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Supramolecular Engineering of Discrete Pt(II)…Pt(II) Interactions for Visible-Light Photocatalysis

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ABSTRACT: Visible-light photosensitizers have emerged as a sustainable and environmentally friendly medium for organic transformation. Herein, we have developed a supramolecular strategy to manipulate visible-light photosensitization and photocatalytic efficiencies. With the elaborate manipulation of aggregated Pt(II)···Pt(II) interactions, the discrete tetra-nuclear Pt complexes not only show high binding affinity ($K_a \sim 10^6 \text{ M}^{-1}$), but also feature bathochromic-shifted metal-metal-to-ligand charge transfer transitions. Both factors are crucial for their ${}^{1}\text{O}_{2}$ generation capability upon low-energy visible light irradiation ($\lambda \geq 590 \text{ nm}$). More interestingly, when terpyridine moiety is embedded in the structure of supramolecular photosensitizer, breakup of tetra-nuclear Pt(II)···Pt(II) complexation can be realized upon addition of Zn(OTf)₂. As a consequence, photo-oxidation of secondary amine to the corresponding imine can be deactivated and reactivated, *via* the sequential addition of Zn(OTf)₂ and unsubstituted terpyridine as the competitive ligand. Hence, the current study proves that intelligent visible-light photocatalysts can be achieved *via* rational supramolecular design.

KEYWORDS: Photocatalysis; photosensitizer; organometallic chemistry; Pt(II)…Pt(II) metal-metal bonds; supramolecular chemistry

Introduction

Visible-light photosensitizers, widely adopted by nature for photosynthesis, have also become a sustainable and environmentally friendly medium for artificial organic transformation.¹ To optimize the photocatalytic efficiency, precise manipulation of photosensitizers' photo-physics is of crucial importance. Especially, interplay between monomeric and π -aggregated optical signals needs to be addressed.²⁻³ Supramolecular engineering of the photosensitizers represents a feasible strategy to circumvent this issue. Currently, it mainly focuses on the noncovalent complexation of photosensitizers with macrocyclic receptors (such as cyclodextrins and cucurbiturils).⁴⁻⁹ These studies, despite recent advances, are restricted in the concept of hampering photosensitizers' π aggregation, thus leading to the predominance of monomeric optical signals. Conversely, deliberate utilization of π aggregated signals for photosensitization has been rarely exploited. One possible advantage for this approach is the employment of less destructive irradiation for photo-catalysis, since excitonic coupling of the photosensitizers gives rise to broader absorption ranges.¹⁰⁻¹¹ In addition, photosensitization and photocatalysis can be "on-demand" activated/deactivated, by exploiting the reversibility of π -aggregation process.¹²

Organoplatinum(II) complexes represent an intriguing building block to attain this objective, thanks to their squareplanar geometry and coordination-unsaturated property.¹³⁻¹⁶ For the resulting supramolecular organoplatinum assemblies, Pt(II)…Pt(II) metal-metal interactions tend to form,¹⁷⁻¹⁹ leading to the appearance of metal-metal-to-ligand charge transfer (MMLCT) optical transitions.²⁰⁻²² Due to the decrease of HOMO–LUMO gap,¹⁷ the MMLCT signals shift bathochromically than those of the parent organoplatinum species, which are promising for low-energy photosensitization in a reversible and highly controlled manner.

Herein, we sought to develop an unprecedented type of supramolecular visible-light photosensitizers and photocatalysts, which consist of discrete Pt(II)...Pt(II) metal-metal interactions. Specifically, pre-organized molecular tweezers 1a-b and 2 are designed (Scheme 1) and synthesized (Schemes S1-S3). Two cofacial electron-deficient alkynylplatinum(II) terpyridine and electron-rich isocyanideplatinum(II) diphenylpyridine pincers are incorporated into their structures, respectively. Upon mixing **1a-b** and **2** together, it is prone to form discrete tetra-nuclear Pt complexes (1a/2 or 1b/2, see Scheme 1), along with the emergence of MMLCT signals. As a consequence, highly reactive oxygen species tend to generate upon visible light irradiation, which can be successively utilized to oxidize amine **3** to the corresponding imine **4** (Scheme 1).²³⁻²⁶ Notably, we can modulate the stacking number of discrete Pt assemblies (tetra-nuclear complex 1a/2 versus the corresponding tri-nuclear complexes),²⁷⁻³⁵ facilitating to establish their structure-photocatalysis relationships. Furthermore, stimuliresponsive elements (such as cation-responsive terpyridine unit on 1b, Scheme 1) can be embedded in the molecular tweezer's rigid backbone, $^{36.39}$ and thereby enabling the switching-on and -off of photocatalytic efficiency. As a result, elaborate supramolecular control over noncovalent Pt(II)...Pt(II) interactions offers an efficient approach toward intelligent photosensitizers and photocatalysts.

Scheme 1. Schematic representation for the construction of discrete supramolecular platinum complexes 1a-b/2 for intelligent photosensitization and photocatalysis.



Results and discussion

Before studying heterodimeric recognition between **1a–b** and **2**, we first examined self-complexation behavior of the individual monomer. For **1a** in CHCl₃ solution, the MLCT/LLCT (metal-to-ligand and ligand-to-ligand charge transfer, $\lambda_{max} = 460$ nm) absorbance³⁰ obeys the Beer–Lambert law (Figures S2). Meanwhile, ¹H NMR spectra show slight resonance changes upon varying the concentration (Figure S1), denoting its rather weak self-association tendency. We rationalized that, due to the presence of sterically bulky *tert*butyl groups, intermolecular overlapping of alkynylplatinum(II) terpyridine pincers is severely inhibited.

In terms of **2**, polyhedral oligomeric silsesquioxane (POSS) is introduced to increase its solubility in CHCl₃. Based on the concentration-dependent ¹H NMR chemical shift changes, the homodimeric K_a value is determined to be 51.5 ± 16.9 M⁻¹ (Figure S3 and Eq. S1). Moreover, no Pt(II)…Pt(II) metal-metal interactions are involved in the self-complexation processes, as validated by the absence of MMLCT signals for either **1a** or **2**.

On this basis, equivalent amounts of **1a** (bright yellow solution) and **2** (colorless solution) were mixed together in CHCl₃, resulting in the appearance of a dark brown color (Figure 1, inset). Simultaneously, a new UV-Vis absorption centered at 564 nm emerges (Figure 1a), which is bathochromic-shifted than the MLCT/LLCT absorption of **1a** ($\lambda_{max} = 460$ nm) and intra-ligand absorption⁴⁰ of **2** ($\lambda_{max} = 350$ nm). In addition, complex **1a**/2 shows a low-energy emission band in the near-infrared region ($\lambda_{max} = 800$ nm, Figure 1b). With reference to the previous literatures,³⁰ these red-shifted spectroscopic bands suggesting the close proximity of Pt atoms in complex **1a**/2.

Non-covalent binding thermodynamics was further investigated. Depending on the isothermal titration calorimetry (ITC) experiment, the binding stoichiometry between 1a and 2 is determined to be 1 : 1, as manifested by the abrupt change in the titration curve (Figure 1c). Fitting the exothermic isotherm data with one-site model provides the K_a value of (2.89 \pm 0.23) $\times 10^6$ M⁻¹ for complex **1a**/2. Comparable value ($K_a = (4.55 \pm$ $(0.89) \times 10^6 \text{ M}^{-1}$) is acquired from UV–Vis titration measurement, by fitting (Eq. S2) the collected MMLCT absorbance at 550 nm (Figure 1a, inset). For complex 1b/2, similar binding affinity is obtained $(K_{a, \text{ITC}} = (4.36 \pm 0.83) \times 10^6 \text{ M}^{-1}, K_{a, \text{UV-Vis}} = (7.03 \pm 0.84) \times 10^6 \text{ M}^{-1}$, Figure S12–S13). It is worthy to note that the binding affinity of tetra-nuclear complex 1a/2 (or 1b/2) is 2-3 order of magnitude higher than those of the tri-nuclear Pt counterparts 1a/6 and 2/5 (structures of 5-6, see Figure 2; $K_{a, \text{UV-Vis}} = (5.67 \pm 0.47) \times 10^4 \text{ M}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ J}^{-1} \text{ for } \mathbf{1a/6} \text{ and } (5.05 \pm 0.26) \times 10^{-1} \text{ J}^{-1} \text{ J}^$ 10^3 M⁻¹ for 2/5, Figures S8 and S11). Such results illustrate the huge impact of stacking number on the non-covalent binding strength.

The difference for non-covalent complexation among 1a/2, 1a/6 and 2/5 was further elucidated by means of ¹H NMR experiments. Briefly, for tri-nuclear Pt complexes 1a/6 and 2/5, their aromatic resonances are highly discernable at room temperature (Figure 2a–b). In stark contrast, broadened and ill-resolved signals appear for complex 1a/2 (Figure 2c), denoting its relatively slow complexation/decomplexation exchange rates. Upon elevating the temperature to 373 K, the exchange rates are dramatically accelerated, giving rise to sharpened and well-defined peaks for the aromatic resonances of 1a/2 (Figure 2d). Remarkably, when comparing to those of the individual monomer (Figure 2d–f), the terpyridine protons on 1a and diphenylpyridine protons on 2 undergo drastic upfield shifts (– 0.50, –0.60, –0.36, –0.42, –0.75 and –0.64 ppm for H₁₋₄ and H_{d-e}, respectively). Meanwhile, protons H₅ and H_g, which lo-

cate in the inner cavity of 1a and 2, shift to the downfield region (0.32 and 0.39 ppm, respectively) in 1a/2. Hence, it can be concluded that non-covalent complexation between 1a and 2 maintains even at high temperature.



Figure 1. a) UV-Vis spectra of 1a (blue line), 2 (black line), and complex 1a/2 (red line) in CHCl₃ (c = 0.20 mM). Inset: intensity changes of UV-Vis absorbance at 550 nm, upon titrating 2 into the CHCl₃ solution of 1a. b) Fluorescent spectra of 1a (blue line) and 1a/2 (red line) in CHCl₃ (c = 0.20 mM). c) ITC data performed by consecutive injecting of 1a (4.00 mM in CHCl₃) into the CHCl₃ solution of 2 (0.20 mM). Inset: colors of 1a, 2, and complex 1a/2 (0.20 mM in CHCl₃). d) Optimized structure of 1a/2 *via* DFT calculation.

Deeper insights into the non-covalent complexation structure were achieved by means of DFT (density functional theory) calculations. For the optimized geometry of 1a/2 (Figure 1d and Figure S14), quadruple stacking of Pt atoms is validated by the short Pt---Pt distances of 3.43, 3.43 and 3.50 Å. Hence, it supports the existence of Pt(II)...Pt(II) metalmetal interactions, which coincides very well with the aforementioned UV/Vis and fluorescent measurements. Meanwhile, the inter-planar distances between alkynylplatinum(II) terpyridine and isocyanideplatinum(II) diphenylpyridine pincers are determined to be 3.43, 3.61 and 3.54 Å, respectively, revealing the mutual π -intercalation character of 1a/2. Accordingly, the high binding affinity of 1a/2 can be ascribed to the implement of multivalent donoracceptor and Pt---Pt metal-metal interactions in a synergistic manner.

Subsequently, we turned to examine visible-light photosensitization behavior of the tetra-nuclear Pt complex **1a/2**. In detail, when photo-exciting the mixture of **1a/2** and diamagnetic 2,2,6,6-tetramethylpiperidine (TEMP) with an OLED lamp (12 w, 590 nm), three lines with equal intensity are observed in electron paramagnetic resonance (EPR) spectrum (Figure 3a). It indicates the capture of singlet oxygen ($^{1}O_{2}$) generated *in-situ* by TEMP, leading to the formation of TEMPO radical. On the other hand, when 5,5-dimethylpyrroline-*N*-oxide (DMPO), a superoxide radical anion (O_2^-) scavenger, is utilized instead of TEMP, the O_2^- adduct with DMPO can be hardly detected in the presence of **1a/2** (Figure S15). From these results, it is apparent that 1O_2 , rather than O_2^- , is the active reactive oxygen species during the visible-light photosensitization process.²⁶



Figure 2. Partial ¹H NMR spectra (300 MHz, $C_2D_2Cl_4$, 2.00 mM for each monomer) of a) 1a/6; b) 2/5; c) 1a/2 at 298 K; and d) 1a/2; e) 1a and f) 2 at 373 K.

¹O₂ photosensitization capability was further verified via UV-Vis experiments, by monitoring time-dependent absorbance of 9,10-dimethylanthracene (DMA) at 401 nm (Figure S16). Since DMA is rapidly consumed by ${}^{1}O_{2}$ to afford 9,10-dimethylanthracene-9,10-endoperoxide, the absorption of DMA completely decays within 60 min. Photogeneration of ¹O₂ can be explained as follows: due to the spectral overlapping between photo-irradiation wavelength and MMLCT absorption, 1a/2 is excited and inter-system crossed to the triplet excited state, which undergoes successive energy transfer with the surrounding oxygen.¹⁴ On the contrary, slight changes of EPR and UV-Vis signals occur for either 1a or 2 (Figure 3a and Figure S16), ascribed to the absence of MMLCT transitions for the individual species.

Considering that tri-nuclear Pt complexes 1a/6 and 2/5 also possess MMLCT absorbance ($\varepsilon_{max} = 2.70 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and 0.68 × 10³ dm³ mol⁻¹ cm⁻¹ for $\lambda = 564$ nm, respectively), their ¹O₂ generation capabilities were further evaluated and compared with those of 1a/2 ($\varepsilon_{max} = 5.66 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). When the monomer concentration is 1 × 10⁻⁵ M, ¹O₂ generation rate of 1a/2 (727 min⁻¹•M⁻¹) is nearly one-fold higher than that of 1a/6 (348 min⁻¹•M⁻¹), and significantly higher than that of 2/5 (75 min⁻¹•M⁻¹) (Figure 3b, Figure S17– S19 and Eq. S3). More interestingly, when lowering the concentration to 1 × 10⁻⁶ M, ¹O₂ production capability shows a slight drop for 1a/2 (669 min⁻¹•M⁻¹), whilst 1a/6 suffers from 7 times decrease (49 min⁻¹•M⁻¹) (Figure 3b). In view of the fact that both 1a/2 and 1a/6 are in dynamic equilibrium between complexed and uncomplexed states, we resorted to mathematical calculation to elucidate their distinct behaviors (Eq. S4). Briefly, when the concentration reaches 1×10^{-6} M, only 5.4% of **1a/6** exists in the complexed form, which acts as the active species for photosensitization. In contrast, the complexed species accounts for 62.7% in terms of **1a/2**. Such results definitely support that, besides the emergent bathochromic-shifted MMLCT band, non-covalent binding strength also plays a key role for the visible-light photosensitization efficiency.



Figure 3. a) EPR spectra (0.02 mM in CHCl₃) of 1a/2 (red line), 1a (blue line), and 2 (black line), in which TEMP captures ${}^{1}O_{2}$ generated *in-situ via* visible light irradiation (590 nm, 12 W). b) Concentration-dependent ${}^{1}O_{2}$ generation capability of 1a/2 (\blacksquare), 1a/6 (\blacksquare) and 2/5 (\blacksquare).

Table 1. Photo-catalytic oxidation of **3** to **4**.^[a]

\land		Catalys	t, purging O_2		\gg
	∫ ∦ ` 3		2590 mm, 100		4
Entry	Catalyst	Time [h]	Conversion [%]	Yield [%]	TON [h
1	1a/2	6	100	98	163.3
$2^{[b]}$	1a/2	3	100	96	160.0
3 ^[c]	1a/2	12	97	92	153.3
4	1a/6	6	49	47	80.0
5	2/5	6	12	11	18.0
$6^{[d]}$	1a/2	24	7	n.d.	
$7^{[e]}$	1a/2	24	2	n.d.	
8 ^[f]	1a/2	3	100	96	320.0
9 ^[g]	1a/2	0.8	100	97	1212.5
10	1b/2	6	100	96	160.0

[*a*] Amine (5.00 mmol/L), photosensitizers (0.1 mol%), CHCl₃ (10 mL), O₂ bubbling in 10 seconds. After reaction, the solvent was evaporated and

the residue was subjected to ¹H NMR analysis. Conversion was determined by crude ¹H NMR analysis using 4,4'-dimethyl-2,2'-bipyridine as the internal standard, while yield was calculated based on the starting amount of substrate. Same reaction conditions described in [*a*] were proceeded except that: [*b*] catalyst loading was 0.2 mol%; [*c*] catalyst loading was 0.05 mol%; [*d*] N₂ was purged into the solution for 30 seconds; [*e*] the solution was kept in darkness; [*f*] CHCl₃/CH₃CN (2 : 1, *v*/*v*) and [*g*] CHCl₃/CH₃CN (1 : 3, *v*/*v*) were employed as the solvent. *n.d.* = not determined.

Due to the high reactivity of ¹O₂, oxidation of secondary amine 3 to imine 4 was further investigated, by employing the discrete Pt complexes as the homogeneous photocatalysts (Table 1). Both complexes 1a/2 and 1b/2 show excellent conversion rates, as evidenced by the progressive decrease of the benzylic ¹H NMR resonance (3.73 ppm) on **3**, together with the gradual increase of imine signal (8.28 ppm) on 4 (Figure S20). When 0.10 mol% of 1a/2 is loaded, 100% conversion with 98% product yield (85% isolation yield, Table S1) can be achieved upon 6 h irradiation (entry 1 in Table 1). TON (turnover number) values show slight changes upon varying the amount of 1a/2 (0.05-0.20 mol%) (entries 2-3), while they increase remarkably in polar medium (entries 8-9). In sharp contrast, the photocatalytic efficiency declines significantly for the tri-nuclear Pt counterparts 1a/6 (49% conversion, TON $= 80.0 \text{ h}^{-1}$, entry 4) and 2/5 (12% conversion, TON = 18.0 h^{-1} , entry 5). Such phenomena should be ascribed to their weakened photosensitized ¹O₂ generation capabilities. No conversion can be detected with the absence of oxygen or light (entries 6–7), validating that ${}^{1}O_{2}$ is the active oxidant during the organic transformation process.



Figure 4. a) UV/Vis spectral changes of **1b**/2 in CHCl₃/CH₃CN (2 : 1, v/v) upon sequential addition of Zn(OTf)₂ and terpyridine. Inset: intensity changes of absorbance at 563 nm upon sequential addition of Zn(OTf)₂ and terpyridine. b) Photo-catalytic conversion of **3** to **4** upon

sequential addition of $Zn(OTf)_2$ and terpyridine into 1b/2 (CHCl₃/CH₃CN (2 : 1, v/v)).

Finally, dynamic property of the non-covalent Pt complex 1b/2 was exploited, which provided an extra control over their photo-catalytic efficiency. As previously reported by Lehn et al., terpyridine and its derivatives are capable of displaying Zn^{2+} ion-controlled nanomechanical motion.³⁶⁻³⁹ Herein, upon adding 2 equivalent of Zn(OTf)2, conformational switch from U- to W-shape occurs for 1b (Scheme 1 and Figure S21). As a consequence, breakup of tetra-nuclear Pt complex 1b/2 can be directly reflected by 3-fold decrease of MMLCT absorbance intensity ($\lambda = 563$ nm, Figure 4a). Such phenomena denote the structural conversion from 1b/2 to $1b \cdot Zn^{2+}/2$ (Scheme 1 and Figure S22). Simultaneously, no conversion from amine 3 to imine 4 can be detected (Figure 4b). Deactivation of the photocatalytic efficiency should be primarily ascribed to the disruption of tetra-nuclear Pt(II)-Pt(II) interactions involved in **1b**/2, thus preventing ${}^{1}O_{2}$ generation for the resulting complex **1b**• $Zn^{2+}/2$ (Figure S23).⁴¹ When unsubstituted terpyridine (4 equivalence) was subsequently added and served as the competitive ligand, the original MMLCT signals completely restore (Figure 4a), accompanying with the re-activation of photocatalytic efficiency (Figure 4b and Figure S24). Remarkably, attributed to the fully reversibility of 1b/2 (Figure 4a, inset), sequential addition of Zn(OTf)₂ and terpyridine enables the revival and loss of the photo-catalytic properties for several repeated cycles (Figure 4b).

Conclusion

In summary, herein we have demonstrated the first example of supramolecular photosensitizers and photocatalysts derived from discrete Pt(II)...Pt(II) metal-metal complexation. The designed Pt complexes 1a-b/2 not only display strong binding strength, but also feature bathochromic-shifted MMLCT transition signals, both of which are crucial for their excellent ${}^{1}O_{2}$ generation capabilities upon low-energy visible light irradiation. More importantly, when terpyridine moiety is embedded in the rigid backbone of 1b, breakup of tetra-nuclear Pt(II)...Pt(II) complexation can be achieved upon adding $Zn(OTf)_2$ to the resulting supramolecular photosensitizer 1b/2. Consequently, photo-oxidation of secondary amine to the corresponding imine can be precisely deactivated/reactivated, upon the sequential addition of Zn(OTf)₂ and unsubstituted terpyridine as the competitive ligand. Hence, the current system opens up a new avenue toward smart photocatalytic materials via elaborate supramolecular design.

ASSOCIATED CONTENT

Supporting Information. Synthesis, characterization, UV-Vis, ¹H NMR and ITC titration data, photosensitization and photocatalytic experiments, theoretical calculations and other materials. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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Notes

The authors declare no completing interest.

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- 41. When complex 1a/2 is employed instead of 1b/2 for the photocatalytic transformation of 3 to 4, addition of $Zn(OTf)_2$ hardly influence the conversion efficiency (Figure S25). Hence, direct capture of singlet oxygen by $Zn(OTf)_2$ can be totally excluded. In other word, $Zn(OTf)_2$ is responsible for disrupting tetra-nuclear Pt(II)...Pt(II) interactions involved in 1b/2, thereby preventing the photocatalytic conversion.