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Pre-Organized Molecular Tweezer Stabilized by Intramolecular Hydrogen Bonds: Solvent-Responsive Host–Guest Complexation

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ABSTRACT

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Introduction

Molecular tweezer, representing the pre-organization of two π -aromatic pincers with designated orientation and distance, is capable for guest encapsulation and thereby receives enormous attention for separation, sensor and optoelectronics applications. In recent years, coordination complexes consisting of d⁸ transition metal (such as Pt^{2+} and Pd^{2+}) have been widely utilized as the pincer units, attributing to their square planar geometries and fascinating functionalities.² It is worthy of note that, with the elaborate choice of the complementary organometallic guests, metal-metal interactions could be potentially embedded, leading to intriguing photo-physical properties for the resulting noncovalent complex.³ For example, molecular tweezer 1 with the decoration of two electron-deficient alkynylplatinum(II) terpyridine units has been reported by Yam et al. and us (Scheme 1).⁴⁵ Due to the pre-organization effect imparted by the shapepersistent diphenylpyridine spacer, 1 permits for the accommodation of various electron-rich guest molecules into its cavity. Based on these findings, we have further self-assembled such recognition motifs to afford well-ordered supramolecular polymeric assemblies.⁵

On this basis, it is of particular interest to trigger reversible guest encapsulation/release from molecular tweezer receptor.⁶ One of the feasible protocols to attain the objective is to implement dynamic elements to the backbone unit. In this context, a variety of switchable molecular tweezers have been reported, which undergoes conformational changes in response to external stimuli such as pH,⁷ cations,⁸ anions,⁹ light,¹⁰ voltage¹¹ and mechanical forces.¹² We sought to develop an alternative and convenient strategy to modulate on–off switching behavior for the resulting tweezer/guest recognition system. Based on this consideration, molecular tweezer **2** is designed in this manuscript

Abstract: A novel molecular tweezer consisting of 2,2'-iminodibenzoyl backbone and alkynylplatinum(II) terpyridine pincers is designed and synthesized. It shows moderate binding strengths towards two neutral organometallic guests, accompanying with interesting optical behaviors due to the involvement of donor–acceptor and metal–metal interactions. Notably, addition of polar solvent, hexafluoroisopropanol, cleavages intramolecular NH···O hydrogen bonds and thereby triggers conformational change for the molecular tweezer receptor. Consequently, molecular tweezer/guest complexation could be significantly influenced, benefiting for further construction of intelligent molecular machines and devices.

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(Scheme 1), for which the tweezer-like conformation is stabilized *via* intramolecular NH···O hydrogen bonds.¹³ It is anticipated to form molecular tweezer/guest complexes between **2** and the neutral guests [Pt(C^N^C)(C=N-C₆H₄-OMe-*p*)] **3** and [Au(C^N^C)(C=C-C₆H₄-OMe-*p*)] **4** (Scheme 1) through electron donor–acceptor and metal–metal interactions. Moreover, considering that intramolecular hydrogen bonds embedded into 2,2'-iminodibenzoyl backbone of **2** are highly sensitive to the solvent polarity changes, conformation change for the tweezer receptor, as well as the binding strength for the resulting tweezer/guest complexes is elucidated towards such external stimuli, which is advantageous for the fabrication of intelligent molecular machines and devices.



Scheme 1. Schematic representation for the non-covalent host–guest complexes derived from the tweezer receptors 1–2 and the complementary guests 3–4, as well as the synthetic route towards 2.

Results and discussion

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The designated molecular tweezer 2 was synthesized in a straightforward manner (Scheme 1). Briefly, the esterification reaction between 4-hydroxyphenylacetylene and commercially available 2,2'-dicarboxydiphenylamine 5 in the presence of N-(3dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC•HCl) and 4-dimethylamino pyridine (DMAP) provided the intermediate 6, which was subsequently converted to the targeted compound 2 via copper(I)-catalyzed coupling reaction. The proposed structure for 2 was confirmed by ¹H NMR, ¹³C NMR and MS spectroscopy (Fig. S4-6, ESI[†]). For proton H₁₁, a singlet ¹H NMR resonance peak appears at the noticeably downfield position ($\delta = 11.1$ ppm) (Fig. S4, ESI⁺), supporting the existence of NH···O intramolecular hydrogen bonds between the amine and two adjacent carbonyl oxygen atoms on the 2,2'iminodibenzoyl skeleton.

Since it failed to grow single crystal of **2** suitable for X-ray crystallography measurement, we tuned to use DFT (density functional theory) calculation to understand its structural information. For the optimized geometry of **2** (Fig. 1), both amide hydrogens form intramolecular hydrogen bonds with the oxygen atom (bond length = 1.96 Å and 1.98 Å, respectively), which is highly consistent with the ¹H NMR experimental results. Notably, to avoid steric hindrance for the 2,2'-dicarboxydiphenyl skeleton, two alkynylplatinum (II) terpyridine pincers on **2** tends to distort from each other to form a V-shape structure (Pt–Pt distance: 18.5 Å), which is more twisted than that of **1** (Pt–Pt distance: 7.56 Å based on its single crystal structure).^{4c}



Figure 1. Optimized geometry of **2** *via* DFT calculation. Pt atoms are described by Lanl2dz, whilst the residual atoms in **2** are described by PBEPBE/3-21G.

The optical properties for **2** in dilute CHCl₃ solution (1×10^{-4}) M) were investigated by means of UV-Vis and fluorescent spectroscopy. In detail, two absorption bands with the maximum peaks locating at 379 nm and 463 nm appear in the visible region (Fig. 2a). Such phenomena are distinct from that of 1, for which only one broad absorption peak dominates in the same region (Fig. S7, ESI⁺). According to the previously reported literatures, the visible light absorption for 1 is predominately assigned to the admixture of $\pi(C \equiv CR) \rightarrow \pi^*(^tBu_3tpy)$ ligand-to-ligand charge transfer (LLCT) and $d\pi(Pt) \rightarrow \pi^*(^tBu_3tpy)$ metal-to-ligand charge transfer (MLCT) bands. Since 2 features the ancillary ligand with more electron-rich character, LLCT bands would be significantly influenced. As a consequence, the band centred at 463 nm is primarily assigned to the MLCT band, whilst the relatively highenergy absorption band (379 nm) should be designated to the LLCT absorption band. Meanwhile, an emission band centred at 600 nm is visualized for 2 (Fig. 2a), which is similar to that of 1 and thereby originates from the ³MLCT alkynylplatinum(II) terpyridine band.

We then turned to study molecular tweezer/guest complexation, by mixing equivalent amounts of 2 (bright yellow solution) and 3 (pale yellow solution) together. For the resulting mixture in chloroform solution, a dark brown color promptly appears (Fig. 2a, inset, middle), indicating non-covalent

complexation for these two compounds. For the resulting complex 2/3, an obvious bathochromic-shifted band ($\lambda_{max} = 552$ nm) emerges in UV-Vis spectrum (Fig. 2a), which is characteristic for the communication between electron-rich alkynylplatinum(II) diphenylpyridine guest 3 and electron-poor alkynylplatinum(II) terpyridine pincers on 2. Simultaneously, a metal-metal-to-ligand charge-transfer (MMLCT) emission band appears in the near infrared region ($\lambda_{max} \approx 800$ nm) (Fig. 2a), together with a broad excitation peak ranging from 400 nm to 600 nm (Fig. S8, ESI[†]). The presence of MMLCT absorption and emission bands provides direct evidence for the involvement of Pt…Pt metal-metal interactions in complex 2/3.



Figure 2. a) UV-Vis absorption and fluorescent spectra (CHCl₃, 0.10 mM for each component) of 2 (red lines), and 1 : 1 mixture of 2 and 3 (black lines). b) UV-Vis absorption and fluorescent spectra of 2 (red lines), and 1 : 1 mixture of 2 and 4 (black lines).

When equivalent amount of alkynylgold(III) diphenylpyridine guest 4 is added into the chloroform solution of 2, no significant colour change occurs for the resulting complex 2/4 (Fig. 2b, inset, middle). Meanwhile, only intensity changes occur for the MLCT absorption (460 nm) and emission (600 nm) bands (Fig. 2b). Such phenomena are quite different from those of the aforementioned complex 2/3. It is evident that, although both guests 3 and 4 possess the square planar d⁸ metal ions, different metal ions exert distinct impact on their photo-physical behaviours.



Figure 3. Partial ¹H NMR spectra (300 MHz, $CDCl_3$, 298 K, 1.00 mM for each component) of a) **3**; b) 1 : 1 mixture of **2** and **3**; c) **2**; d) 1 : 1 mixture of **2** and **4**; and e) **4**.

¹H NMR measurements were performed to get more detailed information on the non-covalent tweezer/guest complexation behaviours. For complex 2/3, the terpyridine protons on 2 (-0.44, -0.43, -0.46 and -0.54 ppm for H_{1.4}, respectively), as well as the diphenylpyridine protons on 3 (-0.71 and -0.27 ppm for H_{e,h}, respectively) undergo obvious upfield shifts, whilst proton H_f on 3 moves downfield (0.29 ppm) (Fig. 3a–c). In the meantime, only slight chemical shift changes occur for the 2,2'-iminodibenzoyl protons such as H₈₋₁₁. Such phenomena support the close spatial proximity between guest 3 and the two pincers on 2. The maximum point for Job plots,¹⁴ deriving from the chemical shift

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changes for H_4 , locates at the mole fraction of 0.5 (Fig. S9–S11, ESI†), revealing 1: 1 binding stoichiometry between 2 and 3. In terms of 2/4, similar chemical shift tendencies are also observed, with the exception that $H_{h'}$ exhibits a slightly downfield shift (-0.12 ppm) (Fig. 3c–e).

Next, we shed light on the molecular tweezer/guest binding thermodynamics by means of isothermal titration calorimetry (ITC) measurements (Fig. 4a-b). For both complexes 2/3 and 2/4, the appearance of exothermic signals suggests the enthalpydriven non-covalent complexation. Moreover, the abrupt exothermic isotherm changes validate 1:1 binding stoichiometries, which are highly consistent with the ¹H NMR Job plots' results. Depending on the non-linear curve fitting of the titration data, the binding constant (K_a) values for complexes 2/3 and 2/4 are determined to be $(1.25 \pm 0.07) \times 10^4 \text{ M}^{-1}$ and $(1.19 \pm 0.09) \times 10^4$ M⁻¹, respectively (Fig. 4a-b). Notably, for both guests 3-4, molecular tweezer 2 exhibits relatively lower binding strengths than those of 1 ($K_a = (3.43 \pm 0.09) \times 10^4$ M⁻¹ and (2.81 ± 0.25) × 10^4 M⁻¹ for 1/3 and 1/4, respectively) (Fig. S12 and S18, ESI[†]), highlighting the crucial role of backbone unit on the stability of tweezer/guest complexation. Moreover, more enthalpies are released for 1 than those of 2 (Δ H values: -5.65 kcal/mol for 1/3 versus -3.66 kcal/mol for 2/3, and -4.47 kcal/mol for 1/4 versus -3.27 kcal/mol for 2/4). Considering that both tweezer receptors possess the same π -pincers, the decreased binding strength for 2 is primarily ascribed to its twisted conformation (Fig. 1), which leads to insufficient π -surface overlapping between the pincers and the complementary guests. Another possible reason lies in the presence of electron-rich ancillary ligand on 2, which presumably influences the tweezer/guest binding affinity via electronic effects.



Figure 4. ITC measurements (CHCl₃, 298 K) for the titration of a) 3 and b) 4 into the chloroform solution of 2.

Subsequently, we envisaged binding reversibility for molecular tweezer/guest complexation. Hexafluoroisopropanol (HFIP), which is a well-known fluorinated solvent capable of interrupting hydrogen bonding interactions,¹⁵ is firstly titrated into the chloroform solution of 2 (2.00 mM). Upon adding 8.33% (v/v) amount of HFIP, significant upfield shift ($\Delta \delta = -0.53$ ppm) is observed for the amine proton H₁₁, accompanying with the obvious downfield shifts ($\Delta \delta = 0.20$ and 0.15 ppm) for the neighbouring protons H₅ and H₆, respectively (Fig. S14, ESI[†]). Such phenomena indicate that intramolecular NH····O hydrogen bonds on the 2,2'-iminodibenzoyl backbone, which are crucial to preserve the tweezer-like conformation for 2, are disrupted towards the HFIP solvent. On this basis, the impact of HFIP on the binding strength of 2/3 was evaluated with the gradual addition of HFIP (Fig. 5). Progressive downfield shifts are visualized for the terpyridine protons H_{1-2} on 2 and the diphenylpyridine proton H_h on **3**, which is contrary to the trend of 2/3 complexation process. Hence, ¹H NMR results suggest the HFIP-triggered release of guest 3 from the cavity of molecular tweezer 2.



Figure 5. Partial ¹H NMR spectra (CDCl₃, room temperature) of a) **3**; b) **2**; and an equimolar mixture of **2** and **3** ([**2**] = [**3**] = 1.00 mM) with different percentage of HFIP (ν/ν): c) 0%; d) 5%; e) 10%; f) 15%; g) 20%.

UV-Vis absorption spectroscopy was further employed to evaluate molecular tweezer/guest binding strength in response to HFIP. When 0%, 4%, 6% (v/v) amounts of HFIP are titrated into the chloroform solution of 2/3, K_a values are determined to be $(7.55 \pm 0.33) \times 10^3 \text{ M}^{-1}$, $(1.81 \pm 0.19) \times 10^3 \text{ M}^{-1}$, and (0.63 ± 0.16) \times 10³ M⁻¹, respectively (Fig. 6 and Fig. S16, ESI⁺), denoting that small amount of HFIP gives rise to several ten times decreases for the binding affinity. Similar tendencies are also observed for 2/4 (K_a values are determined to be (6.18 ± 0.19) × 10³ M⁻¹ and $(1.32 \pm 0.05) \times 10^3$ M⁻¹ for 0%, 6% amounts of HFIP, respectively, Fig. 6 and Fig. S17, ESI⁺). In contrast, for the counterpart receptor 1, 6% (v/v) amounts of HFIP lead to only 2.7 and 1.8 times decrease for $K_{a,1/3}$ and $K_{a,1/4}$, respectively (Fig. S18). Hence, it is evident that the main function of HFIP is disrupting intra-molecular NH····O hydrogen bonds on 2, whilst solvent polarity changes brought by HFIP play a minor role for the binding strength variations. Interestingly, when trace amount of HFIP (1%) is added, an abnormal binding strength reinforcement is observed for both 2/3 ($K_a = (1.17 \pm 0.07) \times 10^4$ M⁻¹) and 2/4 $(K_a = (9.01 \pm 0.34) \times 10^3 \text{ M}^{-1})$ (Fig. 6). Such phenomena are probably ascribed to the strengthening of dipole-dipole van der Walls interactions, which offsets the weakening effect of hydrogen bonds to a certain extent.



Figure 6. K_a values of 2/3 (**n**) and 2/4 (**n**) upon varying the amounts of HFIP (v/v) in chloroform.

Conclusion

In summary, a novel molecular tweezer 2 has been designed and synthesized, for which the tweezer-like conformation is preorganized by virtue of intramolecular NH····O hydrogen bonds on 2,2'-iminodibenzoyl skeleton. Molecular tweezer 2 exhibits moderate binding affinities towards the neutral guests, which are 4

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primarily driven by electron donor-acceptor and metal-metal interactions. Notably, molecular tweezer/guest complexation is liable to solvent polarity changes, mainly attributing to the cleavage of intramolecular hydrogen bonds on the tweezer receptor. The current study demonstrates the efficiency to

† Electronic Supplementary Information (ESI) available. Synthesis, characterization, UV-Vis titration data and other materials. See DOI: 10.1039/x0xx00000x.

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develop switchable π -aromatic receptor, which is promising for the further development of stimuli-responsive supramolecular materials and devices.

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Highlights

- 1. The designed molecular tweezer is pre-organized by intramolecular hydrogen bonds;
- It shows moderate binding affinity towards the organometallic guests; 2.
- The molecular tweezer/guest complexes display interesting optical behaviours; 3.
- Addition of HFIP leads to the release of guest from the molecular tweezer receptor. 4.

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