

Supramolecular aggregation/disaggregation-based molecular sensing: a review focused on investigations from China

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ABSTRACT: Supramolecular aggregation and disaggregation induced by external stimuli can impact the optical or electrical signals of the aggregates/constituting units (receptors). Therefore, manipulating supramolecular aggregation/disaggregation has recently been employed to construct novel and promising photoluminescence (PL)-based sensing and recognition systems. The sensing systems were capable of substantially enhancing the sensitivity, relying on cooperative interactions occurring in the assembly/disassembly processes (mostly operating in emission turned-on or emission-enhanced mode). This review focuses mainly on recent advances in the new emerging PL-based sensing platforms, based on manipulating the behaviours of supramolecular aggregation/disaggregation, including aggregation-induced emission (AIE), metallophilic interactions-related sensing (metallophilic interactions-induced aggregation/disaggregation), metal coordination polymers-related sensing, and other sensing systems involving supramolecular aggregation/disaggregation. In particular, those sensing systems developed by scientists in China are summarized and highlighted. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: supramolecular aggregation/disaggregation; sensing; aggregation-induced emission; metallophilicity; metal coordination polymers

Introduction

Supramolecular aggregation and disaggregation, constitute one class of important phenomena occurring in nature, and are mainly driven by various weak non-covalent interactions, such as van der Waals', π - π stacking, hydrogen bonding, metal coordination, electrostatic and even metallophilic interactions. The supramolecular behaviours are of significance for maintaining or weakening the biological functions in living organisms. For example, the aggregation and disaggregation of erythrocytes is believed to be related to the pathological states of human body (1); the aggregation of certain proteins is associated with amyloid diseases, including Alzheimer's and Parkinson's disease (2). With regard to supramolecular chemistry, external stimuli inducing small receptor molecules to assemble or inducing aggregates to disassemble can generally produce an impact on optical or electrical signals of the aggregates/constituting units (receptors) by means of specific interactions, including coordination and hydrogen-bonding interactions. In particular, the behaviour of ordered supramolecular aggregation and disaggregation involves cooperative interaction(s) in some cases. Therefore, manipulating the behaviour of supramolecular aggregation/disaggregation is expected to open a great opportunity to employ observable changes of optical or electrical signals, especially changes of photoluminescence (PL) signals due to their outstanding sensitivity, to signal the targets (or interacting events). With this idea in mind, by employing PL spectral changes resulting from the behaviour of supramolecular aggregation/disaggregation, a series of novel sensing and recognition systems operating by various mechanisms for important target molecules/ions,

including metal ions, proteins, DNA, sugar and even anions, have recently been developed and have received considerably interest. It should be pointed out that these reported supramolecular aggregation/disaggregation-based sensing systems can be classified in several categories, including aggregation-induced emission (AIE), metallophilic interactions-related sensing (metallophilic interactions-induced aggregation/disaggregation), metal coordination polymers-related sensing, and other sensing systems involving supramolecular aggregation/disaggregation, according to sensing mechanisms and/or sensing modes. Particularly, PL-based sensing, mainly relying on cooperative interactions occurring in the assembly processes (two or even several weak non-covalent interactions), was suggested to achieve signal amplification to

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afford excellent signaling sensitivity. Although some of the aggregation- and disaggregation-related sensing mechanisms are still not fully understood these sensing systems can provide us with some important guidelines for constructing new PL-based sensing/recognition platforms, in order to achieve high sensitivity and selectivity capable of meeting the requirements of analytical chemistry.

In this review, we summarize these new emerging PL-based sensing and recognition platforms based on manipulation the behaviours of supramolecular aggregation/disaggregation to generate observable reporting signals, particularly those that have been developed by scientists in China. We offer a general view of the categories of these sensing platforms and afford new insights into the design of these receptor molecules. The current trends in this rapidly growing area are also discussed.

Aggregation-induced emission (AIE)

It is well known that light emission is quenched if the aggregation of traditional organic luminophores occurs. The aggregation-caused quenching (ACQ) effect is usually unfavourable for practical applications, including chemosensors. However, aggregation-induced emission (AIE), primarily observed by Tang's group in 2001 from a solution of 1-methyl-1,2,3,4,5-pentaphenylsilole (**3**), is an abnormal photoluminescence phenomenon, compared to the notorious ACQ effect of traditional organic luminophores. Since then, a cascade of AIE phenomena has been observed, mainly in silole and tetraphenylethylene (TPE) derivatives. On the basis of a series of experimental investigations and theoretical calculations, Tang's group believed that the unique AIE effect is mainly caused by the restriction of the intramolecular rotation in the aggregates (3–6). The intramolecular rotation of AIE-active molecules is considered to be capable of promoting the excited state's non-radiative decay, resulting in these AIE-active molecules being non-emissive. The occurrence of aggregation of AIE-active molecules can cause intramolecular rotation to be restricted and light emission is thus turned on or enhanced substantially. Inspired by the intriguing light emission phenomenon, the AIE effect has been widely exploited to fabricate various functional materials, in particular to create bio-/chemosensors, expected to greatly broaden the application scope of organic luminophores (7–27). In principle, the aggregation of AIE-active molecules can be induced by introducing guest molecules/ions to bind with the AIE-active molecules via various weak non-covalent interactions, such as electrostatic, coordination and hydrophobic interactions, and even some specific interactions, which can afford a promising entry to constructing powerful new sensing platforms expected to substantially enhance the sensitivity to overcome the limitations of traditional organic luminophores (see the following reviews 4,6,28,29). In this section we focus on recent advances of molecules/ions sensing, based on the AIE effect, particularly as developed by scientists in China. The sensing systems were chosen and classified according to the sensing species.

Neutral biomolecules

In order to develop promising and sensitive systems for sensing D-glucose (D-Glu) with high selectivity and a favourable 'turn on' PL-based sensing mode operating in the AIE mechanism, AIE-active receptor **1** (Fig. 1) (TPE derivative containing two boronic acid units) was designed and synthesized (7). It was expected

that **1** could become highly emissive if D-Glu interacts with **1** to form aggregates via the well-known reaction mechanism between phenylboronic acid (PBA) with diols. Detailed spectral experiments revealed that, when small amount of Glu (< 0.2 mmol/L) was added to the carbonate buffer solution containing **1** (pH 10.5), changes in emission spectra of **1** were hardly observed; when the concentration of Glu was increased to 0.2 mmol/L, however, the emission was found to be substantially enhanced with increasing [Glu]; intriguingly, the emission strength of **1** was observed to be hardly enhanced even when large amounts (10 mmol/L) of D-fructose (Fru), D-galactose (Gal) and D-mannose (Man) were respectively added. An assumed working principle for the specific emission response of **1** towards Glu was proposed by the authors: at high pH (10.5), **1** can be transformed to non-emissive **1**-(OH)₂, likely assigned to the enhancement of dissolution resulting from electrostatic repulsive interactions due to the two boronate groups with the same negative charges in **1**; when [Glu] is relatively low (< 0.2 mmol/L), the binding of **1** with Glu occurs to form a 1:1 mono-adduct, i.e. **1**-Glu. The intramolecular rotations of the resulting **1**-Glu adduct are maintained, also leading to the absence of emission; when [Glu] is relatively high (0.2 mmol/L), the bisadduct **1**-Glu₂ could be formed. The intramolecular rotations of the aromatic rings in **1**-Glu₂ are hindered compared to that of free **1** or **1**-Glu, thus leading to **1**-Glu₂ being somewhat emissive. However, if much higher [Glu] is employed, one Glu molecule will interact with two boronic acid groups in **1**, which can cause the occurrence of the polymerization reaction of the two *cis*-diol units in Glu with the boronic acid groups in **1** to create polymerized (**1**-Glu)_n. This polymerization reaction could result in the greatly suppressed intramolecular rotation of the oligomer, thereby turning on the emission of **1**.

Anions

Cationic **2** of silole derivative (Fig. 2) bearing a positively charged ammonium moiety was designed and synthesized to afford a novel sensing platform based on the AIE effect for cyanide, one of the most toxic ions (anions), by means of its binding to hydrophobic **3** (Fig. 2) (8). The working principle was an intermolecular assembly mode. Hydrophobic **3** can be transformed into an amphiphilic species via the nucleophilic addition reaction of cyanide to the trifluoroacetyl amino group in **3**, leading to the aggregation of **3** combined with amphiphilic species **2**, thanks to both hydrophobic and electrostatic attraction, to form an ensemble in aqueous solution, facilitating the occurrence of the AIE effect. As a result, upon addition of cyanide, the original weak emission of the ensemble system of **2** and **3** was found to be enhanced and to be linearly related to the concentration of added cyanide, thereby affording a promising method for sensing cyanide with high selectivity and sensitivity.

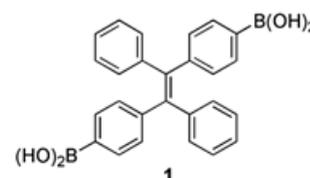


Figure 1. Molecular structure of **1** (7).

Also, cationic silole **2** has been successfully applied to signal the presence of adenosine triphosphate (ATP), a linear polyanion containing four negative charges, with high selectivity (9). In principle, cationic silole **2** can attach on the ATP template via electrostatic attractive interactions, resulting in the aggregation of the silole groups and thereby activating the AIE effect of **2**. This sensing platform can be further developed to continuously and monitor the ATP hydrolysis process *in situ*, because the hydrolysis products (ADP, AMP and adenosine) do not interfere with sensing of ATP. PL-based sensing of other polyanions, such as heparin, have also been achieved by employing this AIE-active receptor molecule (10).

Biomacromolecules (charged biomolecules)

The silole **2** has also been employed to develop a new optical probe for the detection of DNA and for label-free fluorescence nuclease assay with a fluorescence turn-on mode, based on the similar AIE mechanism (11).

Grafting glucosamine moieties to TPE, **4** (Fig. 3) creates a cationic AIE-active molecule of TPE derivative that forms an ensemble by combining with amphiphilic monododecylphosphate operating in both electrostatic attractive and hydrophobic interactions, when the concentration of monododecylphosphate is somewhat lower than its critical micelle concentration (12). The ensemble was found to be highly emissive, due to the AIE effect. Upon the addition of alkaline phosphatase, the emission of the ensemble was found to be significantly weakened, due to the disassembly resulting from the absence of phosphate groups caused by the enzyme-induced cleavage reaction. The substantial PL changes were thus expected to be capable of signalling the presence of alkaline phosphatase.

Anionic disulphonated **5** of the TPE derivative (Fig. 4) was synthesized to demonstrate that **5** could work as an excellent protein probe with high sensitivity and selectivity via binding of anionic **5** to protein molecules, such as bovine serum albumin, in which light emission was turned on due to the restriction of

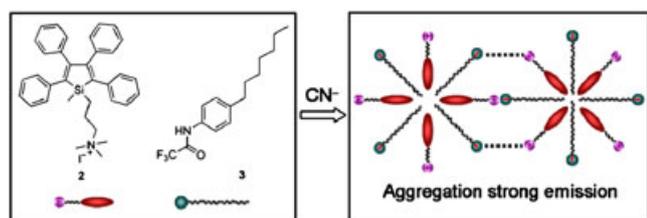


Figure 2. Molecular structures of **2** and **3** (8), and illustration of the design rationale for the emission turn-on detection of cyanide by making use of the AIE feature of silole compounds.

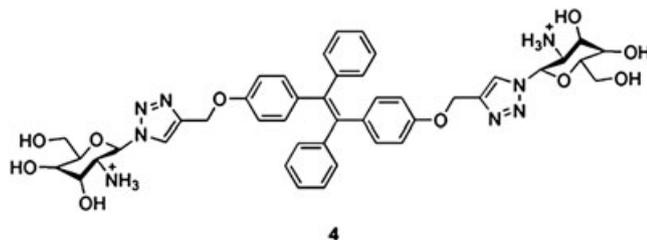


Figure 3. Molecular structure of **4** (12).

intramolecular rotation induced by the formation of aggregates (13). This AIE-active molecule has also been employed to signal human serum albumin and to monitor its conformational transitions, revealing a multistep transition with the involvement of globule intermediates (14).

By combining with cationic myristoylcholine, an amphiphilic compound acting as a substrate of acetylcholinesterase (AChE), anionic **5** can be employed to construct an ensemble for sensing AChE and screening its inhibitors by means of the aggregation-induced emission originating from TPE (15). If the concentration of myristoylcholine is lower than its critical micelle concentration, cationic myristoylcholine could form premicellar aggregations or heteroaggregations combining with negatively charged **5** because of both the electrostatic attractive and hydrophobic interactions, leading to weakly emissive **5** becoming highly emissive. Upon addition of AChE, myristoylcholine can easily be hydrolysed to generate anionic myristic acid and cationic choline, which would cause the disassembly of the ensemble of **5** and myristoylcholine, owing to the electrostatic repulsion interactions. As a result, the emission intensity of the ensemble would be decreased, indicating the presence of AChE and also the AChE inhibitors.

Other molecules/ions

Attaching isopropyl (iPr) groups to the phenyl rings of hexaphenylsilole (HPS), the intramolecular rotation process of HPS would be internally hindered (16). Therefore, a series of silole regioisomers, **6_{x,y}** (Fig. 5), were synthesized to test whether the photoluminescence could be varied with its regiostructures. It was found that the steric effect of the bulky iPr groups enabled the dynamics of the singlet excited states of the HPS derivatives to be suppressed, and **6_{3,4}**, with a high intramolecular rotations barrier, accordingly became highly emissive in solution. Experiments further revealed that **6_{3,4}** was a sensitive chemosensor capable of optically discriminating nitroaromatic regioisomers of *p*-, *o*-, and *m*-nitroanilines.

Hexaphenylsilole (HPS) **7** (Fig. 6) was found to be non-emissive in diluted solution but to be highly emissive in its aggregates, due to the AIE effect caused by the restriction of the intramolecular rotation (17). By combining **7** with dipropylamine

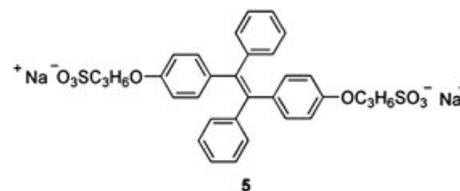


Figure 4. Molecular structure of **5** (13).

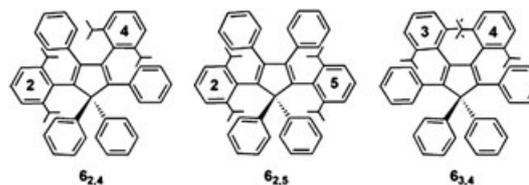


Figure 5. Molecular structure of **6_{x,y}** (16).

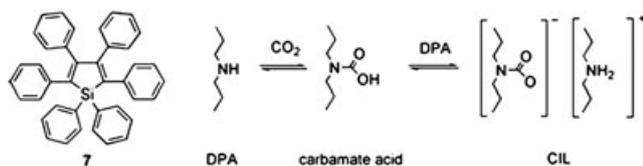


Figure 6. Molecular structure of **7** and the formation of carbamate ionic liquid by reaction of CO₂ gas with dipropylamine (17).

(DPA), a novel sensing strategy for quantifying CO₂ has been developed, based on the AIE effect. The sensing mechanism relied on the finding that the polarity and viscosity of **7** solution could be greatly enhanced because of forming carbamate ionic liquid (CIL), achieved easily by means of bubbling CO₂ gas through DPA, which turned on the light emission of HPS. This was because the HPS molecule could be clustered, and thus the intramolecular rotation process was inactivated. Therefore, the presence of CO₂ could be detected and quantified over the concentration range 0–100% using this PL-based sensing platform. Other gas-sensing chemodosimeters based on AIE-active molecules have also been developed (18).

Besides the silole and TPE derivatives, other AIE-active molecules were also successfully employed to construct novel PL-based sensing platforms (19–27). For example, Tong's group has found that a series of salicylaldehyde azine (SA) derivatives linked by N–N single bonds could demonstrate an aggregation-induced enhanced emission (AIEE) effect. These SAs have also been used to signal biomolecules, such as cationic protamine protein, and small molecules, including hydrazine, with good sensitivity and selectivity (19).

Metallophilic interactions-related sensing

Numerous experiments have observed that attractive metallophilic interactions, mainly referred to d¹⁰...d¹⁰ and d⁸...d⁸ interactions, as a new class of weak non-covalent interactions, will occur if the distance of between two identical metal ions with the same charge is shorter than the sum of the van der Waals' radii of the corresponding metal ions. This is an abnormal phenomenon compared to the traditional view involving the repulsive interactions between two cations that are the same. The metal-to-metal distances, therefore, are considered to be able to provide an indicator for these attractive interactions. It should be pointed out that, in particular, aurophilic interactions have attracted extensive and increasing attention, compared to its counterparts; for example, the attractive interactions have been effectively employed in numerous fields, including crystal engineering (30–33), supramolecular chemistry (34), nanostructures (35–38), molecular devices (39–42) and metal ion sensing (43). This is because gold exhibits a maximum relativistic effect among all other local neighbours in the elemental periodic table, which also leads to the attractive aurophilic interactions having an order-of-magnitude strength similar to that of hydrogen bonding, thus accelerating the development of the chemistry of gold over the past two decades (44,45). The attractive aurophilic interactions can lead to a strong tendency for the Au(I) complexes to associate into dimers, oligomers or even uni- and multidimensional polymers. The Au(I)...Au(I) interactions are thought to arise from the stabilization of the filled 5d-orbital-based molecular orbital with the empty molecular orbitals of appropriate symmetry

derived from the 6s and 6p orbitals by configuration mixing (46–48). In view of the unique photochemical and photophysical properties (49), the metallophilic interactions-related complexes have also been employed to develop novel PL-based sensing/recognition platforms for various analytes in recent years, by means of manipulating the attractive interactions to achieve 'on' or 'off' states of metallophilicity, resulting in the occurrence of the 'aggregation/disaggregation' of the d¹⁰ or d⁸ complexes. It should be pointed out that the mechanisms of metallophilic interactions-related PL are still not fully understood at present. In this section, we focus on the recently related advances on the sensing/recognition systems based on manipulating the metallophilic interactions (referring to d¹⁰ and d⁸ systems), developed by scientists in China. All highlighted examples are classified into two categories, according to the elemental group of metal ions.

d¹⁰...d¹⁰ interactions systems

A pioneering work for the PL-based sensing systems based on modulating the aurophilic interactions reported by Yam's group is that the addition of K⁺ could induce the occurrence of the Au(I)...Au(I) interactions in Au(I) complexes **8** and **9** bearing two benzo(15)crown-5 moieties (Fig. 7) (39). In the absence of K⁺, the two benzo(15)crown-5 moieties of **8** are in the floppy state in solution; however, the addition of K⁺ is suggested to coordinate with the benzo(15)crown-5 moieties of **8** to sandwich between the two crown rings according to induced absorption spectral changes, thereby bringing the two Au(I) centres into close proximity to facilitate the occurrence of Au(I)...Au(I) interactions. The aurophilic interactions could promote the 'aggregation' state of **8**, leading to the appearance of a long-lived, low-energy emission band at 720 nm. The newly emerging emission was considered to originate from ligand-to-metal charge-transfer transition, mixed with the metal-centred state that is modified by metallophilic interactions (LMMCT), accompanied by a decrease in luminescence intensity at 502 nm assigned to ligand-to-metal charge-transfer transitions mixed without metallophilic interactions (LMCT), with a clear isoemissive point located at 600 nm. A reversal of the emission trend could also be observed upon successive addition of free benzo(15)crown-5 to the mixture of **8** and K⁺, since that the sandwiched K⁺ could be extracted from **8** by free benzo(15)crown-5, leading to weakening of or even the disappearance of aurophilic interactions. Addition of Na⁺ to **8** did not give rise to the growth of a new emission band at 720 nm, despite the well-known high affinity

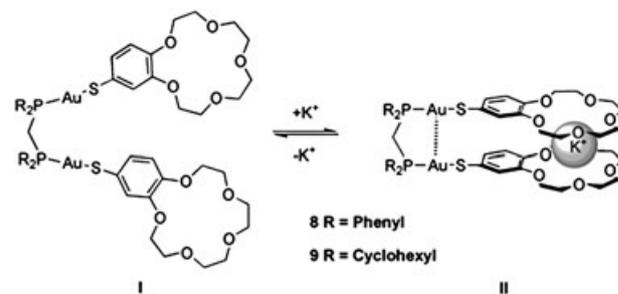


Figure 7. Molecular structures of **8** and **9**, and proposed floppy and sandwich-binding modes of **8** and **9** in the absence (I) and presence (II) of potassium ion, respectively (39).

of benzo(15)crown-5 for Na^+ , indicative of the importance of a sandwiched structure formed from K^+ and **8**. Similar spectral behaviours could be observed in the case of **9**. This work is believed to demonstrate a new concept of utilization of the on/off switching of the $\text{Au(I)} \dots \text{Au(I)}$ interactions for sensing molecules/ions.

To extend this sensing concept, Yam's group has subsequently developed a series of luminescent Au(I) complexes containing crown ether pendants of different ring sizes to show that the $\text{Au(I)} \dots \text{Au(I)}$ interactions can be on/off switched upon the binding of specific metal ions to form a sandwich-binding mode, with the capacity of sensing metal ions (40–42). Recently, a tripodal alkynylgold(I) complex **10** bearing three oligoether pendants (Fig. 8) has also been designed and synthesized to serve as a selective luminescent probe for Mg^{2+} , based on the similar switch on of the $\text{Au(I)} \dots \text{Au(I)}$ interactions (50). Encapsulating Mg^{2+} in among the three intramolecular oligoether pendant units of **10**, the rigid and linear arylalkynylgold(I) units with a given floppy nature could be forced into close proximity, leading to turning on of the $\text{Au(I)} \dots \text{Au(I)}$ interactions, evidenced by the appearance of the low-energy emission band at 675 nm. Other alkaline earth and alkaline metal ions were found to hardly induce changes of the absorption spectra of **10**, indicative of high sensing selectivity towards Mg^{2+} . These investigations opened up a promising entry for developing new PL-based sensing platforms for molecules/ions via sophisticatedly manipulating metallophilic interactions.

Although the strength of the $\text{Ag(I)} \dots \text{Ag(I)}$ interactions is in general considered to be less than that of the $\text{Au(I)} \dots \text{Au(I)}$ interactions, manipulating the $\text{Ag(I)} \dots \text{Ag(I)}$ interactions have recently been employed to construct novel sensing systems for metal ions and biomolecules (51,52). It was found that when Ag(I) was mixed with cysteine (Cys) in aqueous solution, Ag(I) –Cys coordination polymers could be immediately generated *in situ*, which was facilitated by both the $\text{Ag(I)} \dots \text{Ag(I)}$ and electrostatic attractive interactions among the side-chains along the polymeric backbone (Fig. 9) (51). The coordination polymers formed could be featured by argentophilicity-related absorption and

circular dichroism (CD) spectra, with practically no spectral background because both Ag(I) and Cys are spectrally transparent in these spectral windows. Therefore, the ensemble was expected to afford high sensitivity and selectivity for sensing Cys by employing the absorption and CD spectra, in particular featured by the Cys enantiomeric discrimination capacity. It should be pointed out that the electrostatic interactions (electrostatic attractive or electrostatic repulsion) among the side-chains along the polymeric backbone were of crucial importance for enhancing or weakening the argentophilicity in the Ag(I) –Cys or Ag(I) –GSH cases. Indeed, experiments showed that, at the low pH of 5.0, hardly any absorption or CD signals were observed from Ag(I) –GSH, whereas appreciable optical signals were found in Ag(I) –Cys solution, which can be attributed to the differed isoelectric points of GSH and Cys. The Ag(I) –GSH or Ag(I) –Cys coordination polymers, however, are weakly luminescent or even non-luminescent. Therefore, it can be envisioned that replacing the electrostatic interactions among the side-chains of Ag(I) –SR polymers via introducing π – π stacking interactions by including an aromatic fluorophore into the RSH ligand, the formed coordination polymers might also be luminescent. It will be useful if the emission of these ensembles can also be manipulated by introduced π – π stacking interactions. To succeed in this regard, a novel –SH-containing receptor **11** (Fig. 10), NCys, was designed, in which the amine group in the Cys moiety was derivatized with 2-(1-naphthyl)-acetamide (52). The aromatic fluorophore is expected to afford the π – π stacking interactions when the Ag(I) –NCys coordination polymers are formed in aqueous solution, making the polymers luminescent. Therefore, a ratiometric luminescent sensing ensemble for Ag^+ ions in aqueous solution was successfully established, evidenced by the fact that, upon addition of Ag^+ , the strong emission at 337 nm of NCys in the aqueous buffer solution originating from its naphthyl moiety was substantially quenched, while a new emission appeared and developed at 441 nm, together with an isoemissive point at 399 nm considered to originate from the LMMCT state. Such coordination polymers have also been used to construct supramolecular hydrogels facilitated by cooperative interactions of

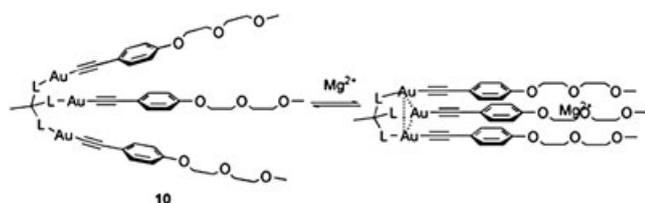


Figure 8. Molecular structure of **10** and proposed binding mode for **10** and Mg^{2+} (50).

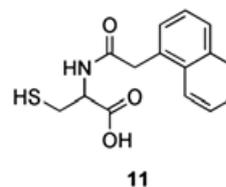


Figure 10. Molecular structure of **11** (52).

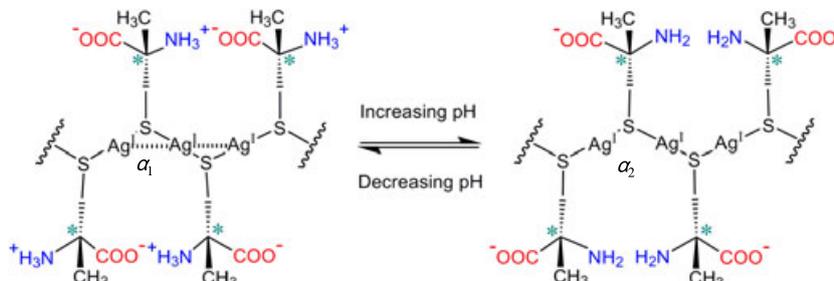


Figure 9. Proposed switching of argentophilic attraction via pH-modulating electrostatic interaction between adjacent ligands along the Ag(I) –Cys polymeric backbone. α_1 and α_2 are the Ag – S – Ag angles at low and high pH, respectively. $\alpha_1 < \alpha_2$ (51).

the metallophilicity, electrostatic and hydrogen-bonding interactions, providing a novel visual sensing platform for iodide with high selectivity based on iodide-triggered gel–sol state transition (53). It should be noted that signal amplification was also suggested in these cases, considering the involvement of cooperative interactions.

$d^8 \dots d^8$ interactions systems

Due to the properties of coordinate-unsaturation and square-planar geometry of platinum(II) complexes, Pt(II) \dots Pt(II) interactions, believed to have a strong tendency to aggregate in solid states into linear chains or oligomeric structures, have in particular attracted considerable attentions in the $d^8 \dots d^8$ systems over the past few decades, with intriguing spectroscopic and photophysical behaviours. Understanding of and applications of the Pt(II) \dots Pt(II) interactions are also expected to promote rapid development of other $d^{10} \dots d^{10}$ systems. However, most of the investigations of Pt(II) \dots Pt(II) interactions have focused on Pt(II) complex crystals in their solid states, due to the strong aggregation tendency, resulting in poor solubility in common solvents; related studies on the aggregation behaviours involving the Pt(II) \dots Pt(II) interactions in solution states remain largely unexplored, whereas introducing long alkynyl groups into platinum(II) complexes was suggested to be able to significantly enhance solubility, affording a promising entry to investigating metal \dots metal interactions-induced aggregation in solution states accompanied by corresponding spectral changes related to the metal \dots metal interactions.

The aggregation behaviours will occur if positively charged alkynylplatinum(II) terpyridyl complexes with a square planar structure are employed to interact with some polyanionic species, such as nucleic acids and polyelectrolytes, due to both Pt(II) \dots Pt(II) and electrostatic attractive interactions. Yam's group has reported that the self-assembly of [Pt(terpy)(C \equiv C–C \equiv C–CH₂–OH)]OTf **12** and [Pt(terpy)(C \equiv C–C \equiv CH)]OTf **13** (Fig. 11) could be achieved in the presence of various single-stranded oligonucleotides, including poly(dT)₂₅, poly(dC)₂₅, poly(dG)₂₅ and poly(dA)₂₅, via modulating the metal \dots metal and π – π stacking interactions (54). The investigation demonstrated that, electrostatic binding of the designed platinum(II) complexes to the single-stranded nucleic acids in buffer solutions could induce the aggregation and self-assembly of the platinum(II) complexes, featured by the newly formed UV-vis absorption and emission bands at $\lambda_{\text{abs}} > 520$ nm and at ca. 760–800 nm, respectively, upon the addition of nucleic acids. The newly formed

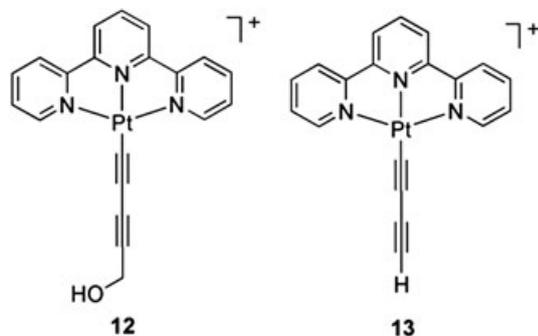


Figure 11. Molecular structures of **12** and **13** (54).

spectral signals indicated the formation of aggregates of **12** and **13** by means of metal \dots metal and π – π interactions, and could be tentatively attributed to the transitions of metal–metal-to-ligand charge-transfer (MMLCT). Observed evolution of the intensity and change of pattern of CD spectra also supported the assembly of the platinum(II) complexes into helical structures. These self-assembly properties could be employed for monitoring the formation of DNA G-quadruplex and the activity of nuclease, based on the platinum(II) indicators being bound to DNA via non-covalent interactions. The excellent sensitivity shown by this strategy is thereby capable of providing a new sensing platform for indicating micro-environmental and conformational changes of biomolecules.

As a class of artificial DNAs, aptamers are employed in the design of biosensors, thanks to their remarkable selectivity and binding capacity towards specific targets. Based on the aforementioned metal \dots metal and electrostatic interactions, a 'proof-of-principle' concept for quantifying lysozyme and thrombin has been achieved by means of the aggregation of platinum(II) complexes-induced spectral changes (55). A 42-mer lysozyme aptamer (LA), a 15-mer thrombin binding aptamer (TBA) and a water-soluble platinum(II) complex **14** (Fig. 12) were designed to check this sensing concept. The spectral changes of **14** in the presence of each aptamer were examined. It was found that, upon addition of LA and TBA, a broad absorption shoulder with no clear band maximum emerged at ca. 538 and 512 nm, respectively, and the emission intensity at longer wavelength has also been observed to be significantly enhanced. These induced spectral signals were suggested to be related with the Pt(II) \dots Pt(II) interactions, since electrostatic attractive interactions between the positively charged metal complexes and polyanionic aptamers could result in the close proximity of **14**, facilitating the aggregation of **14** via both metal \dots metal and π – π stacking interactions. It was also observed that adding various concentrations of target proteins, lysozyme or thrombin, could cause a gradual decrease in both the intensities of absorption and of emission related to the Pt(II) \dots Pt(II) interactions, owing to the high binding affinity of aptamers towards lysozyme or thrombin. This system can provide a new PL-based sensing strategy for label- and immobilization-free probing lysozyme or thrombin with good selectivity and specificity.

Similar aggregation-induced sensing mechanisms based on metal \dots metal and π – π stacking interactions have also been employed to probe glucose and α -glucosidase activity by means of the assembly of alkynylplatinum(II) terpyridyl complexes (56).

Metal coordination polymers-related sensing

Metal coordination polymers, also known as metal–organic frameworks, generally contain metal cation centres with selected

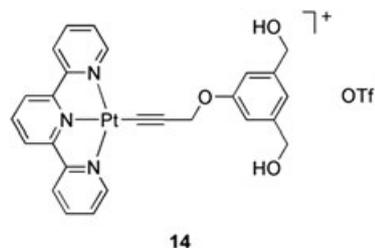


Figure 12. Molecular structure of **14** (55).

different coordination geometries as connectors linked by suitable organic ligands with certain spacers, infinitely extending in an array (57). These supramolecular architectures can also be described as polymers possessing one-, two- and even three-dimensional structures, with the coordination-based complexes as repeat units, depending on the type, oxidation state and coordination number of the metal ions. The intermolecular driving forces maintaining the architectures include coordination bonding, van der Waals' forces, π - π stacking and hydrogen bonding. Applications of metal coordination polymers have been a focus in various fields (58–62), including crystal engineering, molecular devices, luminescent materials, catalysis and sensors. Particularly, developing chemo-/biosensors based on metal coordination polymers is a current topic of considerable interest (63–69). It should be pointed out that a preorganized process between receptor molecules and metal ions is expected to occur to afford cooperative interactions, facilitating the formation of the supramolecular polymeric structure that is an 'aggregation' state in solution.

An early fluorescent sensor for Cu(II), involving the formation of coordination polymers, is 5,10,15,20-tetra[*p*-*N,N*-bis(2-pyridyl)amino]phenyl]porphyrin zinc **15** bearing two functional moieties (Fig. 13), in which one is porphyrin containing Zn(II), serving as a fluorophore, and another is 2,2'-dipyridylamine (dpa), acting as the recognition and binding site for metal ions, which has been synthesized to provide an 'on-off' fluorescent sensing system for Cu²⁺ with excellent selectivity (63). In this case, Cu(II) was believed to be coordinated by two dpa groups from two **15** molecules to create coordination polymeric structures featured by four-coordination of **15** and two-coordination of Cu(II). Such a coordination mode was supported by Job's plot, ESI-MS spectra and fluorescence spectra titration, respectively. In general, the metal coordination-induced supramolecular aggregation is suggested to be capable of facilitating PL quenching or enhancing in the reported cases, providing observable analyte-dependent changes in PL signals (or in absorption signals) to allow a new class of chemosensors to be developed.

Considering the high selectivity of coordination interactions between thymine (T) and Hg²⁺ or adenine (A) and Ag⁺, Zhang's group has designed and synthesized a series of novel PL-based receptors with favourable luminescence 'turn-on' or ratiometric emission mode, to construct novel sensing platforms for Ag⁺ and Hg²⁺ (64,65).

Taking advantage of formed metal coordination polymers to obtain aggregation-induced emission, PL-based receptors **16** and **17** of TPE derivatives bearing adenine and thymine moieties (Fig. 14), were synthesized to probe Ag⁺ and Hg²⁺, respectively (64). Experiments revealed that intrinsic weakly emissive **16** could become highly emissive, with a maximum at 470 nm upon addition of Ag⁺. This suggests that the coordination of adenine moieties of **16** with Ag⁺ to form rigid coordination polymeric structures leads to substantially restricting the intramolecular rotations of **16**, thus causing AIE effect originating from the TPE units. Similar emission spectral responses were also observed in the case of weakly emissive **17** towards Hg²⁺, with quite good selectivity because of the specific binding of T with Hg²⁺ to form supramolecular aggregates by extended complexation.

Based on chromophore (excimer) interactions, the same research group has further developed a ratiometric fluorescence sensing system for Ag⁺ by means of coordination of receptor **18** of pyrene derivative bearing adenine moieties (Fig. 15) with Ag⁺ (65). Upon the addition of Ag⁺, **18** could be coordinated

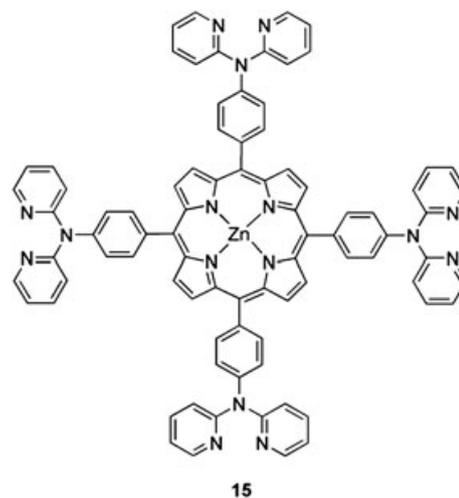


Figure 13. Molecular structure of **15** (63).

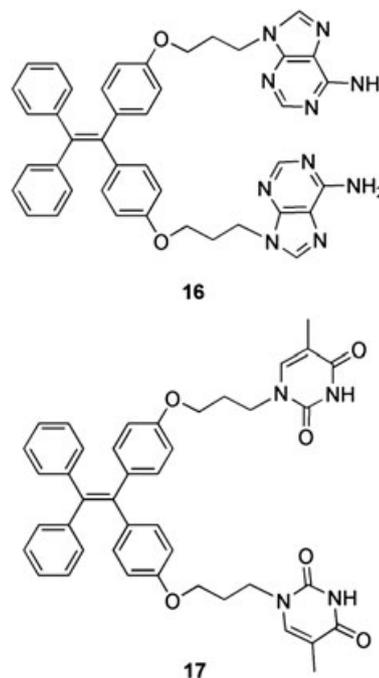


Figure 14. Molecular structures of **16** and **17** (64).

with Ag⁺ to generate extended coordination polymeric structures bringing the pyrene moieties of **18** close together, facilitating the occurrence of excimer emission of pyrene and the disappearance of original emission resulting from pyrene monomers featured by a ratiometric emission mode, which is favourable for sensing Ag⁺.

Such T-Hg-T interactions could also be employed to construct other chemosensing platforms for Hg²⁺ with high sensitivity and selectivity, by means of other PL-based receptor molecules containing thymine groups (66,67). For example, by integrating phthalocyanine and thymine into the backbone of receptor **19** (Fig. 16), a novel strategy of fluorescence-sensing Hg²⁺ could also be achieved (66). In the presence of Hg²⁺, analyte concentration-dependent fluorescence quenching was observed for **19**, assigned to the aggregation-induced self-quenching via coordination of

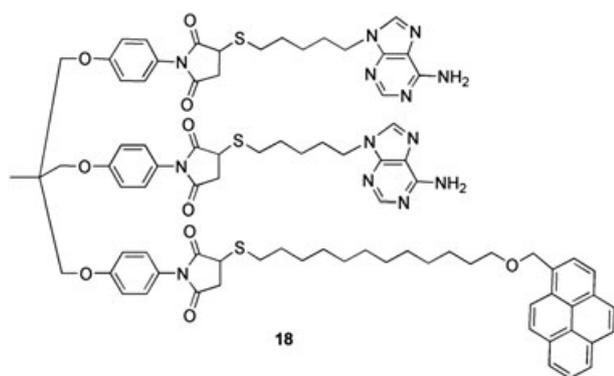


Figure 15. Molecular structure of **18** (65).

thymine moieties in **19** with Hg^{2+} to offer a T–Hg–T binding motif. Thymine-containing PL-based receptor **20** of perylene derivate, possessing a favourable zigzag structure (Fig. 17), has also been fabricated to afford a novel basis for chemosensing Hg^{2+} with extremely high selectivity and sensitivity operating by a fluorescence quenching mechanism, believed to be caused by metal coordination-induced aggregation originating from the formation of the T–Hg–T binding motif (67).

Considering that thymine contains an imide moiety acting as a coordination site for the formation of T–Hg–T interactions when the imide loses a proton from –NH, a pioneering study has been performed to determine if thymine in the traditional T–Hg–T binding mode could be replaced by other receptors also containing imide moieties to create a T–Hg–T-like binding motif (68). Since perylene bisimide (PBI) **21** (Fig. 18) contains two imide groups and serves as a robust class of fluorophores with quite high quantum yield, good photostability and strong aggregation tendency, PBI was chosen to substitute for thymine, (expected to produce a T–Hg–T-like binding motif), to construct novel fluorescence sensing platforms for Hg^{2+} and Cys. As monomers are arranged in a face-to-face fashion to form *H*-aggregates, an efficient fluorescence quenching would occur, accompanied by a hypsochromic shift of the absorption band. Indeed, it was observed that, with increasing concentration of Hg^{2+} , emission at 532 nm originating from the PBI monomers gradually decreased and was almost completely quenched, featured by a superquenching effect. The spectral changes could be assigned to Hg^{2+} -induced *H*-aggregation of PBI. The excellent binding selectivity towards Hg^{2+} has been verified by testing other metal ions and metal ions competition experiments, supporting PBI with imide groups as being able to retain the excellent selectivity, of its counterpart thymine, to form a T–Hg–T-like binding motif via specific interaction with Hg^{2+} . In fact, Hill plot experiments showed a cooperative interaction of Hg^{2+} with PBI to support the observed superquenching effect. Introducing Cys or other thiol species into the PBI– Hg^{2+} ensemble, the original emission was found to be gradually restored, because of the much stronger Hg–S interaction than that of Hg–N causing the Hg–imide interactions to be replaced by the interactions of Hg–S, facilitating the dissociation of 'PBI–Hg' aggregates. The disassembly could thus regenerate the radiative channels and restore the original emission. This study is expected to substantially extend the structural diversity of selective chemosensors for Hg^{2+} , in which the imide group may at large be considered as a selective binding site for Hg^{2+} .

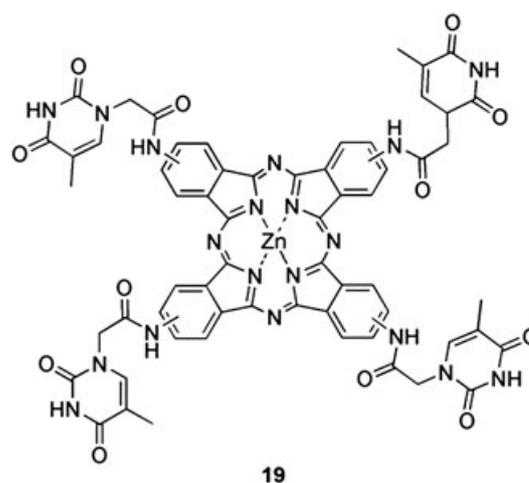


Figure 16. Molecular structure of **19** (66).

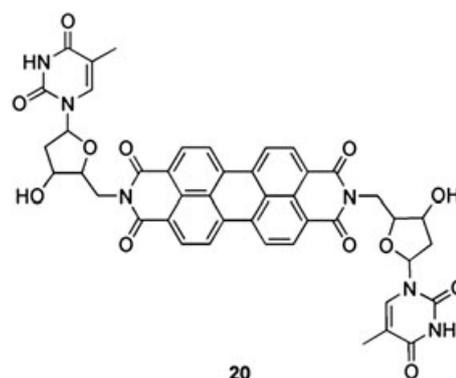


Figure 17. Molecular structure of **20** (67).

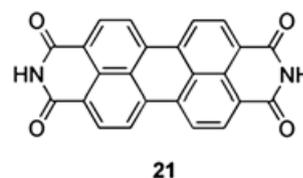


Figure 18. Molecular structure of **21** (68).

Other sensing systems involving supramolecular aggregation/disaggregation

Other PL-based sensing systems relying upon modulating the behaviours of supramolecular aggregation/disaggregation have also been developed to probe target molecules/ions (70–81). For example, compound **22**, a water-soluble (> 30 mmol/L) perylene derivative, bearing two positively charged groups (Fig. 19), has been designed and synthesized. There is an equilibrium between aggregated and monomeric forms, therefore, strong emission originating from free monomers is observed in aqueous solution (70). An anti-lysozyme aptamer (5'-ATC AGG GCT AAA GAG TGC AGA GTTACT TAG-3') was designed to signal lysozyme by employing cationic **22** to interact with the designed aptamer. When the polyanionic aptamer was added to an aqueous solution of **22**, strong electrostatic attractive interactions between the dye monomers/aggregates and the

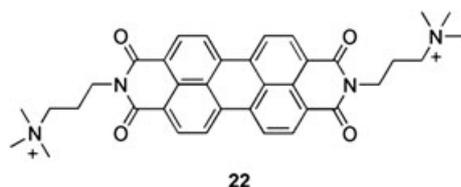


Figure 19. Molecular structure of **22** (70).

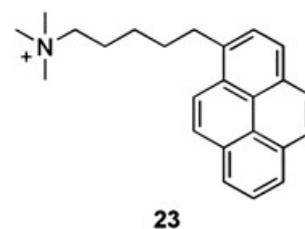


Figure 20. Molecular structure of **23** (72).

aptamer would occur, leading to rapid binding of the dye to the DNA and enhancing the aggregation of **22**. This behaviour could result in a significant decrease in the intensity of the original emission originating from perylene monomers, in view of the ACQ effect. This also indicated that electrostatic repulsive interactions among the dye molecules were greatly suppressed, since the positive charges on the dye were largely neutralized by negative charges of added DNA. Upon the addition of lysozyme to the solution of **22** and aptamer, specific binding of lysozyme to aptamer would weaken the binding between the aptamer and the dye monomers/aggregates. As a result, many more dye-monomer molecules were released; thus, an observable emission signal was turned on and the recovered luminescence intensity was directly proportional to the concentration of the added protein.

Compound **22** has also been employed to probe toxic Hg^{2+} , by means of forming T-Hg-T binding interactions to induce the disaggregation of the ensemble of **22** and a thymine-rich oligonucleotide (oligo-M) (71). When oligo-M was added to **22** aqueous solutions, **22** could be induced to aggregate, leading to significant quenching of the original emission originating from the perylene monomers. In the presence of Hg^{2+} , the specific binding interactions between oligo-M and Hg^{2+} operating in the well-known T-Hg-T binding motif could induce oligo-M to generate a hairpin structure, resulting in disaggregation of the ensemble of **22** and oligo-M. Therefore, enhanced emission originating from perylene monomers could be observed, since free dye monomers were released, obtaining considerably high sensitivity towards Hg^{2+} (LOD \approx 1 nmol/L).

A similar receptor (**23**) based on a pyrene derivative bearing only one positively charged group (Fig. 20) has also been synthesized to probe nucleic acids by means of electrostatic attractive interactions between polyanionic nucleic acid and **23** induced aggregation of pyrene, leading to the formation of an excimer (72). This receptor molecule was also employed to construct a ratiometric fluorescence sensing system for glucose, via glucose binding to an artificial polymer containing boronic acid functional groups, facilitating the polymer to form a polyanion, resulting in the occurrence of strong pyrene excimer emission because of the aggregation of **23** (73).

Conclusions and perspectives

Tremendous numbers of PL-based sensing and recognition systems have been explored and successfully applied in a versatile range of applications, operating in various sensing mechanisms, during the past 30 years. Developing novel and promising PL-based sensitive and selective sensing systems for various target molecules is an important research aim. Supramolecular aggregation and disaggregation can modulate optical or electrical signals of the aggregates/constituting units (receptors) to different extents upon the addition of external stimuli. Therefore,

manipulating the behaviours of supramolecular aggregation/disaggregation has recently been employed to construct novel sensing systems to signal the targets (or interacting events). It is expected to substantially enhance the sensitivity in general given cooperative interactions appearing in the supramolecular assembly/disassembly processes (mostly operating in emission turned-on or emission-enhanced mode).

In this review, we have highlighted the recent advances in PL-based sensing and recognition platforms, based on manipulating the behaviours of supramolecular aggregation/disaggregation to generate observable reporting signals, particularly those developed by scientists in China. These reported sensing systems can be classified in several categories, including AIE, metallophilic interactions-related sensing (metallophilic interactions-induced aggregation/disaggregation), metal coordination polymers-related sensing, and other sensing systems involving supramolecular aggregation/disaggregation, according to sensing mechanisms and/or sensing modes. This review offers a general view of the categories of sensing platforms and affords new insights into designing these receptor molecules.

Acknowledgements

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References

- Lademann J, Weigmann HJ, Sterry W, Roggan A, Muller G, Priezzhev AV, Firsov NN. Investigation of the aggregation and disaggregation properties of erythrocytes by light scattering measurements. *Laser Phys* 1999;9(1):357–62.
- Stefani M, Dobson CM. Protein aggregation and aggregate toxicity: new insights into protein folding, misfolding diseases and biological evolution. *J Mol Med Jmm* 2003;81(11):678–99.
- Luo JD, Xie ZL, Lam JWY, Cheng L, Chen HY, Qiu CF, Kwok HS, Zhan XW, Liu YQ, Zhu DB, Tang BZ. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. *Chem Commun* 2001;18:1740–41.
- Hong YN, Lam JWY, Tang BZ. Aggregation-induced emission: phenomenon, mechanism and applications. *Chem Commun* 2009;29:4332–53.
- Yu G, Yin SW, Liu YQ, Chen JS, Xu XJ, Sun XB, Ma DG, Zhan XW, Peng Q, Shuai ZG, Tang BZ, Zhu DB, Fang WH, Luo Y. Structures, electronic states, photoluminescence, and carrier transport properties of 1,1-disubstituted 2,3,4,5-tetraphenylsiloles. *J Am Chem Soc* 2005;127(17):6335–46.
- Wang M, Zhang GX, Zhang DQ, Zhu DB, Tang B. Fluorescent bio/chemosensors based on silole and tetraphenylethene luminogens with aggregation-induced emission feature. *J Mater Chem* 2010;20(10):1858–67.

- Liu Y, Deng CM, Tang L, Qin AJ, Hu RR, Sun JZ, Tang BZ. Specific detection of D-glucose by a tetraphenylethene-based fluorescent sensor. *J Am Chem Soc* 2011;133(4):660–63.
- Peng LH, Wang M, Zhang GX, Zhang DQ, Zhu DB. A fluorescence turn-on detection of cyanide in aqueous solution based on the aggregation-induced emission. *Org Lett* 2009;11(9):1943–6.
- Zhao MC, Wang M, Liu H, Liu DS, Zhang GX, Zhang DQ, Zhu DB. Continuous on-site label-free ATP fluorometric assay based on aggregation-induced emission of silole. *Langmuir* 2009;25(2):676–8.
- Wang M, Zhang DQ, Zhang GX, Zhu DB. The convenient fluorescence turn-on detection of heparin with a silole derivative featuring an ammonium group. *Chem Commun* 2008;37:4469–71.
- Wang M, Zhang DQ, Zhang GX, Tang YL, Wang S, Zhu DB. Fluorescence turn-on detection of DNA and label-free fluorescence nucleic acid assay based on the aggregation-induced emission of silole. *Anal Chem* 2008;80(16):6443–8.
- Chen Q, Bian N, Cao C, Qiu XL, Qi AD, Han BH. Glucosamine hydrochloride functionalized tetraphenylethylene: a novel fluorescent probe for alkaline phosphatase based on the aggregation-induced emission. *Chem Commun* 2010;46(23):4067–9.
- Tong H, Hong YN, Dong YQ, Haussler M, Li Z, Lam JWY, Dong YP, Sung HHH, Williams ID, Tang BZ. Protein detection and quantitation by tetraphenylethene-based fluorescent probes with aggregation-induced emission characteristics. *J Phys Chem B* 2007;111(40):11817–23.
- Hong YN, Feng C, Yu Y, Liu JZ, Lam JWY, Luo KQ, Tang BZ. Quantitation, visualization, and monitoring of conformational transitions of human serum albumin by a tetraphenylethene derivative with aggregation-induced emission characteristics. *Anal Chem* 2010;82(16):7035–43.
- Wang M, Gu XG, Zhang GX, Zhang DQ, Zhu DB. Convenient and continuous fluorometric assay method for acetylcholinesterase and inhibitor screening based on the aggregation-induced emission. *Anal Chem* 2009;81(11):4444–49.
- Li Z, Dong Y, Mi BX, Tang YH, Haussler M, Tong H, Dong YP, Lam JWY, Ren Y, Sung HHH, Wong KS, Gao P, Williams ID, Kwok HS, Tang BZ. Structural control of the photoluminescence of silole regioisomers and their utility as sensitive regiodiscriminating chemosensors and efficient electroluminescent materials. *J Phys Chem B* 2005;109(20):10061–6.
- Liu Y, Tang YH, Barashkov NN, Irgibaeva IS, Lam JWY, Hu RR, Birimzhanova, D, Yu Y, Tang BZ. Fluorescent chemosensor for detection and quantitation of carbon dioxide gas. *J Am Chem Soc* 2010;132(40):13951–3.
- Ning ZJ, Chen Z, Zhang Q, Yan YL, Qian, SX, Cao Y, Tian H. Aggregation-induced emission (AIE)-active starburst triarylamine fluorophores as potential non-doped red emitters for organic light-emitting diodes and Cl₂ gas chemodosimeter. *Adv Funct Mater* 2007;17(18):3799–807.
- Chen XT, Xiang Y, Li N, Song PS, Tong AJ. Fluorescence turn-on detection of protamine based on aggregation-induced emission enhancement characteristics of 4-(6'-carboxyl)hexyloxysilyl aldehyde azine. *Analyst* 2010;135(5):1098–105.
- Wang J, Mei J, Yuan WZ, Lu P, Qin AJ, Sun JZ, Ma YG, Tang BZ. Hyperbranched polytriazoles with high molecular compressibility: aggregation-induced emission and superamplified explosive detection. *J Mater Chem* 2011;21(12):4056–9.
- Zheng YS, Hu YJ. Chiral recognition based on enantioselectively aggregation-induced emission. *J Org Chem* 2009;74(15):5660–63.
- Li DM, Zheng YS. Highly enantioselective recognition of a wide range of carboxylic acids based on enantioselectively aggregation-induced emission. *Chem Commun* 2011;47(36):10139–41.
- Lu HG, Xu B, Dong YJ, Chen FP, Li YW, Li ZF, He JT, Li H, Tian WJ. Novel fluorescent pH sensors and a biological probe based on anthracene derivatives with aggregation-induced emission characteristics. *Langmuir* 2010;26(9):6838–44.
- Tong H, Hong YN, Dong YQ, Haussler M, Lam JWY, Li Z, Guo ZF, Guo ZH, Tang BZ. Fluorescent 'light-up' bioprobes based on tetraphenylethylene derivatives with aggregation-induced emission characteristics. *Chem Commun* 2006;35:3705–7.
- Dong YQ, Lam JWY, Qin A, Li Z, Liu JZ, Sun JZ, Dong YP, Tang BZ. Endowing hexaphenylsilole with chemical sensory and biological probing properties by attaching amino pendants to the silolyl core. *Chem Phys Lett* 2007;446(1–3):124–7.
- Peng LH, Zhang GX, Zhang DQ, Xiang JF, Zhao R, Wang YL, Zhu DB. A fluorescence 'turn-on' ensemble for acetylcholinesterase activity assay and inhibitor screening. *Org Lett* 2009;11(17):4014–17.
- Hong YN, Haussler M, Lam JWY, Li Z, Sin KK, Dong YQ, Tong H, Liu JZ, Qin AJ, Renneberg R, Tang BZ. Label-free fluorescent probing of G-quadruplex formation and real-time monitoring of DNA folding by a quaternized tetraphenylethene salt with aggregation-induced emission characteristics. *Chem Eur J* 2008;14(21):6428–37.
- Liu J, Lam JWY, Tang BZ. Aggregation-induced emission of silole molecules and polymers: Fundamental and applications. *J Inorg Organometallic Polym Mater* 2009;19(3):249–85.
- Wu JS, Liu WM, Ge JC, Zhang HY, Wang PF. New sensing mechanisms for design of fluorescent chemosensors emerging in recent years. *Chem Soc Rev* 2011;40(7):3483–95.
- Bau R. Crystal structure of the antiarthritic drug gold thiomalate (myochrysin): a double-helical geometry in the solid state. *J Am Chem Soc* 1998;120(36):9380–81.
- Chui SSY, Chen R, Che CM. A chiral [2]catenane precursor of the antiarthritic gold(I) drug auranofin. *Angew Chem Int Ed* 2006;45(10):1621–4.
- Dance IG, Fitzpatrick LJ, Rae AD, Scudder ML. The intertwined double (–AgSR–)_n strand chain structure of crystalline (3-methylpentane-3-thiolato) silver, in relation to (AgSR)₈ molecules in solution. *Inorg Chem* 1983;22:3785–8.
- Howard-Lock HE. Structures of gold(I) and silver(I) thiolate complexes of medicinal interest: a review and recent results. *Met-Based Drugs* 1999;6:201–9.
- Kishimura A, Yamashita T, Aida T. Phosphorescent organogels via 'metallophilic' interactions for reversible RGB-color switching. *J Am Chem Soc* 2005;127(1):179–83.
- Lu XM, Yavuz MS, Tuan HY, Korgel BA, Xia YN. Ultrathin gold nanowires can be obtained by reducing polymeric strands of oleylamine–AuCl complexes formed via aurophilic interaction. *J Am Chem Soc* 2008;130(28):8900–901.
- Huo ZY, Tsung CK, Huang WY, Zhang XF, Yang PD. Sub-two nanometer single crystal Au nanowires. *Nano Lett* 2008;8(7):2041–4.
- Viau G, Piquemal JY, Esparrica M, Ung D, Chakroune N, Warmont F, Fievet F. Formation of assembled silver nanowires by reduction of silver thiolate in polyol/toluene medium. *Chem Commun* 2003;17:2216–17.
- Heaven MW, Dass A, White PS, Holt KM, Murray RW. Crystal structure of the gold nanoparticle [N(C₆H₁₁)₄][Au₂₅(SCH₂CH₂Ph)₁₈]. *J Am Chem Soc* 2008;130(12):3754–5.
- Yam VWW, Li CK, Chan CL. Proof of potassium ions by luminescence signaling based on weak gold–gold interactions in dinuclear gold(I) complexes. *Angew Chem Int Ed* 1998;37(20):2857–9.
- Yam VWW, Chan CL, Li CK, Wong KMC. Molecular design of luminescent dinuclear gold(I) thiolate complexes: from fundamentals to chemosensing. *Coord Chem Rev* 2001;216:173–94.
- Li CK, Cheng ECC, Zhu NY, Yam VWW. Luminescent phosphino-crown-containing gold(I) complexes: their syntheses, spectroscopic studies and host–guest chemistry. *Inorg Chim Acta* 2005;358(14):4191–200.
- Li CK, Lu XX, Wong KMC, Chan CL, Zhu NY, Yam VWW. Molecular design of luminescence ion probes for various cations based on weak gold(I)–gold(I) interactions in dinuclear gold(I) complexes. *Inorg Chem* 2004;43(23):7421–30.
- Xie JP, Zheng YG, Ying JY. Highly selective and ultrasensitive detection of Hg²⁺ based on fluorescence quenching of Au nanoclusters by Hg²⁺–Au⁺ interactions. *Chem Commun* 2010;46(6):961–3.
- Hutchings GJ, Brust M, Schmidbauer H. Gold – an introductory perspective. *Chem Soc Rev* 2008;37(9):1759–65.
- Schmidbauer H. The aurophilicity phenomenon: a decade of experimental findings, theoretical concepts and emerging applications. *Gold Bull* 2000;33(1):3–10.
- Yam VWW, Lo KKW. Luminescent polynuclear d(10) metal complexes. *Chem Soc Rev* 1999;28(5):323–34.
- Schmidbauer H, Schier A. A briefing on aurophilicity. *Chem Soc Rev* 2008;37(9):1931–51.
- Pyykko P. Strong closed-shell interactions in inorganic chemistry. *Chem Rev* 1997;97(3):597–636.
- Chen CM, Lai SW. Structural and spectroscopic evidence for weak metal–metal interactions and metal–substrate exciplex formations in d(10) metal complexes. *Coord Chem Rev* 2005;249(13–14):1296–309.

50. He XM, Cheng ECC, Zhu NY, Yam VWW. Selective ion probe for Mg^{2+} based on Au(I)–Au(I) interactions in a tripodal alkynylgold(I) complex with oligoether pendants. *Chem Commun* 2009;(27):4016–18.
51. Shen JS, Li DH, Zhang MB, Zhou J, Zhang H, Jiang YB. Metal–metal–interaction-facilitated coordination polymer as a sensing ensemble: a case study for cysteine sensing. *Langmuir* 2011;27(1):481–6.
52. Li DH, Shen JS, Chen N, Ruan YB, Jiang YB. A ratiometric luminescent sensing of Ag^+ ion via *in situ* formation of coordination polymers. *Chem Commun* 2011;47(20):5900–902.
53. Shen JS, Li DH, Cai QG, Jiang YB. Highly selective iodide-responsive gel–sol state transition in supramolecular hydrogels. *J Mater Chem* 2009;19(34):6219–24.
54. Yu C, Chan KHY, Wong KMC, Yam VWW. Single-stranded nucleic acid-induced helical self-assembly of alkynylplatinum(II) terpyridyl complexes. *Proc Natl Acad Sci USA* 2006;103(52):19652–7.
55. Yeung MCL, Wong KMC, Tsang YKT, Yam VWW. Aptamer-induced self-assembly of a NIR-emissive platinum(II) terpyridyl complex for label-and immobilization-free detection of lysozyme and thrombin. *Chem Commun* 2010;46(41):7709–11.
56. Chung CYS, Chan KHY, Yam VWW. 'Proof-of-principle' concept for label-free detection of glucose and α -glucosidase activity through the electrostatic assembly of alkynylplatinum(II) terpyridyl complexes. *Chem Commun* 2011;47(7):2000–2002.
57. Kitagawa S, Kitaura R, Noro S. Functional porous coordination polymers. *Angew Chem Int Ed* 2004;43(18):2334–75.
58. Desiraju GR. Supramolecular synthons in crystal engineering – a new organic synthesis. *Angew Chem Int Ed Engl* 1995;34 (21):2311–27.
59. Reineke TM, Eddaoudi M, Fehr M, Kelley D, Yaghi OM. From condensed lanthanide coordination solids to microporous frameworks having accessible metal sites. *J Am Chem Soc* 1999;121(8):1651–7.
60. Pan L, Adams KM, Hernandez HE, Wang XT, Zheng C, Hattori Y, Kaneko K. Porous lanthanide–organic frameworks: synthesis, characterization, and unprecedented gas adsorption properties. *J Am Chem Soc* 2003;125(10):3062–7.
61. Pschirer NG, Ciurtin DM, Smith MD, Bunz UHF, zur Loye HC. Non-interpenetrating square-grid coordination polymers with dimensions of $25 \times 25 \text{ \AA}^2$ prepared by using N,N' -type ligands: The first chiral square-grid coordination polymer. *Angew Chem Int Ed* 2002;41(4):583–5.
62. Canali L, Sherrington DC. Utilisation of homogeneous and supported chiral metal(salen) complexes in asymmetric catalysis. *Chem Soc Rev* 1999;28(2):85–93.
63. Weng YQ, Yue F, Zhong YR, Ye BH. A Copper(III) ion-selective on-off-type fluoroionophore based on zinc porphyrin-dipyridylamino. *Inorg Chem* 2007;46(19):7749–55.
64. Liu L, Zhang GX, Xiang JF, Zhang DQ, Zhu DB. Fluorescence 'turn on' chemosensors for Ag^+ and Hg^{2+} based on tetraphenylethylene motif featuring adenine and thymine moieties. *Org Lett* 2008;10(20):4581–4.
65. Liu L, Zhang DQ, Zhang GX, Xiang JF, Zhu DB. Highly selective ratiometric fluorescence determination of Ag^+ based on a molecular motif with one pyrene and two adenine moieties. *Org Lett* 2008; 10(11):2271–4.
66. Liu XJ, Qi C, Bing T, Cheng XH, Shangguan DH. Highly selective phthalocyanine–thymine conjugate sensor for Hg^{2+} based on target induced aggregation. *Anal Chem* 2009;81(9):3699–704.
67. Che Y, Yang XM, Zang L. Ultraselective fluorescent sensing of Hg^{2+} through metal coordination-induced molecular aggregation. *Chem Commun* 2008;(12):1413–15.
68. Ruan YB, Li AF, Zhao JS, Shen JS, Jiang YB. Specific Hg^{2+} -mediated perylene bisimide aggregation for highly sensitive detection of cysteine. *Chem Commun* 2010;46(27):4938–40.
69. Yagi S, Hyodo Y, Hirose M, Nakazumi H, Sakurai Y, Ajayaghosh A. Metallo supramolecular assemblies of bis-squaraines by allosteric Ca^{2+} ion binding. *Org Lett* 2007;9(10):1999–2002.
70. Wang B, Yu C. Fluorescence turn-on detection of a protein through the reduced aggregation of a perylene probe. *Angew Chem Int Ed* 2010;49(8):1485–8.
71. Wang B, Wang FY, Jiao HP, Yang XY, Yu C. Label-free selective sensing of mercury(II) via reduced aggregation of the perylene fluorescent probe. *Analyst* 2010;135(8):1986–91.
72. Zhang RX, Tang D, Lu P, Yang XY, Liao DL, Zhang YJ, Zhang MJ, Yu C, Yam VWW. Nucleic acid-induced aggregation and pyrene excimer formation. *Org Lett* 2009;11(19):4302–5.
73. Yu C, Yam VWW. Glucose sensing via polyanion formation and induced pyrene excimer emission. *Chem Commun* 2009;11: 1347–9.
74. Gonzalez DC, Savariar EN, Thayumanavan S. Fluorescence patterns from supramolecular polymer assembly and disassembly for sensing metallo- and non-metalloproteins. *J Am Chem Soc* 2009;131(22): 7708–16.
75. Mancin F, Scrimin P, Tecilla P, Tonellato U. Amphiphilic metalloaggregates: catalysis, transport, and sensing. *Coord Chem Rev* 2009;253(17–18):2150–65.
76. Slavnova TD, Gorner H, Chibisov AK. Cyanine-based J-aggregates as a chirality-sensing supramolecular system. *J Phys Chem B* 2011;115(13): 3379–84.
77. Yao ZY, Bai H, Li C, Shi GQ. Analyte-induced aggregation of conjugated polyelectrolytes: role of the charged moieties and its sensing application. *Chem Commun* 2010;46(28):5094–6.
78. Shinoda S, Okazaki T, Player TN, Misaki H, Hori K, Tsukube H. Cholesterol-armed cyclens for helical metal complexes offering chiral self-aggregation and sensing of amino acid anions in aqueous solutions. *J Org Chem* 2005;70(5):1835–43.
79. Matile S, Tanaka H, Litvinchuk S. Analyte sensing across membranes with artificial pores. *Top Curr Chem* 2007;277:219–50.
80. Das G, Talukdar P, Matile S. Fluorometric detection of enzyme activity with synthetic supramolecular pores. *Science* 2002;298(5598): 1600–602.
81. Sakai N, Mareda J, Matile S. Rigid-rod molecules in biomembrane models: from hydrogen-bonded chains to synthetic multifunctional pores. *Acc Chem Res* 2005;38(2):79–87.