensors make it challenging to conduct precise quantitative determination. The key to promote the quantitative detection is to control the ratio among different states and investigate the reliable sensing information for each state, thus calling for vast simulation researches with experimental verification. Further design of photochromic sensors will be continued to focus on novel photochromic molecules and composite materials, which contributes to improving high performance detection and multi-analyte discrimination, as well as practical recognition.

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