Non-Covalent Molecular Tweezer/Guest Complexation with Pt(II)···Pt(II) Metal–Metal Interactions: Toward Intelligent Photocatalytic Materials

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1. Materials and methods

9,10-Dimethylanthracene (DMA), copper(I) iodide (CuI), 2,6-diphenylpyrididine, 1-(4-ethynyl-2-pyridinyl)-ethanone were reagent grade and used as received. [Pt(C^N^C)(DMSO)], [Pt(tpy)Cl](BF_4), compounds 2a–b were synthesized according to the previously reported procedures. Other reagents and solvents were employed as purchased.

^1^H NMR spectra was collected on a Varian Unity INOVA-300 spectrometer with TMS as the internal standard. ^1^3^C NMR spectra were recorded on a Varian Unity INOVA-300 spectrometer at 75 MHz. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Breman, Germany), equipped with an ESI interface and ion trap analyzer. Time-of-flight mass spectra (TOF-MS) were obtained on matrix-assisted laser desorption ionization-time of flight (autoflex speed MALDI/TOF, Bruker). UV/Vis spectra were recorded on a UV-1800 Shimadzu spectrometer. Fluorescent spectra were recorded on a Fluoromax-4 spectrofluorometer. Titration Calorimetry (ITC) experiments were carried out with a Microcal VP-ITC apparatus at 298 K. For DFT calculations, all of the optimized geometries were optimized via Gaussian 09 (revision D.01) software package. Light elements such as C, H, O and N were depicted by 3–21G, whilst the S atoms were described by 6–31G(d) calculation level. Notably, the corresponding Los Alamos core potentials Lanl2dz were deliberately set as basis sets for the heavy Pt^{2+} atoms.

**General method for the determination of heterodimeric binding constants via UV-Vis titration measurements:** It depends on the UV/Vis intensity changes of MMLCT absorption band upon UV–Vis titration. Briefly, treating the collected absorbance data (A) vs concentration of the titrating species (C_A) with a non-linear least-squares curve-fitting equation affords the binding constants. For 1 : 1 host/guest complexation, the binding constant is calculated according to the following equation:

\[
A = A_0 + \frac{A_{\text{lim}} - A_0}{2C_0} \left( C_0 + C_A + 1/K_S - \left[ (C_0 + C_A + 1/K_S)^2 - 4C_0C_A \right]^{1/2} \right)
\]  
(Eq. S1)

In particular, A_0 and A are the absorbance intensity of the titrated sample at the MMLCT band with and without presence of the titrating species, respectively. [C_0] is the total concentration of the titrated sample, while [C_A] is the concentration of the titrating species. A_{lim} is the limiting value of absorbance in the presence of excess donor and K_S is the binding constant.
2. Preferential conformation determination for 1b

Theoretically, molecular tweezer 1b, together with the counterpart receptor 1a, could possibility adopt “U”- and “W”-shaped conformations. To clarify which conformation is more stable, we resorted to the thermotical calculations. Specifically, the model molecules (M1a-U, M1a-W, M1b-U, and M1b-W, see Figure S1) were submitted to the DFT calculations. As can be seen, no obvious preference takes place for M1a, because of the relatively low energy barrier between “U”- and “W”-shaped conformations ($\Delta E = 1.77$ kJ/mol). In sharp contrast, M1b prefers the “U”-shaped conformation, since it is much more stable than the “W”-shaped one ($\Delta E = 71.20$ kJ/mol). Such phenomena could be primarily ascribed to the electronic repulsion between nitrogen lone pairs. Depending on these theoretical studies, it can be concluded that molecular tweezer receptor 1b also prefers to adopting “U”-shaped conformation, with the co-facial conformation for two electron-deficient alkynylplatinum(II) terpyridine pincers.

![Figure S1. DFT calculations for a) M1a and b) M1b. All calculations are based on B3LYP/6-31G(d) level.](image-url)

$$E = -894.7794 \text{ a.u.}$$
$$\Delta E = 0.027 \text{ a.u.} = 71.20 \text{ KJ/mol}$$

$$E = -862.6937 \text{ a.u.}$$
$$\Delta E = 0.0067 \text{ a.u.} = 1.77 \text{ KJ/mol}$$
3. Photophysical behaviors of 1a and 1b

Figure S2. a) UV/Vis and b) fluorescent spectra (CHCl₃/CH₃CN = 1 : 1, 0.05 mM) of molecular tweezers 1a (blue line) and 1b (red line). As can be seen, the MLCT/LLCT absorption and emission bands of 1b are blue-shifted than those of 1a.
4. Non-covalent complexation between 1b and 2a

Upon mixing 1b and 2a together, the aromatic terpyridine protons on 1b and aromatic diphenylpyridine protons on 2a undergo obvious upfield shifts (−0.22, −0.30, −0.58 and −0.71 ppm for H₃, H₄, H₅ and H₆, respectively). Hence, electron donor–acceptor interactions exist between electron-deficient terpyridine pincers on 1b and electron-rich diphenylpyridine unit on 2a.

Figure S3. Partial ¹H NMR spectra (300 MHz, CDCl₃/CD₃CN = 1 : 1, 298 K, 2.00 mM) of a) 1b; b) 1 : 1 mixture of 1b and 2a; c) 2a. Upon mixing 1b and 2a together, the aromatic terpyridine protons on 1b and aromatic diphenylpyridine protons on 2a undergo obvious upfield shifts (−0.22, −0.30, −0.58 and −0.71 ppm for H₃, H₄, H₅ and H₆, respectively). Hence, electron donor–acceptor interactions exist between electron-deficient terpyridine pincers on 1b and electron-rich diphenylpyridine unit on 2a.

Figure S4. a) UV/Vis spectra for the mixture of 1b and 2a, by keeping the total concentration constant (CHCl₃/CH₃CN = 1 : 1, [1b] + [2a] = 0.10 mM). b) Job’s plot. The curve shows 1 : 1 binding stoichiometry between 1b and 2a, by plotting the absorbance at 500 nm against the mole fraction of guest 2a.
Figure S5. a) UV/Vis spectral changes of 1b (0.05 mM, CHCl₃ : CH₃CN = 1 : 1) upon gradual addition of 2a. b) Intensity changes of absorbance at 515 nm. The MMLCT band of 1b, predominately locating on the region of approximately 450–600 nm, undergoes gradual increase for the absorption intensity upon progressive addition of 2a. Nonlinear curve-fitting of the collected absorbance data at 515 nm provides the $K_a$ value of $(2.53 \pm 0.29) \times 10^5$ M$^{-1}$. 
5. *Non-covalent complexation between 1b and 2b*

**Figure S6.** a) UV/Vis absorption spectral changes of 1b (0.05 mM, CHCl₃: CH₃CN = 1 : 1) upon gradual addition of 2b. Inset: intensity changes of absorbance at 515 nm. b) Fluorescent spectra (0.05 mM, CHCl₃: CH₃CN = 1 : 1) of 1b (black line) and 1b/2b (red line). The emergence of MMLCT absorption/emission bands support the presence of Pt--Pt metal–metal interactions for complex 1b/2b. Nonlinear curve-fitting of the collected absorbance data at 515 nm provides the $K_a$ value of $(2.30 \pm 0.22) \times 10^5$ M⁻¹ for complex 1b/2b.

**Figure S7.** ITC experiments by consecutive injecting of 2b (8.00 mM) into the solution of 1b (0.40 mM, CHCl₃: CH₃CN = 1 : 1). The binding stoichiometry between 1b and 2b is determined to be 1 : 1, as reflected by the abrupt change in the curve. Fitting the exothermic binding isotherm data with one-site model provides the $K_a$ value of $(3.90 \pm 0.17) \times 10^5$ M⁻¹ for 1b/2b. Such results are highly consistent with those of the UV/Vis titration experiments (Figure S6a).
6. Non-covalent complexation between 1a and 2a

Figure S8. a) UV/Vis absorption spectral changes of 1a (0.05 mM, CHCl₃: CH₃CN = 1:1) upon gradual addition of 2a. Inset: intensity changes of absorbance at 550 nm. b) Fluorescent spectra (0.05 mM, CHCl₃: CH₃CN = 1:1) of 2a (black line) and 1a/2a (red line). The emergence of MMLCT absorption/emission bands support the existence of Pt---Pt metal–metal interactions for complex 1a/2a. Nonlinear curve-fitting of the collected absorbance data at 550 nm provides the $K_a$ value of (4.69 ± 0.13) × 10⁴ M⁻¹ for complex 1a/2a.

Figure S9. ITC experiments by consecutive injecting of 2a (8.00 mM) into the solution of 1a (0.40 mM, CHCl₃: CH₃CN = 1:1). The binding stoichiometry between 1a and 2a is determined to be 1:1, as reflected by the abrupt change in the curve. Fitting the exothermic binding isotherm data with one-site model provides the $K_a$ value of (6.20 ± 0.17) × 10³ M⁻¹ for complex 1a/2a.
7. **DFT calculation for complex 1b/2a**

X-ray crystallography provides the reliable structural information for non-covalent complexation systems. On this account, we tried to grow high-quality single crystals for the supramolecular tweezeering complexes. Even though considerable attempts have been carried out, unfortunately it fails to get the desired crystals. As an alternative way, we turned to clarify the non-covalent complexation structures via density functional theory (DFT) calculations.

For the optimized geometry of **1b/2a** (Figure S10), triple stacking of Pt(II) atoms is validated by the short Pt---Pt distances of 3.48 and 3.53 Å. Hence, it supports the existence of Pt---Pt metal–metal interactions, which is consistent with the UV/Vis and fluorescent experimental results. Meanwhile, inter-planar distances between the alkynylplatinum(II) terpyridine and isocyanideplatinum(II) diphenylpyridine pincers are determined to be 3.63 Å. Accordingly, it can be concluded that both Pt---Pt metal–metal and donor–acceptor interactions are involved in complex **1b/2a**.

![Figure S10. Optimized geometry of complex 1b/2a.](image-url)
8. Photosensitization capability test

$^1$O$_2$ generation rate ($\nu$ min$^{-1}$M$^{-1}$) can be calculated on the basis of the UV/Vis measurements (Figure S11a). Specifically, it is determined by the following equation,

$$\nu = \frac{k}{c}$$  \hspace{1cm} (Eq. S2)

In particular, $k$ is the slope of the corresponding curve, while $c$ denotes the monomer concentration.

![Figure S11](image)

**Figure S11.** a) UV/Vis absorption changes of DMA (0.25 mM, CHCl$_3$ : CH$_3$CN = 1 : 1) upon visible light irradiation (590 nm, 12 W), with the employment of complex 1b/2a ($c = 0.03$ mM) as the photosensitizer. b) Photosensitization efficiency of complexes 1a/2a (■) and 1b/2a (●), by monitoring time-dependent absorbance of DMA at 401 nm. It is obvious that 1b/2a displays reinforced photosensitive efficiency than that of 1a/2a ($725$ min$^{-1}$M$^{-1}$ vs $322$ min$^{-1}$M$^{-1}$).
9. Photo-oxidative cyanation of tertiary amine 3

General procedure for the photo-catalytic reaction: tertiary amine 3 (0.10 mmol), TMSCN (0.15 mmol), and the corresponding photosensitizers were dissolved in 10 mL CHCl₃/CH₃CN (1 : 1, v/v) in a 13 cm-tall quartz tube. The reaction mixture was bubbled with solvent-saturated oxygen gas in 20 seconds, and irradiated with a 100 W OLED lamp (λ > 590 nm) as the light source at room temperature. Upon light irradiation, the benzylic resonance Hₐ of 3 locating at 4.41 ppm progressively decreases. In the meantime, the newly-formed benzylic signal Hₐ' locating at 5.52 ppm gradually increases (Figure S12). After irradiating for several hours, the solvent was evaporated and the product yield was calculated, by using 4,4'-dimethyl-2,2'-bipyridine as the internal ¹H NMR standard. Turnover numbers (TON) value was calculated by product yield vs reaction time and catalyst loading percentage.

Figure S12. Photo-oxidative cyanation of tertiary amine 3 to 4. Herein complex 1b/2a was employed as the photosensitizer to illustrate the organic conversion.
10. Photo-cleavage reaction of coumarin derivative 5

![Diagram showing the photo-cleavage reaction of coumarin derivative 5 to 6.]

Figure S13. Photo-cleavage of coumarin derivative 5 to 6. Conversion of 5 to 6 can be monitored by $^1$H NMR experiments (CD$_3$CN : D$_2$O = 1:1, complex 1b/2a was employed as the photo-catalyst).

![Fluorescence intensity vs. wavelength graph.]

Figure S14. Photo-cleavage reaction of 5 to 6 (20 μM in 95% water/5% DMF, complex 1b/2a as the photocatalyst, 590 nm, 12w), accompanying with the “turning-on” fluorescence at 450 nm.
11. Cation-triggered responsiveness of 1b and 1b/2a

Figure S15. UV/Vis absorption spectral changes of 1b (0.05 mM, CHCl$_3$ : CH$_3$CN = 1 : 1) upon the successive addition of a) Zn(OTf)$_2$ and b) cyclen. Fluorescent spectral changes of 1b (0.05 mM, CHCl$_3$ : CH$_3$CN = 1 : 1) upon the successive addition of c) Zn(OTf)$_2$ and d) cyclen. The addition of Zn$^{2+}$ ion leads to the blue-shifting of MLCT/LLCT absorption band, as well as the decline of fluorescent intensity. Such phenomena suggest the “U”- to “W”-shaped conformational transition of 1b. The absorption and fluorescent spectra completely restore after the successive addition of cyclen as the competitive ligand.

Figure S16. UV/Vis absorption spectral changes of 1b/2a (0.05 mM, CHCl$_3$ : CH$_3$CN = 1 : 1) upon the successive addition of a) Zn(OTf)$_2$ and b) cyclen. Fluorescent spectral changes of 1b/2a (0.05 mM, CHCl$_3$ : CH$_3$CN = 1 : 1) upon the successive addition of c) Zn(OTf)$_2$ and d) cyclen. The addition of Zn$^{2+}$ ion leads to the vanish of MMLCT absorbance and emission band, suggesting the disruption of complex 1b/2a. The MMLCT absorption and fluorescent spectra completely restore after the successive addition of cyclen.
Figure S17. ITC experiments by consecutive injecting of 2a (8.00 mM) into the solution of a) 1b + Zn²⁺ (0.40 mM, CHCl₃ : CH₃CN = 1 : 1), and b) 1a + Zn²⁺ (0.40 mM, CHCl₃ : CH₃CN = 1 : 1). Notably, negligible heat exchange occurs when titrating 2a into the mixture solution of 1b and Zn²⁺. Such phenomena suggest that 1b undergoes “U”- to “W”-shaped conformational transition upon adding Zn²⁺ ion, which influences non-covalent binding capability toward the complementary guest 2a. In stark contrast, the presence of Zn²⁺ ion hardly affects the non-covalent binding affinity between 1a and 2a (with Zn²⁺ ion, \( K_a = (4.08 \pm 0.12) \times 10^4 \) M⁻¹ for 1a/2a; without Zn²⁺ ion, \( K_a = (6.20 \pm 0.17) \times 10^4 \) M⁻¹ for 1a/2a, see Figure S9), validating the importance of dynamic switching elements for the stimuli-responsive molecular tweezer/guest complexation behaviors.
12. “On-demand” photo-catalytic efficiency of 1b/2a

Figure S18. Monitoring photo-catalytic efficiency upon sequential addition of Zn(OTf)_2 and terpyridine (as the competitive ligand) to complex 1b/2a (0.2% equivalent to 3). Depending on ¹H NMR measurements, “on-demand” photo-oxidative cyanation of tertiary amine 3 can be achieved, by manipulating the revival and loss of photosensitization capability of 1b/2a.
13. Synthesis of 1b

![Scheme S1. Synthetic route to molecular tweezer 1b.](image)

Compound 7 (0.13 g, 0.32 mmol), [Pt(tpy)Cl](BF₄) (0.58 g, 0.80 mmol), CuI (0.02 g, 0.32 mmol) and NEt₃ (4 mL) in CH₂Cl₂ (60 mL) were stirred at room temperature for 48 hours. The mixture was evaporated under reduced pressure, and the residue was purified by column chromatography (alumina, CH₃OH/CH₂Cl₂, 1: 100 v/v as the eluent) to afford 1b as an orange solid (0.51 g, 91%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 9.32 (s, 2H), 7.99 (d, J = 6.2 Hz, 8H), 7.89 (s, 4H), 7.47 (d, J = 4.9 Hz, 2H), 7.06 (s, 2H), 6.83 (dd, J = 6.0, 1.8 Hz, 4H), 6.76 (d, J = 3.4 Hz, 4H), 6.66 (d, J = 4.5 Hz, 2H), 3.73 (s, 3H), 1.22 (s, 36H), 1.11 (s, 18H). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 166.4, 165.0, 160.5, 157.3, 154.2, 153.7, 153.1, 152.7, 147.6, 146.4, 135.0, 128.9, 127.0, 124.9, 122.9, 120.9, 115.1, 107.1, 100.6, 67.0, 55.6, 52.0, 36.8, 36.0, 29.9, 29.6. ESI–MS m/z: [M – 2BF₄]²⁺, calcd for C₈₀H₇₅N₉OPt₂, 788.8087; found, 788.8057; error, 3.8 ppm.

![Figure S19. ¹H NMR spectrum (300 MHz, CDCl₃, room temperature) of 1b.](image)
Figure S20. $^{13}$C NMR spectrum (75 MHz, DMSO-$d_6$, room temperature) of 1b.

Figure S21. Electrospray ionization spectrum of 1b.
References: