

Photofunctional organometallics—from fundamentals to design, assembly and functions*

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Abstract: A number of soluble platinum(II) and gold(I) complexes have been designed and synthesized. Their luminescence and photophysical behavior have been studied. Their assembly properties, which were governed by the noncovalent metal–metal interactions, have also been investigated with the introduction of various external stimuli. The UV–vis and emission spectral changes of these complexes, which arose from the modulation of their assembly and disassembly behavior, have demonstrated the establishment of a convenient and sensitive detection strategy for various types of analytes. These studies suggested the potential applications of these metal complexes as detection probes for a diverse range of target substrates.

Keywords: gold; luminescence; platinum; self-assembly; sensors.

INTRODUCTION

Platinum(II) and gold(I) complexes, the third-row transition-metal complexes of d⁸ and d¹⁰ electronic configurations, respectively, have been known to possess rich photophysical and luminescence properties. Particular attention has been focused on those complexes coordinated with sterically undemanding ligands, owing to the presence of noncovalent metal–metal interactions that would give rise to their interesting structural and spectroscopic features [1–10].

Square-planar platinum(II) polypyridine complexes are one of the representative classes of d⁸ metal complexes possessing a strong propensity to assemble into linear chains or oligomers in the solid state [2–4]. Chloroplatinum(II) terpyridine complexes, [Pt(tpy)Cl]⁺ (tpy = 2,2':6',2''-terpyridine), of various counter-anions, for example, exhibit different colors and display intense low-temperature solid-state emission of diverse energies [3a]. These were ascribed to the different nature of the counter-anions, which governed the packing of the complex molecules and hence the extent of the metal–metal and π–π stacking interactions that imparted them with the different spectroscopic properties [3a]. These complexes, however, were shown to be non-emissive in fluid solution at ambient temperature, owing to the quenching of the triplet metal-to-ligand charge transfer (³MLCT) excited state by the low-lying d-d excited state via non-radiative decay [2b,3c]. Upon coordination of solubilizing alkynyl ligands of strong σ-donating properties to the metal center, a new class of alkynylplatinum(II) terpyridine complexes, [Pt(tpy)(C≡CR)]⁺, of enhanced solubilities was obtained [4]. Their ³MLCT emission in solution state at ambient temperature could be achieved [4], and a new research dimension for the study and

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exploration of the assembly behavior of this class of complexes in the solution state has also been made available.

The aurophilic nature of d^{10} gold(I) metal complexes, which is a consequence of a combination of relativistic and correlation effects [5,11], endows this class of complexes with a diverse range of supramolecular assembly features and intriguing spectroscopic properties that are associated with the inter- and intramolecular metal–metal interactions [5–10]. Numerous gold(I) complexes of different nuclearities coordinated with phosphine [6], thiolate [7], chalcogenide [8], and alkynyl [9] ligands have been reported. The choices of ligands and synthetic approaches have been shown to impart critical influence on these properties as well. Our recent works have demonstrated the utilization of the aurophilic interaction in directing the supramolecular assembly of polynuclear gold(I) macrocyclic frameworks with supramolecular chirality and guest-binding capability observed [8d–g]. These findings illustrated the potential applications stemming from such aurophilic interactions.

In light of the prominent sensitivity of the metal–metal interactions towards various environmental factors, the self-assembly or supramolecular assembly behaviors of these soluble metal complexes, governed by such noncovalent interactions, are believed to be capable of being altered upon introduction of external stimuli in the solution state. It is envisaged that their spectroscopic properties, which exhibit a strong dependence on the metal–metal interactions, not only would reflect the extent of the assembly behaviors but also may serve as optical transduction signals for the detection of various analytes. Such detection strategy would be an interesting subject to be explored.

SOLVENT-INDUCED SELF-ASSEMBLY

A dimorphic complex, $[\text{Pt}(\text{tpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$ (**1-OTf**), in acetonitrile was found to exhibit high-energy intraligand $[\pi \rightarrow \pi^*]$ absorptions of terpyridine and alkynyl ligands and a low-energy MLCT $[\text{d}\pi(\text{Pt}) \rightarrow \pi^*(\text{tpy})]$ absorption at 416 nm in the UV–vis absorption spectrum, which correspond to the presence of the monomeric species and suggested the lack of ground-state aggregation [12]. By making use of its poor solvation in diethyl ether, remarkable color changes from yellow to green then to blue were observed upon increasing the diethyl ether composition in the mixed acetonitrile-diethyl ether solution of **1-OTf**. Along with the diminution of the intraligand and MLCT absorptions, a lower-energy absorption band at 615 nm was observed and enhanced, which has been assigned as originated from the metal–metal-to-ligand charge transfer (MMLCT) transition (Fig. 1, left) [12]. These observations indicated the aggregate formation of **1-OTf** in such solvent mixture with appreciable amounts of intermolecular metal–metal and $\pi-\pi$ stacking interactions involved. Accordingly, a near-infrared (NIR) emission at 785 nm was turned on with intensity enhanced upon increasing the diethyl ether content (Fig. 1, right), which is assigned as emission derived from the excited state of triplet MMLCT (${}^3\text{MMLCT}$) character.

The effect of the nature of the counter-anions on the solvent-induced self-assembly of **1⁺** has been examined as well. Drastic colorimetric responses from yellow to blue (**1-OTf**), magenta (**1-PF₆**), pink (**1-ClO₄**), and orange (**1-BF₄**) were observed with increasing diethyl ether content in the acetonitrile solution of the metal complexes [13]. Newly emerged MMLCT absorption and ${}^3\text{MMLCT}$ emission bands of different energies were obtained for each of them, indicative of the self-assembly of the complex molecules [13]. Together with the variation in the composition of diethyl ether required for turning on the MMLCT absorption or reaching the saturated intensity enhancement, the size and geometry of the counter-anions have been shown to be of pivotal importance in controlling the extent of intermolecular metal–metal and $\pi-\pi$ stacking interactions [13].

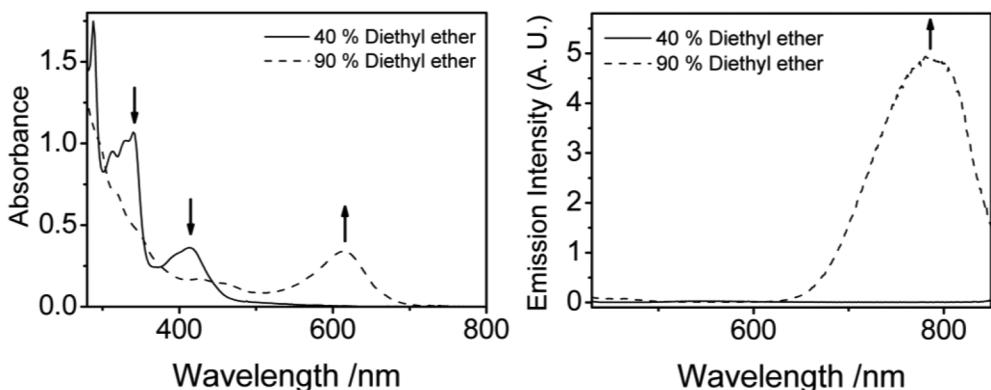


Fig. 1 UV-vis absorption (left) and emission (right) spectral changes of **1-OTf** (147 μM) in acetonitrile-diethyl ether solution with increasing composition of diethyl ether.

POLYELECTROLYTE-INDUCED SELF-ASSEMBLY

In the mimicry of the counter-anions arranging in organized fashion, synthetic polyelectrolytes of a polyanionic nature were envisioned to be capable of serving as templates for the study of the assembly behavior of alkynylplatinum(II) terpyridine complexes. With the introduction of **1-OTf** to poly(acrylic acid) in the presence of tetra-*n*-butylammonium hydroxide (TBAH) in the acetonitrile-methanol mixture, the resultant solution was changed from light yellow to red in color [14]. Intensity reduction in the MLCT absorption and the emergence of MMLCT absorption band at 543 nm were observed, concomitant with the turning on of NIR $^3\text{MMLCT}$ emission at 800 nm, suggesting that the deprotonation of poly(acrylic acid) into polyanionic polyacrylate would allow electrostatic interaction between the polymer and **1-OTf**. The complex molecules were thus brought into close proximity, leading to the formation of supramolecular assembly via metal–metal and π – π stacking interactions.

In light of a change in the $\text{p}K_a$ value of boronic acid upon binding with saccharide, a phenylboronic acid-containing synthetic polymer, PAAPBA, was believed to be turned into polyanionic nature under basic conditions upon binding with glucose [15]. The glucose-bound PAAPBA was employed to investigate the assembly behavior of the water-soluble $[\text{Pt}(\text{tpy})\{\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{CH}_2\text{N}(\text{CH}_3)_3\}](\text{OTf})_2$ (**2**) in aqueous buffer-acetonitrile solution under basic conditions [16]. Upon addition of glucose, diminution of the absorption band at 417 nm originated from MLCT transition mixed with alkynyl-to-terpyridine ligand-to-ligand charge transfer (LLCT) transition, as well as the emergence of MMLCT absorption tail were observed for **2** in the presence of PAAPBA. Concomitantly, decrease in $^3\text{MLCT}/^3\text{LLCT}$ emission at 577 nm together with remarkable $^3\text{MMLCT}$ emission intensity enhancement at 800 nm were observed upon the introduction of glucose (Fig. 2, left) [16]. These indicated that the binding of glucose with boronic acid functionalities would result in charge conversion from charge neutral to polyanionic nature, and thus the polymer would interact electrostatically with **2** and give rise to the formation of their supramolecular assembly (Fig. 2, right). The results demonstrated a “proof-of-principle” concept on utilizing the self-assembly behavior of **2** for the detection of glucose. Such a detection strategy based on the polymer–complex ensemble has been extended to the probing of the enzymatic activities of α -glucosidase [16]. By monitoring the emission intensity changes as a function of time, which signaled the conversion of maltose to glucose, with the presence of different substrate concentration, a Lineweaver–Burk plot was obtained and the K_M and V_{\max} values determined were both in good agreement with the literature values determined from a coupled enzyme assay [16].

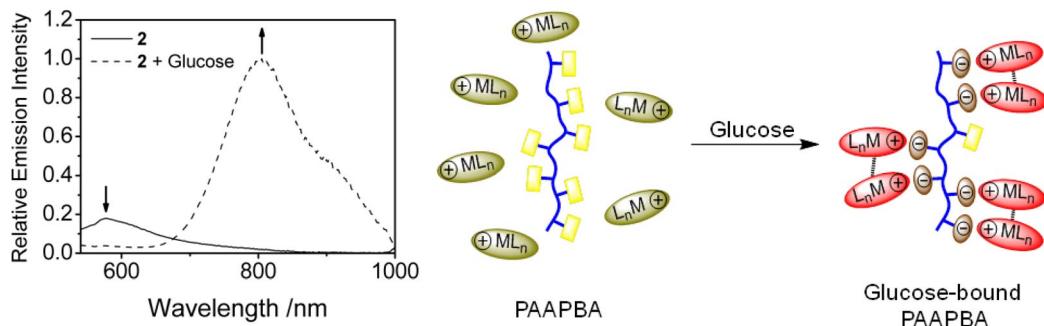


Fig. 2 (Left) Emission spectral changes of **2** (83.3 μ M) and PAAPBA (83.3 μ M of boronic acid unit) in aqueous buffer-acetonitrile solution upon addition of glucose (93.7 mM). (Right) Schematic cartoon showing the self-assembly of platinum(II) complexes onto the glucose-bound PAAPBA.

Taking the merits of the strong absorption and fluorescence nature of conjugated polyelectrolytes, together with the close spectral overlap between the emission energy of PPE-SO_3^- and the absorption energy of the aggregated **2**, the study of Förster resonance energy transfer (FRET) from PPE-SO_3^- to aggregated **2** was explored. Upon addition of **2**, the UV-vis absorption spectrum of PPE-SO_3^- was red-shifted, and this was attributed to the induced self-assembly of **2** by the polyanionic polymer as well as the polymer aggregates formed upon the electrostatic interaction with **2** [17]. With the presence of **2**, the fluorescence emission of PPE-SO_3^- at 535 nm decreased remarkably (Fig. 3, left) together with a switching-on of the ${}^3\text{MMLCT}$ emission of the aggregated **2** at 795 nm observed (Fig. 3, right). Time-resolved emission study of PPE-SO_3^- and resonance light scattering experiment have further confirmed the FRET process between PPE-SO_3^- and the aggregated **2** [17]. Such FRET process has also been employed to demonstrate a “proof-of-principle” concept for the detection of human serum albumin (HSA) under low pH condition [17]. The hydrophobic and electrostatic interactions between PPE-SO_3^- and HSA would displace the assembled **2** from PPE-SO_3^- and lead to a less efficient FRET process, giving rise to a decreased ${}^3\text{MMLCT}$ emission intensity but an enhanced fluorescence intensity of PPE-SO_3^- .

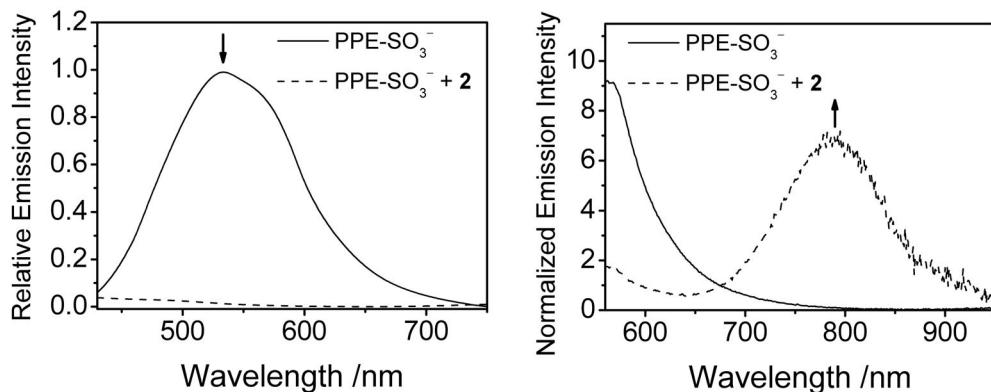


Fig. 3 Emission spectral changes of PPE-SO_3^- (45 μ M) in aqueous buffer solution upon addition of **2** (45 μ M) in wavelength region of (left) 430–750 nm and (right) 560–950 nm.

OLIGONUCLEOTIDE-INDUCED SELF-ASSEMBLY

As inspired by the polyelectrolyte serving as a template for inducing the self-assembly of alkynylplatinum(II) terpyridine complexes, oligonucleotides containing multiple negatively charged phosphate backbones were employed to investigate the induced self-assembly behavior of this class of complexes. MMLCT absorption and $^3\text{MMLCT}$ emission of $[\text{Pt}(\text{tpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_2\text{OH})]\text{OTf}$ (**3**) were enhanced upon addition of oligonucleotides with different nucleic acid sequences, indicating the self-assembly of **3** upon their electrostatic interactions with the oligonucleotides [18]. The extents of the spectral changes were found to show strong correlations with the primary and secondary structures of these oligonucleotides. Induced circular dichroism (CD) signals were observed for the mixtures of oligonucleotides and achiral **3** from the wavelength region of 190–550 nm, which were different from those of oligonucleotides alone [18]. These CD spectral changes suggested that they originate from the electronic transition of **3** and revealed the formation of the supramolecular helical assembly of the oligonucleotide–complex ensemble. Such variation in the spectral changes could be employed to differentiate these oligonucleotides effectively.

Advantageous by the pronounced binding affinity towards specific targets, aptamers, which are the artificial oligonucleotides of particular sequences, have been employed to study the self-assembly of platinum(II) complexes and their applications for the detection of some biologically important proteins were explored. With the presence of lysozyme aptamer (LA) or thrombin-binding aptamer (TBA)-preformed G-quadruplex with the inclusion of hemin and K^+ ion, water-soluble $[\text{Pt}(\text{tpy})\{\text{C}\equiv\text{C}-\text{CH}_2\text{OC}_6\text{H}_3-(\text{CH}_2\text{OH})_2-3,5\}]\text{OTf}$ (**4**) was found to self-assemble via metal–metal and $\pi-\pi$ stacking interactions, as revealed from the MMLCT absorption and NIR $^3\text{MMLCT}$ emission enhancement [19]. Addition of lysozyme to the LA–complex mixture resulted in diminution in both MMLCT absorption and $^3\text{MMLCT}$ emission intensities (Fig. 4, left), suggesting the reduced extent of the self-assembly behavior of **4**. These were ascribed to the preferential interaction between LA and lysozyme, which would induce a gradual surface charge reversal over LA and hence lower the availability of negative charges on LA for the electrostatic interactions with **4**. Similarly, addition of thrombin to the TBA–hemin–complex mixture would give rise to MMLCT absorption and $^3\text{MMLCT}$ emission with reduced intensities as well (Fig. 4, right) [19]. Hence, the spectral changes correlating with the induced self-assembly and disassembly of **4** could be used for probing these two important proteins. In addition, selectivity over a range of interfering candidates and potential applicabilities of such detection strategies in fetal bovine serum have also been assessed with positive results obtained.

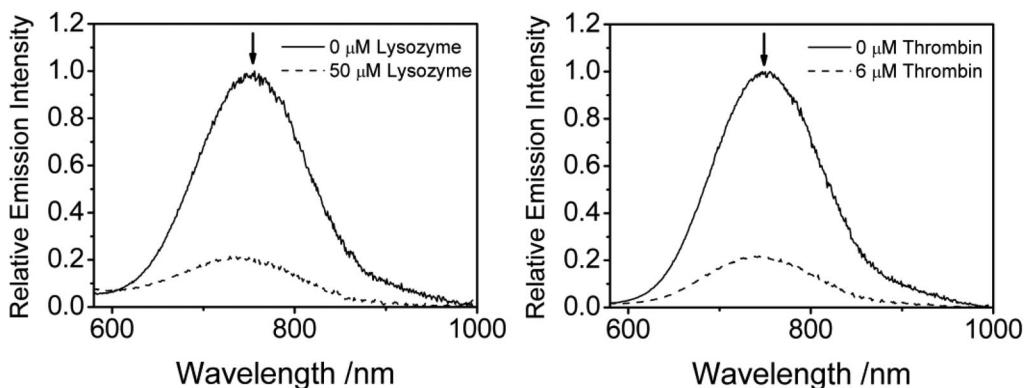


Fig. 4 Emission spectral changes of **4** upon addition of (left) lysozyme to LA–complex mixture [LA (2 μM); **4** (42 μM)] and (right) thrombin to TBA–hemin–complex mixture [TBA (6 μM); hemin (6 μM); **4** (42 μM)] in respective aqueous buffer solution.

TEMPERATURE-CONTROLLED SELF-ASSEMBLY

The exploration of the use of the platinum(II) terpyridine units as signal transduction reporter upon their coordination to a thermoresponsive polymer, poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-PPO-PEO), has also been made. This triblock copolymer has been known to form compact micelles in aqueous environment at or above the critical micelle temperature (CMT). Two metallo-supramolecular triblock copolymers, $[R\text{-Pt(tpy-O-PEO}_{20}\text{-PPO}_{70}\text{-PEO}_{20}\text{-O-tpy)Pt-R}](\text{OTf})_2$ [$R = \text{Cl}$ (**5**); $R = \text{C}\equiv\text{C-Ph}$ (**6**)] have been synthesized [20]. A decrease in the MLCT absorption and an increase in the MMLCT absorption in their UV-vis absorption spectra were observed upon an increase in temperature. Parallel to the UV-vis spectral changes, their NIR $^3\text{MMLCT}$ emissions were turned on as well (Fig. 5, left). As confirmed by the broadening and less-resolved $^1\text{H NMR}$ signals of PPO and terpyridine moieties obtained at temperature above CMT, these spectral changes symbolized the phase transition from unimer to micelles with a core of PPO and coronas of PEO because of the dehydration of the hydrophobic PPO functionality with an increase in temperature (Fig. 5, right). Such transformation has led to the close vicinity of the platinum(II) terpyridine units and the involvement of appreciable amount of metal–metal and π – π stacking interactions. Both transmission electron microscopy (TEM) images and dynamic light scattering (DLS) experiments confirmed the formation of spherical micelles at a temperature higher than CMT [20]. The 19-fold of emission intensity enhancement of **5** within the temperature range of 15–31 °C has allowed it to serve as a sensitive thermoresponsive material.

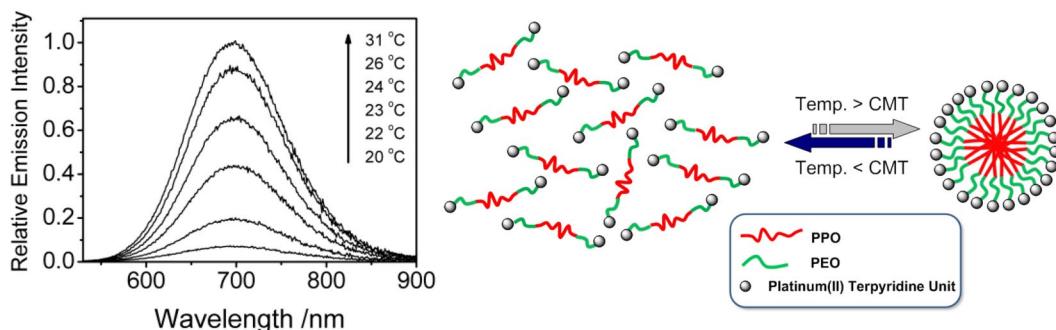


Fig. 5 (Left) Emission spectral changes of **5** (2 mg mL⁻¹) in water with increasing temperature. (Right) Schematic cartoon showing the assembly of platinum(II) terpyridine units upon micelle formation.

METAL ION-INDUCED SELF-ASSEMBLY

With the use of dinuclear gold(I) complexes with bridging diphosphine and benzocrown ether functionalized thiolate moieties, a strategy for metal ion sensing based on the utilization of the switching on and off of the Au···Au interaction has been first initiated by us [21]. These works have illustrated that the sandwiching of metal ions within the two intramolecular benzocrown ether functionalities would bring the two gold(I) centers into close vicinity, leading to a weak Au···Au interaction with an emergence of low-energy triplet ligand-to-metal–metal charge transfer ($^3\text{LMMCT}$) emission. Such sensing strategy is interesting and has been subjected to extensive investigation with the construction of other sensing platforms. Calixarene has been one of the representative candidates prevalently employed in the molecular design, because of the ease of functionalization at either the lower or upper rims and the capability for the construction of unique binding cavity upon judicious structural modification. Recently, we reported dinuclear gold(I) complexes of calixarene and calixcrown for sensing studies [22]. A dinuclear gold(I) complex with aryl functionalized isocyanide based on a calix[4]arene bis-alkynyl scaffold (**7**) has also been synthesized (Fig. 6, left) [23]. This complex was shown to exhibit

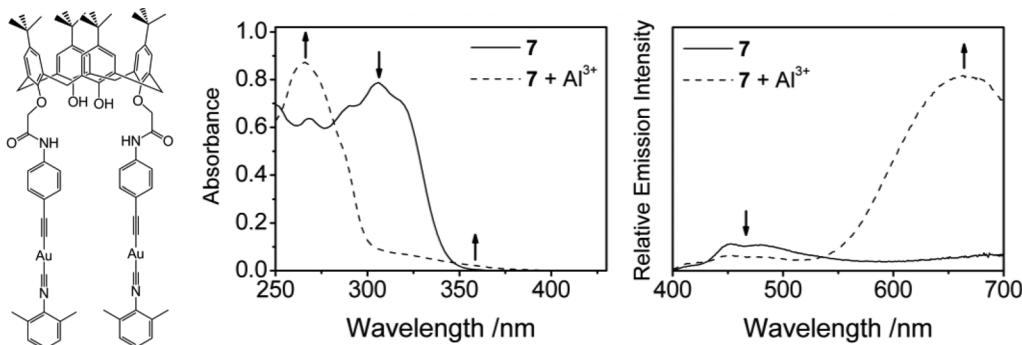


Fig. 6 (Left) Structure of **7**. UV–vis absorption (middle) and emission (right) spectral changes of **7** (124 μM) upon addition of Al^{3+} ion (10.8 μM) in dichloromethane-acetonitrile solution.

strong selectivity towards Al^{3+} ions. Together with the growth of high-energy intraligand absorption of the phenylalkynyl and aryl isocyanide ligands at 264 nm and the diminution of the alkynyl-to-aryl isocyanide LLCT absorption at 306 nm, new low-energy absorption at 350 nm was observed upon addition of such ions. Also, a naked-eye observable luminescence color conversion from green (455 nm) to orange–red (665 nm) was resulted in response to the specific binding of such target ions (Fig. 6, middle and right). These spectral changes were ascribed to the availability of the carbonyl oxygen on amide functionalities for the interaction with the oxophilic Al^{3+} ions, which would then switch on the intramolecular $\text{Au}\cdots\text{Au}$ interactions and result in a reduced highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) energy gap. Such binding mechanism has been confirmed with a downfield shift observed for the protons of amide upon inclusion of Al^{3+} ions, together with a negative result obtained for a control complex without the amido carbonyl functionalities [23].

CONCLUSIONS

With rational design of the molecular structures or choices of ligands, the self-assembly and supramolecular assembly properties of platinum(II) and gold(I) complexes could be modulated with the introduction of external stimuli. Such properties have provided a convenient detection strategy for a versatile range of targets along with high sensitivity and selectivity. Future development on other interesting applications based on such properties is envisaged.

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