Multiaddressable molecular rectangles with reversible Host–guest interactions: Modulation of pH-controlled Guest release and capture

Key words:
Luminescence,
Non covalent intersection,
platinum complex

Introduction

Host-guest chemistry is a fundamental concept in supramolecular chemistry, where a host molecule binds to a guest molecule through non-covalent interactions. The study of metal–metal interactions has drawn enormous attention since the past two decades because of the intriguing Spectroscopic and photophysical properties arising from the close proximity of the metal centers [1,2].These molecular rectangles are synthesized by endcapping U-shaped diplatinum(II) terpyridine moieties with various bis-alkynyl ligands, resulting in a series of rectangles with different rigidities and cavity sizes [1,2,3]. Square planar d8 Platinum(II) complexes with coordination unsaturation are one Of the important classes of metal complexes that have been Extensively explored because of their capability to exhibit metal–Metal interactions and display rich photophysical properties [3,26].Platinum(II) terpyridine complexes have been found to ex-hibit rich polymorphism in the solid state [16,20] owing to their Square planar coordination geometry, which permits facile access To Pt(II)···Pt(II) interactions as well as π–π interactions between. The chromophores. It was not until 2001 that the first successful Synthesis of platinum(II) terpyridine alkynyl complexes, which Possess enhanced solubility and luminescence compared with the Chloro counterpart, was reported [16].Additional efforts have been devoted to the use of the system to respond to external Stimuli, such as variation in solvent composition [17, 18], pH [19, 20], temperature [21, 22], addition of ionic [24,26], and poly-meric species [27, 28], in which spectral changes induced by strong Pt(II)···Pt(II) and π–π interactions have been displayed.

There has been continuous interest in the construction of stimuli-responsive metallosupramolecular architectures with diverse sizes, shapes, and symmetries to rationalize the criteria for molecular recognition and impart them on unique areas of applications, such as stereoselective guest encapsulation and molecular transporting devices [29,30] . Althogh such a variety of metal–organic macrocyclic architectures has been reported, those involving the use of noncovalent Interactions

other than those of hydrogen bonding, donor–acceptor, electrostatic, and hydrophobic–hydrophobic interactions as well as luminescence changes that depend on the nature of the guests, Which would be attractive for chemo- and biosensing, have been rare and are rather underexplored. Examples of such systems that can exhibit reversible host–guest association are also limited.

Since the discovery of anticancer properties of cisplatin in 1969[31], the coordination chemistry and the development of related Species with enhanced properties and reduced cytotoxicity have received enormous attention. Although the potency and cytotoxicity studies are important, the availability of the drugs and their transport and release to the site of action are equally important. Thus, the design of smart drug delivery systems has been an area of growing interest. The first phosphorescent molecular tweezers making use of the alkynylplatinum(II) terpyridine moiety. To accomplish the controlled drug delivery functionalities, the first main strategy is to rigidify the molecular architecture of the host from tweezers to a rectangle, so that the guest molecules would be better accommodated within the cavity, which may lead to a more selective encapsulation of guests within a definite size and steric environment. The possibility of introducing responsive functionalities into the molecular rectangles, which may serve as models for the study of on-demand controlled guest capture and release systems, has also been explored. pH-sensitive pyridine moieties have, therefore, been incorporated into the backbone of the rectangle to modulate the reversible host–guest interaction within the constrained rectangle environment on protonation/deprotonation of the pyridine nitrogen atom to achieve multiaddressable functions that would not have been readily achievable with the molecular tweezers structure. Additionally, the use of various platinum and gold complexes as guest molecules, which have been shown to display anticancer therapeutic behavior [31,30], may lead to the design of a smart multiaddressable molecular rectangle system that could capture and release specific guest molecules under different pH conditions to achieve proof-of-

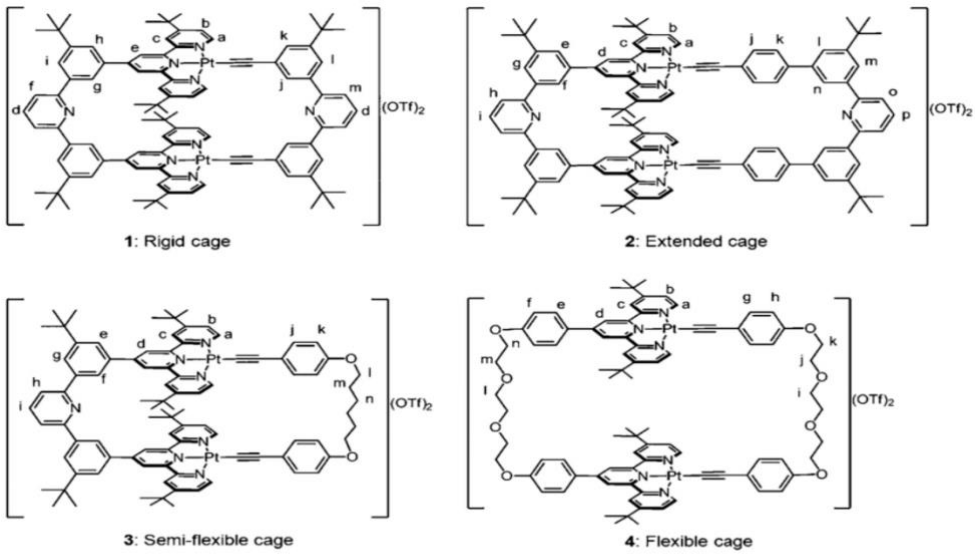


Fig .1. Molecular structure of rectangles 1-4

principle on-demand controlled drug delivery. Herein, the design and synthesis of a series of alkynylplatinum(II) terpyridine molecular rectangles (Fig. 1) with different geometries, topologies and electronic properties are reported. Moreover, the encapsulation of various guest molecules is also investigated in detail to provide a proof-of-principle model for the design of artificial drug delivery systems with the modulation of drug release by pH.

In this review, we focus on the design and synthesis of multiaddressable molecular rectangles with reversible host- guest interactions, which have been engineered to modulate pH-controlled guest release and capture.

Result & Discussion

The alkynylplatinum(II) terpyridine molecular rectangles generally display rich photophysical properties. The electronic absorption spectra of alkynylplatinum(II) terpyridine molecular rectangles 1−4 in dichloromethane solution at room temperature displayed intense intraligand [$\pi \rightarrow \pi^*$] transitions of the terpyridine and the alkynyl ligands at 250−345 nm together with the moderately intense absorptions at 420−490 nm, which are assigned as admixtures of metal-to-ligand charge transfer (MLCT) [$d\pi(Pt) \rightarrow \pi^*$(terpyridine)] and ligand-to-ligand charge transfer (LLCT) [$\pi(C{\equiv}CR) \rightarrow \pi^*$(terpyridine)] transitions according to previous spectroscopic studies on alkynylplatinum(II) terpyridine systems [13,28]. Molecular rectangles 1−4 in degassed acetonitrile solution and solid state at 298 K exhibited structure-less emission bands at 620−700 nm, which are tentatively assigned as originated from the ^{3}MLCT/^{3}LLCT [$d\pi(Pt)/\Pi(C{\equiv}CR) \rightarrow \pi^*$(terpyridine)] excited state with similar trends to their electronic absorptions.

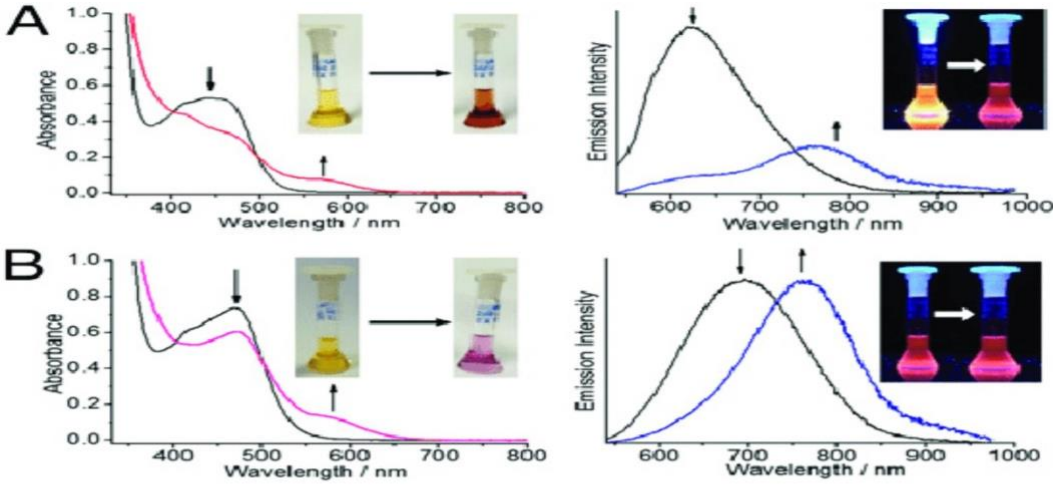
Host Guest Interaction:

The molecular rectangles exhibit excellent guest confinement and selectivity, with the ability to host various square planar platinum(II), palladium(II), and gold(III) complexes, as well as low-dimensional gold(I) complexes, many of which are potential anticancer therapeutics [3]. The reversible host-guest interactions are strongly influenced by metal-metal and π-π interactions, and to a certain extent, electrostatic interactions, leading to various spectroscopic changes depending on the nature of the guest molecules[3]. The host–guest interaction was first investigated with various guest molecules of cationic, neutral, and anionic platinum(II) complexes which are known to be potential anticancer drugs that induce apoptosis on binding to DNA of cancer cells [31,32], in acetonitrile by UV-visible (UV-vis) absorption and emission spectroscopic titration studies to gain the insight into the design of controlled drug delivery systems with the modulation of the nature of drugs. The binding constants for the host–guest interactions were also determined by means of UV-vis absorption and/or emission titration studies to compare their relative affinities.

UV-vis absorption and emission spectra:

On addition of the neutral [Pt(C^N^C)(C≡N−C6H4−OMe−p)] complex to an acetonitrile solution of the molecular rectangles, the color was found to change drastically from yellow to orange-brown (rectangle 1 in Fig. 2A) or from yellowish orange to purple (rectangle 2 in Fig. 2B) with the emergence of a new lower-energy absorption band at about 520–650 nm in the electronic absorption

spectra together with a drop in the orange-red emission of the ^{3} MLCT/^{3} LLCT band and a simultaneous growth of a low-energy emission band in the near-IR (NIR) region (Fig.2). It is believed that the newly formed low-energy absorptions and emissions are derived from a metal–



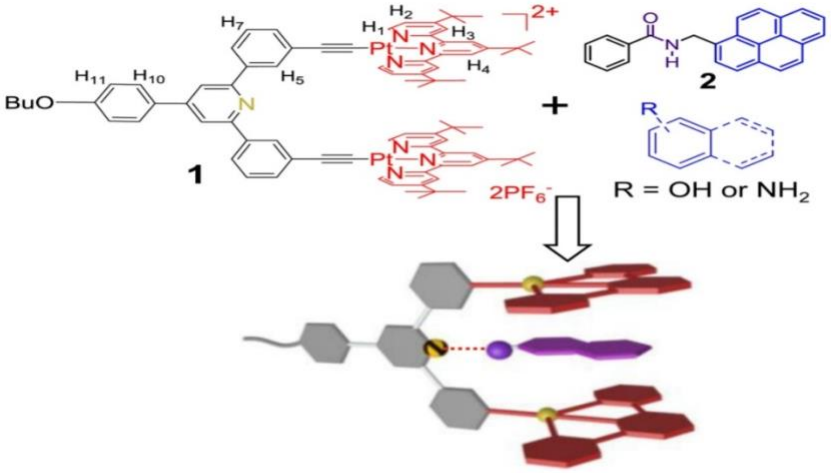
(Left) UV-vis absorption and (Right) emission spectral changes on addition of [Pt(C^N^C)(C≡N−C 6 H 4 −OMe−p)] into (A) 1 and (B) 2 in acetonitrile. Insets show the color/emission changes on addition of guest.

metal-to-ligand charge-transfer (MMLCT) transition and ^{3} MMLCT excited state, respectively, as a result of the Pt(II)···Pt(II) and π–π interactions associated with the host–guest interaction on guest capture [23,28].However, the flexible molecular rectangle 4 only resulted in very small changes in the electronic absorptions on addition of the same guest , resulting from poor confinement of the guest in the flexible architectures. Similar spectroscopic changes have been observed for the titration studies with the negatively charged complexes of [Pt(C^N^C)(C≡C–C6H4–OMe–p)](NBu4), whereas the less π-conjugated [Pt(O^N^O)Cl](NBu4) and positively charged [Pt(N^N^N)Cl](PF6) guests only resulted in a drop of the MLCT/LLCT band at 460 nm and the emission quenching of the ^{3} MLCT/^{3} LLCT band.

Tweezer/Guest Recognition Enhanced by Intermolecular Hydrogen Bonds:

For the bottom-up fabrication of self-assembled nanostructured materials, the fundamental molecular recognition behaviors exert significant impacts on their structural and functional complexities.1 Over the past decade, a variety of host−guest recognition systems have been exploited, which primarily consist of crown ether-, cyclodextrin-, calixarene-, and cucurbituril-type macrocyclic receptors.[4–5] Beyond this scope, acyclic molecular tweezers, representing the preorganization of two π-aromatic pincers with designated orientation and distance, are capable of encapsulating the complementary guests into their cavities.[6] It is highly desirable to develop a molecular tweezer/guest recognition motif with high binding affinity, which would benefit its potential applications in the fields of separation, sensing, and optoelectronics. In this context, introduction of intermolecular hydrogen

bonds represents an alternative strategy to improve non-covalent molecular tweezer/guest binding strength, due to its highly directional and stimuli-responsive character[8]. The alkynylplatinum(II) terpyridine molecular tweezer receptor 1, guest 2 displays a remarkable 80 times enhancement of the binding affinity with respect to that of unsubstituted pyrene (Ka = (1.80 ± 0.11) × 105 M^{-1} for ½ versus (2.27 ± 0.05) × 103 M^{-1} for 1/pyrene) (Scheme 1).[9] This is primarily ascribed to the formation of an intermolecular N−H---N hydrogen bond between the amide unit on 2 and the pyridine moiety on 1.



Molecular tweezer/guest recognition motif with the involvement of intermolecular hydrogen bond

It is anticipated that different types of hydrogen bonds (such as O−H---N and N−H---N) can be formed between 1 and the complementary guests, facilitating the examination of the versatility to enhance molecular tweezer/guest complexation via the assistance of hydrogen bonds. More importantly, the strength of inter-molecular hydrogen bonds can be elaborately modulated, by "caging" the hydroxyl and amine units on the guests,[10] which could efficiently revert to their original forms in respond to external stimuli. Hence, it is highly expected that stimuli responsiveness can be assigned to the resulting molecular tweezer/guest recognition system via the "caging" strategy.

Noncovalent complexation was first examined between 1 and the complementary guests naphthalene and 2-naphthol for 1 itself, severe signal broadening behaviors are observed for the aromatic proton resonances in ^{1}H NMR spectrum, primarily ascribed to the formation of self-associated structures in $CHCl_3$ solution. This phenomenon is still maintained upon adding an equimolar amount of naphthalene to 1. In stark contrast, for a 1:1 mixture of 1 and 2-naphthol, well-defined sharp signals emerge for the resulting 1 H NMR spectrum. In particular, H5 appears in the remarkably downfield region (δ = 8.79 ppm), whereas the terpyridine protons H1−4 on 1 are located at 8.66, 7.31, 8.21, and 8.29 ppm, respectively. Such phenomena indicate distinct complexation behaviors between naphthalene and 2-naphthol guests toward the same molecular tweezer receptor.

For the optimized geometries of ½-naphthol, it is capable of forming an intermolecular O−H---N hydrogen bond between the hydroxyl group on 2-naphthol and the pyridine unit on 1, as

manifested by the short H---N distance of approximately 1.6 Å, together with the O−H---N angle of 173° (Figure 4).Moreover, the electron density predominately distributes over the electron-rich 2-

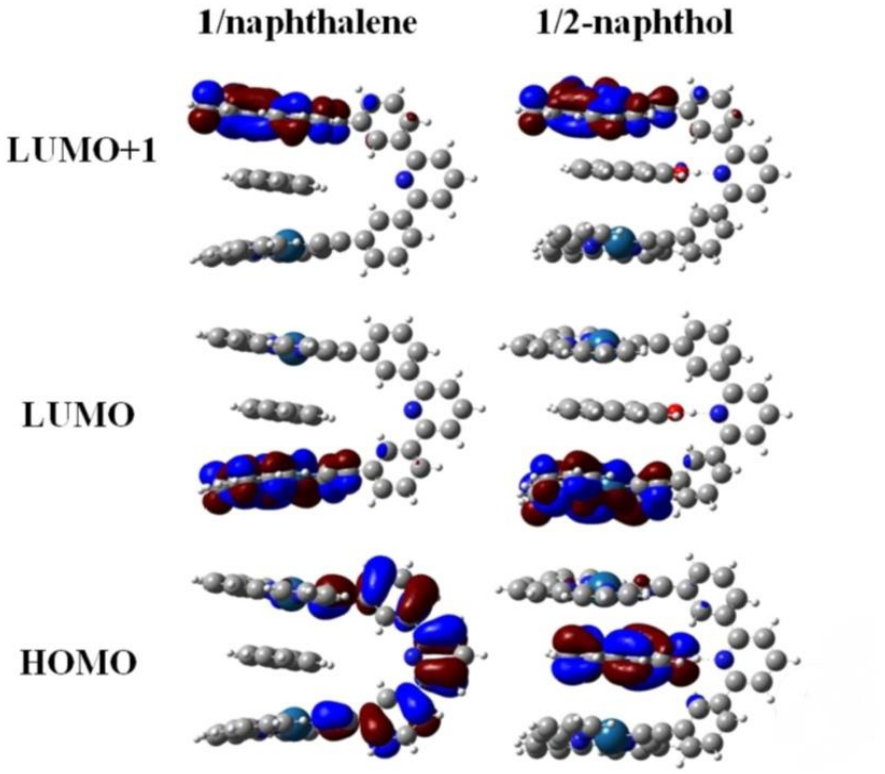


Figure 4. Optimized structures of complexes **1**/2-naphthol and **1**/naphthalene via DFT methods.

naphthol moiety in the HOMO orbital, while it is fully occupied by electron-deficient alkynylplatinum- (II) terpyridine motifs in LUMO and LUMO+1 orbitals. Such phenomena definitely support the involvement of sufficient electron donor−acceptor interactions between 1 and 2-naphthol. In terms of 1/naphthalene (Figure 4), although the electron distribution in LUMO and LUMO+1 orbitals is analogous to that of ½-naphthol, in the HOMO orbital it mainly distributes on the diphenylpyridine backbone, which unambiguously indicates a rather weak charge transfer interactions between naphthalene and the electron-deficient pincers on 1. Hence, it is evident that the formation of an intermolecular hydrogen bond, together with the strengthening donor−acceptor interactions, contributes to the remarkably enhanced binding affinity for ½-naphthol.

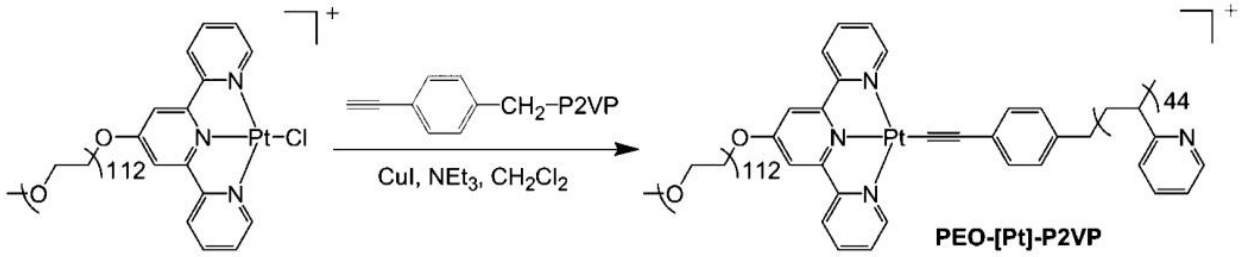
pH – Responsive Guest Release and Capture :

Introduction of pH-responsive functionalities to the ligand backbone generates multifunctional molecular rectangles that exhibit reversible guest release and capture upon the addition of acids and bases [7 11 12]. This pH-controlled behavior indicates the potential of these systems in controlled therapeutics delivery through pH modulation [13].

Phosphorescent transition-metal complexes play an important role as optoelectronic[14] and chemosensory[15] materials. platinum(II) complexes have attracted much attention in recent years because of their rich spectroscopic and luminescence properties.[13,33] It has been known that square planar platinum(II) complexes with polypyridyl ligands could form extended linear chain or oligomeric structure with diverse colors depending on the extent of the metal- - -metal and the ligand π–π stacking interactions.[8–10] Recently, we reported a number of luminescent alkynylplatinum(II) terpyridyl complexes that exhibit remarkable spectroscopic changes upon aggregation via metal-metal and π–π stacking inter- actions in the solution and solid state.[10] Detailed studies on polyelectrolyte-induced self-assembly of platinum(II) complexes via electrostatic binding of the cationic metal complexes to the anionic sites on the polymer have been performed,[10b–e] in which the different nature of hydrophobicity, acidity and chirality of various synthetic polymers and biopolymers, including poly(amino acid)s and single-stranded nucleic acids, have been explored.

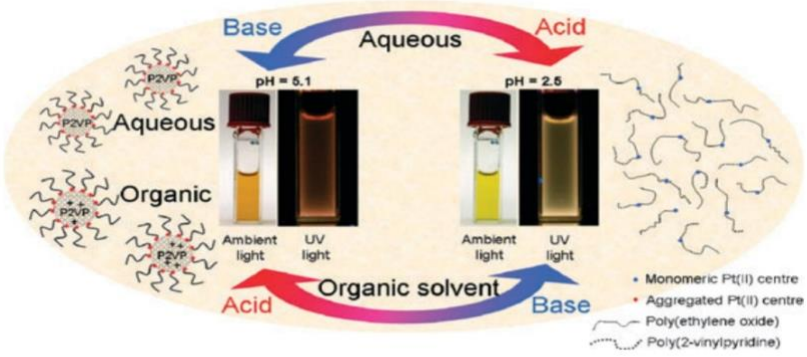
Amphiphilic block copolymers have also attracted much interest as they are known to be capable of undergoing self-assembly into nanosized micelles in selected solvents due to the different nature of the polymer chains when a certain critical micelle concentration (cmc) is achieved. The size and morphologies of the micellar structures are dependent on the molecular weight, block length ratio and interaction parameter of the polymer blocks.11a A simple way to prepare polymeric micelles in aqueous solution is to control the pH of the solution containing the double hydrophilic diblock copolymer such that one block is made insoluble and results in self-assembled micelles. Poly(ethylene oxide)-block-poly-(2-vinylpyridine) (PEO-b-P2VP) diblock copolymers are one class of such candidates that exist as unimers at low pH while micellization occurs at pH higher than 4.811b as a result of deprotonation of the pyridinium moieties, leading to the poor solvation of the poly(2-vinylpyridine) block. Although numerous metallosupramolecular polymers are reported,12 to the best of our knowledge, macromolecules containing bipyridine and/or terpyridine platinum(II) complexes are extremely rare or almost unexplored.12g,h Very recently, during the course of our studies, a report on the self-assembly and photophysics of platinum(II) complexes containing triblock copolymers has been made, that showed interesting FRET modulation upon polymer aggregation.12j We believe that the platinum(II) polypyridyl system, with its rich and intriguing spectroscopic properties may serve as environment-sensitive reporters of polymer conformation and micro-environmental changes. These, together with our recent interest in polyelectrolyte-induced self-assembly of alkynyl-platinum(II) terpyridyl complexes10b–e and the development of colorimetic and luminescence chemosensors,13 have prompted us to design stimuli-responsive block copolymers based on the incorporation of the platinum(II) terpyridyl moiety. Amphiphilic diblock copolymer, poly(ethylene oxide)-b-poly(2-vinylpyridine) copolymer incorporating the alkynylplatinum(II) terpyridyl moiety (PEO–[Pt]–P2VP) in both acidic and basic media. [(PEO112-

tpy)Pt(C=C–P2VP)]OTf (PEO–[Pt]–P2VP) was synthesized by the reaction of [Pt(PEO112-tpy)Cl]OTf with alkynyl-terminated poly(2-vinylpyridine) in the presence of a base and a catalytic



Scheme 1 Synthesis of **PEO–[Pt]–P2VP**.

amount of copper(I) iodide using dichloromethane as solvent, followed by several precipitation/ recrystallization steps in deionized water and 2-propanol to give the final product as a reddish brown solid (Scheme 1). The amphiphilic platinum(II) diblock copolymer was characterized by 1 H NMR and GPC that shows a number-average molecular weight (Mn) of 10 100 g mol-1 (NMR) and 14 065 g mol-1 (GPC), and a polydispersity index (PDI) .The platinum-containing diblock copolymer was found to be readily soluble in deionized water which would give an orange solution that exhibited high-energy absorption bands at 250–340 nm and a low-energy band at ca. 450 nm with an absorption tail extending beyond 550 nm. With reference to previous spectroscopic work on alkynylplatinum(II) terpyridyl complexes,6,10 the higher-energy absorption bands are ascribed as intraligand (IL) [π – π*] transitions of the terpyridyl and alkynyl ligands, and the absorption at ca. 450 nm is assigned as a metal-to-ligand charge transfer (MLCT) [dπ(Pt) – π*(tpy)] transition mixed with an alkynyl-to-terpyridine ligand-to-ligand charge transfer (LLCT) [π(CRC)-π*(tpy)] transition. The electronic absorption at l 4 500 nm probably originates from a metal–metal-to-ligand charge transfer (MMLCT) transition as a result of the possible existence of intermolecular Pt--- Pt contacts and π–π interactions in aqueous solution brought about by micelle formation as revealed in the TEM image. The occurrence of MMLCT bands at similar energies were found in other related platinum(II)



Scheme 2 Reversible pH- and solvent-responsive micelle-mediated self-assembly of **PEO–[Pt]–P2VP**.

terpyridyl systems. Upon addition of dilute hydrochloric acid to PEO–[Pt]–P2VP in aqueous solution (2 mg mL-1), a color change from orange to yellow was observed and a change of luminescence color from red to orange–yellow was found upon UV light excitation(scheme 2) . The corresponding electronic absorption and emission spectral changes at various pH were measured . Upon addition of 1 M hydrochloric acid to the orange solution of PEO–[Pt]–P2VP, the band at ca. 450 nm showed a drop in absorbance with a concomitant growth of absorbance at ca. 400 nm. Along with the drop in absorbance of the 450 nm band, the absorption tail in the region of l 4 500 nm also showed a gradual diminution of intensity and the absorbance at 550 nm approached zero when the pH was lower than 3. An isosbestic point was observed at 440 nm upon varying the pH of the solution and the absorbance change at 505 nm as a function of pH.

We have demonstrated the first example of an amphiphilic alkynylplatinum(II) terpyridyl-based poly(ethylene oxide)-b- poly(2-vinylpyridine) diblock copolymer, PEO–[Pt]–P2VP, that shows reversible self-assembly via pH- and solvent- responsive micelle formation. The reversible micellization properties could induce drastic UV-vis and emission spectral changes via modulation of the Pt---Pt and p–p stacking interactions, depending on the pH and the polarity of the solution media. Such stimuli-responsive micelle-mediated self-assembly properties of amphiphilic platinum(II) terpyridyl- based diblock copolymers may be exploited for probing conformational and microenvironmental changes.

Tuning Emission Responses of a Triphenylamine Derivative in Host−Guest Complexes:

Tuning Emission Responses of a Triphenylamine Derivative in Host-Guest Complexes and an Unusual Dynamic Inclusion Phenomenon" reports on the study of a newly synthesized triphenylamine derivative (1Cl3) and its inclusion complex formation with two different macrocyclic hosts. The study aims to tune the emission responses of the triphenylamine derivative by forming complexes with these hosts.

Key Findings

Significant Differences in Inclusion Complex Formation: The study finds significant differences in inclusion complex formation between the triphenylamine derivative and the two macrocyclic hosts.

Dynamic Inclusion Phenomenon: The study observes an unusual dynamic inclusion phenomenon, where the inclusion complex is dynamic and can change its stoichiometry over time.

Tuning Emission Responses: The study demonstrates the ability to tune the emission responses of the triphenylamine derivative by forming complexes with the macrocyclic hosts.

Methods

Synthesis of Triphenylamine Derivative: The triphenylamine derivative (1Cl3) was synthesized using a novel method.

Inclusion Complex Formation: The triphenylamine derivative was mixed with the two macrocyclic hosts to form inclusion complexes.

Emission Spectroscopy: The emission spectra of the inclusion complexes were measured to study the tuning of emission responses.

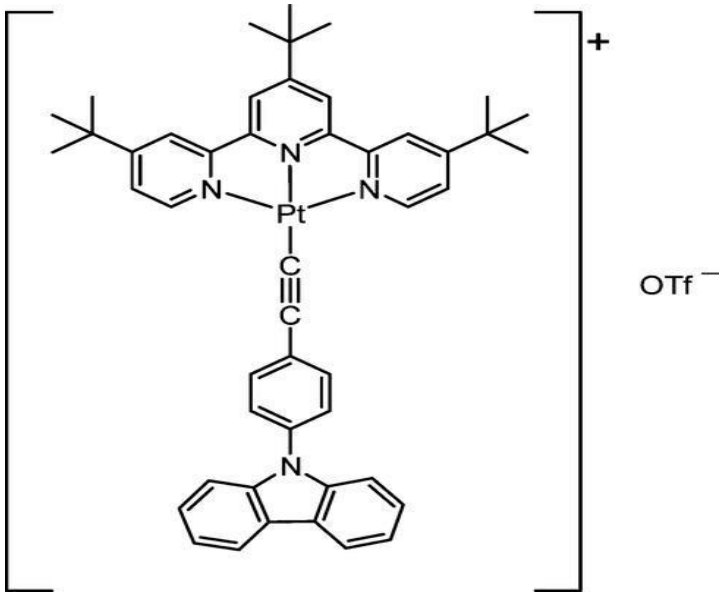
The study demonstrates the ability to tune the emission responses of a triphenylamine derivative by forming complexes with macrocyclic hosts. The unusual dynamic inclusion phenomenon observed in this study highlights the potential for dynamic control of host-guest interactions.

Functionalized Platinum(II) Terpyridyl Alkynyl Complexes as Colorimetric and Luminescence pH Sensors:

Functionalized platinum(II) terpyridyl alkynyl complexes have been demonstrated as colorimetric and luminescence pH sensors. These complexes exhibit dramatic color change and emission enhancement upon the addition of acid, both in organic and aqueous media.

The low-energy absorption bands of these complexes at 432-546 nm are assigned to a [(C≡C) → π*(trpy)] ligand-to-ligand charge-transfer (LLCT) transition with some metal-to-ligand charge-transfer (MLCT) contribution. The energy of this low-energy absorption band is dependent on the electron-donating ability of the alkynyl ligand, with stronger electron donors resulting in a red-shift of the band.

Upon protonation, the emission of these complexes is significantly enhanced, making them useful as luminescence pH sensors. The protonation-induced emission enhancement is attributed to the suppression of nonradiative decay pathways.



Thermodynamic Parameter and Binding Mode:

The binding mode and thermodynamic parameters of the host-guest interactions have been determined by 2D NMR and van't Hoff analysis, and supported by computational studies.[36] These investigations provide valuable insights into the factors governing the reversible guest release and capture in these multiaddressable molecular rectangles. The thermodynamic parameters of host-guest binding can be used to describe, understand, and predict molecular recognition events in aqueous systems. The temperature-dependence of host-guest binding thermodynamics has been studied experimentally and computationally for various host-guest systems[37,38]. The binding enthalpy and entropy of host-guest interactions have been found to vary with temperature, with the binding enthalpy generally decreasing with rising temperature. The heat capacity change upon binding has been observed to be negative for all systems studied, indicating increased enthalpic driving forces for binding at higher temperatures. This trend is attributed to solvation effects, as the solvent properties of water deteriorate as temperature rises. The change in heat capacity upon binding is consistently negative across host-guest systems, indicating increased enthalpic driving forces for binding at higher temperatures. The enthalpy-entropy decomposition suggests that the binding of some guests is entropy driven, while others have large enthalpic contributions.

The thermodynamic parameters that describe host-guest binding interactions include:

1. **Binding Free Energy (ΔG)**: The change in Gibbs free energy upon binding, which determines the spontaneity and strength of the interaction. A negative ΔG indicates a favorable, spontaneous binding process.
2. **Binding Enthalpy (ΔH)**: The change in enthalpy (heat) upon binding, reflecting the strength of direct intermolecular interactions between the host and guest.
3. **Binding Entropy (ΔS)**: The change in entropy upon binding, which can arise from factors like desolvation, conformational changes, and changes in translational/rotational freedom.
4. **Heat Capacity Change (ΔCp)**: The change in heat capacity upon binding, which is often negative and indicates that binding is more favorable at higher temperatures.

These thermodynamic parameters are related by the fundamental equation:

$\Delta G = \Delta H - T\Delta S$

The balance between enthalpic and entropic contributions can vary depending on the specific host-guest system. Generally, favorable binding is driven by a combination of strong host-guest interactions (negative ΔH) and a positive entropic term (TΔS).

Binding Modes in Host-Guest Interactions : ii

The specific binding mode between a host and guest molecule can involve various types of intermolecular interactions, including:

π-π stacking: Interactions between aromatic rings of the host and guest.

Hydrogen bonding: Interactions between hydrogen bond donors and acceptors.

Ion-dipole/Ion-ion: Interactions between charged groups on the host and guest.

Van der Waals forces: Attractive forces between transiently induced dipoles.

Hydrophobic effects: Desolvation of nonpolar surfaces driving binding.

The binding mode is influenced by factors like host preorganization, size/shape complementarity between host and guest, and the ability to minimize the desolvation penalty. Optimal binding often involves a combination of these interactions that maximize the enthalpic and entropic driving forces.[39,40]

The thermodynamics of host-guest binding can be characterized by the changes in free energy, enthalpy, entropy, and heat capacity, which provide insights into the underlying binding mechanisms and interactions. Understanding these principles is crucial for designing effective host-guest systems.

Examples of host-guest complexes with high binding affinity :

Host-guest complexes with high binding affinity are crucial for various applications in chemical sensing, separations, materials science, catalysis, and pharmaceutics. Here are some examples of host-guest complexes with exceptionally high binding affinities:[42]

1. **Cucurbituril (CB) and Cationic Adamantyl Derivatives:**

Binding constants: $10^9 – 10^{13}$ M^{-1}

These complexes have affinities rivaling those of the tightest binding protein-ligand systems, such as biotin with avidin.

2. **CB and Ferrocene Derivatives:**

Binding constants: $10^9 – 10^{13}$ M^{-1}

These complexes have been evaluated as replacements for widely used biomolecular linkers**.**

3. **CB and Hydrocarbon Guests:**

Binding constants: $10^9 – 10^{13}$ M^{-1}

These complexes have been studied for their potential applications in drug delivery, sensing, and stimuli-responsive materials.

4. **Cyclodextrin (CD) and Guest Molecules:**

Binding constants: $10^5 – 10^7$ M^{-1}

These complexes have been used in various applications, including drug delivery, gene delivery, and inclusion complexes for cancer cells.

These examples demonstrate the remarkable binding affinities achievable in host-guest complexes, which can be tailored for specific applications.[40,41]

Role of π-π stacking in host-guest chemistry:

π-π stacking plays a crucial role in host-guest chemistry, particularly in the binding of aromatic guests to hosts with π-acceptor or π-donor sites. This interaction is characterized by the stacking of

aromatic rings, which can be influenced by various factors such as the geometry and orientation of the rings, the presence of substituents, and the solvent environment.

Importance of π-π Stacking:

- Binding Affinity: π-π stacking is a significant contributor to the binding affinity of hosts for guests. The strength of the interaction can be influenced by the electronic properties of the guest and the host, as well as the geometry of the binding site.
- Host-Guest Recognition: π-π stacking is essential for the recognition of guests by hosts. The stacking of aromatic rings allows for specific interactions between the host and guest, which can be used to create highly selective binding sites.
- Supramolecular Assembly: π-π stacking is a key factor in the self-assembly of supramolecular structures. The stacking of aromatic rings can lead to the formation of one-dimensional or two-dimensional arrays, which can be used to create complex architectures.

Examples of π-π Stacking in Host-Guest Chemistry:

- Cucurbiturils (CBs): CBs are a class of hosts that utilize π-π stacking to bind guests. The CB cavity is lined with π-acceptor sites, which interact with π-donor sites on the guest to form a stable complex.
- Cyclodextrins (CDs): CDs are another class of hosts that utilize π-π stacking to bind guests. The CD cavity is lined with π-acceptor sites, which interact with π-donor sites on the guest to form a stable complex.
- Supramolecular Assemblies: π-π stacking is used to create supramolecular assemblies, such as the self-assembly of aromatic molecules into one-dimensional or two-dimensional arrays.

Π-π stacking is a crucial interaction in host-guest chemistry, influencing the binding affinity, recognition, and supramolecular assembly of hosts and guests. The strength and specificity of π-π stacking can be tuned by varying the electronic properties of the guest and host, as well as the geometry of the binding site.

Designing new hosts with high binding affinity:

Designing new hosts with high binding affinity involves a combination of theoretical and experimental approaches. Here are some key strategies and tools used in the design of hosts with high binding affinity:

Theoretical Approaches

1. Molecular Modeling: Computational methods like molecular dynamics simulations and quantum mechanics/molecular mechanics (QM/MM) calculations can be used to predict the binding affinity of a host-guest complex. These methods can help identify the optimal host structure and binding site for a specific guest molecule.
2. Machine Learning: Machine learning algorithms can be trained on large datasets of host-guest interactions to predict the binding affinity of new host-guest complexes. These algorithms can be used to identify the most promising host structures and binding sites for a specific guest molecule.

Experimental Approaches

1. High-Throughput Screening: High-throughput screening methods can be used to rapidly test the binding affinity of a large number of host-guest complexes. This involves synthesizing a library of host molecules and then screening them against a specific guest molecule to identify the hosts with the highest binding affinity.
2. Supramolecular Chemistry: Supramolecular chemistry involves the design and synthesis of host molecules that can bind to specific guest molecules through noncovalent interactions. This approach can be used to create hosts with high binding affinity by optimizing the host structure and binding site for a specific guest molecule.

Design Strategies

1. π-π Stacking: π-π stacking is a key interaction in host-guest chemistry, particularly in the binding of aromatic guests to hosts with π-acceptor or π-donor sites. Designing hosts with π-acceptor or π-donor sites can enhance the binding affinity of the host-guest complex.
2. Electrostatic Interactions: Electrostatic interactions can also play a crucial role in host-guest binding. Designing hosts with electrostatic sites that complement the electrostatic properties of the guest molecule can enhance the binding affinity of the host-guest complex.
3. Hydrogen Bonding: Hydrogen bonding is another important interaction in host-guest chemistry. Designing hosts with hydrogen bond acceptors or donors that complement the hydrogen bonding capabilities of the guest molecule can enhance the binding affinity of the host-guest complex.

Examples of Hosts with High Binding Affinity

1. Cucurbiturils (CBs): CBs are a class of hosts that have been designed to bind to specific guest molecules through π-π stacking and electrostatic interactions. These hosts have been shown to have high binding affinity for a variety of guest molecules.

2. Cyclodextrins (CDs): CDs are another class of hosts that have been designed to bind to specific guest molecules through π-π stacking and hydrogen bonding. These hosts have been shown to have high binding affinity for a variety of guest molecules.
3. Metal-Organic Frameworks (MOFs): MOFs are a class of hosts that have been designed to bind to specific guest molecules through π-π stacking, electrostatic interactions, and hydrogen bonding. These hosts have been shown to have high binding affinity for a variety of guest molecules.

   Designing new hosts with high binding affinity involves a combination of theoretical and experimental approaches. By optimizing the host structure and binding site for a specific guest molecule, it is possible to create hosts with high binding affinity. π-π stacking, electrostatic interactions, and hydrogen bonding are key interactions that can be used to enhance the binding affinity of host-guest complexes.

Role of electrostatic potential in host-guest binding:

The electrostatic potential plays a crucial role in host-guest binding interactions. Here are some key points on how electrostatic potential influences host-guest binding:

1. Complementarity of Electrostatic Potentials: For stable host-guest complexes, the electrostatic potentials of the host and guest molecules should be complementary. The positive regions of the host should align with the negative regions of the guest, and vice versa, to maximize electrostatic attraction and minimize repulsion.
2. Screening of Charges: The presence of ions or salt in the environment can affect the electrostatic interactions between the host and guest. Increased salt concentration can lead to screening of charges, reducing repulsive interactions and potentially enhancing binding affinity.
3. Solvation Effects: The solvation of the host and guest molecules, particularly the desolvation upon binding, can have a significant impact on the electrostatic interactions. The reorganization of solvent molecules around the binding interface can contribute to the overall binding thermodynamics.
4. Induced Polarization: Polarizable force fields, such as the AMOEBA potential, can better capture the induced polarization effects that occur upon host-guest binding. This allows for a more accurate representation of the electrostatic interactions compared to fixed-charge models.
5. Binding Site Preorganization: The preorganization of the host binding site, with optimal placement of charged or polar groups, can enhance the electrostatic complementarity with the guest and lead to tighter binding.

6. Experimental Validation: Techniques like X-ray crystallography and neutron diffraction can provide detailed information about the electrostatic potential distribution within host-guest complexes, which can be used to validate computational models and understand the role of electrostatics in binding.

The electrostatic potential is a crucial factor in determining the binding affinity and stability of host-guest complexes. Accounting for the complementarity of electrostatic potentials, as well as solvation and polarization effects, is essential for accurately modeling and predicting host-guest binding interactions.

Optimizing guest molecules for specific host structures:

Optimizing guest molecules for specific host structures involves designing and synthesizing guest molecules that can effectively bind to the host structure through various intermolecular forces. Here are some key strategies and tools used in optimizing guest molecules for specific host structures:

Strategies

1. Molecular Modeling: Computational methods like molecular dynamics simulations and quantum mechanics/molecular mechanics (QM/MM) calculations can be used to predict the binding affinity of a guest molecule to a specific host structure.
2. High-Throughput Screening: High-throughput screening methods can be used to rapidly test the binding affinity of a large number of guest molecules to a specific host structure.
3. Supramolecular Chemistry: Supramolecular chemistry involves the design and synthesis of guest molecules that can bind to specific host structures through noncovalent interactions. This approach can be used to create guest molecules with high binding affinity for a specific host structure.

Tools

1. Molecular Design Software: Molecular design software like AutoDock, DOCK, and Glide can be used to design and optimize guest molecules for specific host structures.
2. Computational Chemistry Software: Computational chemistry software like Gaussian, Q-Chem, and ORCA can be used to perform quantum mechanics/molecular mechanics (QM/MM) calculations and predict the binding affinity of a guest molecule to a specific host structure.
3. Machine Learning Algorithms: Machine learning algorithms like random forest and support vector machines can be used to predict the binding affinity of a guest

molecule to a specific host structure based on the chemical and physical properties of the guest molecule.

Examples

1. Pillararene-Based Host Structures: Pillararene-based host structures have been designed to bind to specific guest molecules through multiple interactions, including hydrogen bonding, π–π stacking, and metal–ligand coordination.
2. Cucurbituril-Based Host Structures: Cucurbituril-based host structures have been designed to bind to specific guest molecules through π–π stacking and electrostatic interactions.
3. Metal-Organic Frameworks (MOFs): MOFs have been designed to bind to specific guest molecules through π–π stacking, electrostatic interactions, and hydrogen bonding.

Optimizing guest molecules for specific host structures involves a combination of theoretical and experimental approaches. By using molecular modeling, high-throughput screening, and supramolecular chemistry, it is possible to design and synthesize guest molecules with high binding affinity for specific host structures. The use of molecular design software, computational chemistry software, and machine learning algorithms can further enhance the efficiency and accuracy of the optimization process.

Potential application of reversible Host – Guest Interaction:

Reversible host-guest interactions have several potential applications:

Molecular capture and release: Host-guest complexes can be used to reversibly capture and release small molecules or macromolecules. This has applications in drug delivery, separation and purification processes.[43]

Stimuli-responsive materials: The formation and dissociation of host-guest complexes can be triggered by external stimuli like pH, temperature, light, or redox changes. This allows the development of smart, responsive materials for controlled release, self-healing, and shape-memory applications.

Sensing and detection: Changes in the optical or luminescent properties of host-guest complexes upon binding can be used as the basis for colorimetric or fluorescent sensors for analytes.

Catalysis: Host cavities can stabilize reactive intermediates and alter the microenvironment to influence the rate and selectivity of chemical reactions.[44]

Supramolecular assembly: Reversible host-guest interactions can be used to direct the self-assembly of complex, functional supramolecular structures.

In summary, the reversible and stimuli-responsive nature of host-guest interactions makes them a powerful tool for developing smart, functional materials with applications in sensing, delivery, separation, and catalysis.[45]

Applications of reversible host-guest interactions in drug delivery:

Reversible host-guest interactions have several applications in drug delivery:

Stimuli-Responsive Systems: These interactions can be designed to respond to specific stimuli, such as pH, temperature, or light, to control the release of drugs. This allows for more precise and targeted therapy.

Smart Materials: Reversible host-guest interactions can be used to create smart materials that can change their properties in response to external stimuli. This can be used to develop self-healing materials or materials that can release drugs in response to specific conditions.[46,47]

Supramolecular Assembly: These interactions can be used to direct the self-assembly of complex structures, such as nanoparticles or hydrogels, that can encapsulate and release drugs.[48]

Catalysis: Reversible host-guest interactions can be used to stabilize reactive intermediates and alter the microenvironment to influence the rate and selectivity of chemical reactions.

Sensing and Detection: Changes in the optical or luminescent properties of host-guest complexes upon binding can be used as the basis for colorimetric or fluorescent sensors for analytes.

These applications leverage the reversible and stimuli-responsive nature of host-guest interactions to develop smart, functional materials for various therapeutic applications.

Conclusion :

The study on multiaddressable molecular rectangles with reversible host-guest interactions demonstrates significant advancements in pH-controlled guest release and capture mechanisms. By harnessing the reversible nature of host-guest interactions, the research achieves precise control over the release of guests in response to pH changes. Multiaddressable molecular rectangles with

reversible host-guest interactions is that these systems exhibit strong perturbations in their reversible host-guest interactions due to metal-metal and π-π interactions, as well as electrostatic interactions. This modulation of pH-controlled guest release and capture allows for precise control over the binding and release of guest molecules. This capability holds promise for applications in drug delivery systems where targeted and controlled release of therapeutic agents is critical. Furthermore, the modular design of these molecular rectangles allows for versatile manipulation of guest molecules, paving the way for tailored applications in various fields of supramolecular chemistry and materials science.

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