

Vapochromic Behavior of a Chair-Shaped Supramolecular Metallacycle with Ultra-Stability

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S Supporting Information

ABSTRACT: A new discrete supramolecular metallacycle functionalized with an alkynylplatinum(II) bzimpy moiety was successfully prepared via coordination-driven self-assembly, and it displayed a reversible color change in the solid state between yellow and red, triggered by CH₂Cl₂ vapor or mechanical grinding. Notably, unlike many known vapochromic systems, the obtained vapochromic metallacycle exhibits ultra-stability, with the red color remaining unchanged in air for several months at room temperature or even under vacuum for >1 week. Further investigation revealed that the chair conformation of the metallacyclic scaffold, which was thought to prevent intermolecular steric repulsion between the alkyl chain and triethylphosphine, favored close molecular stacking through intermolecular Pt···Pt and π - π stacking interactions, thus allowing such vapochromic behavior with ultra-stability.

Vapochromic materials, which undergo reversible changes in color and/or emission upon exposure to certain volatile organic compounds, have recently received increasing attention because of their wide range of applications in, e.g., chemical sensors, light-emitting diodes, and environmental monitors.¹ In general, the vapor-induced alteration in the molecular packing in the solid state is believed to disturb intermolecular interactions such as hydrogen bonding and metal-metal and π - π stacking interactions, causing changes in the optical properties of vapochromic systems. Notably, although a large number of organometallic and coordination complexes have been extensively explored as vapochromic materials, many known vapochromic systems still suffer from poor stability.² For instance, upon exposure to air or vacuum, some vapochromic materials can desorb the vapor molecules and quickly restore their original color. The development of new vapochromic systems with high stability is in great demand so that vapochromic materials can be applied more widely in chemical sensors and electronic components.

Coordination-driven self-assembly has become one of the most attractive topics within supramolecular chemistry and materials science during the past few decades.³ Various discrete two-

dimensional (2-D) polygons and three-dimensional (3-D) polyhedra with well-defined shapes and sizes have been successfully developed from simple building blocks.⁴ Compared to an individual building block, a system having a well-defined metallacyclic scaffold at the core has been demonstrated to favor the formation of ordered aggregates because of the enhanced intermolecular interactions.^{5,6} Inspired by our previous successful constructions of functionalized discrete metallacycles,⁷ we envisioned that the introduction of the alkynylplatinum(II) bzimpy (bzimpy = 2,6-bis(benzimidazol-2'-yl)pyridine) moiety, a well-explored chromophore based on square-planar Pt(II) complexes,⁸ into a discrete metallacycle would result in a new family of functionalized metallacycles that exhibit novel spectroscopic properties not displayed by their individual components.

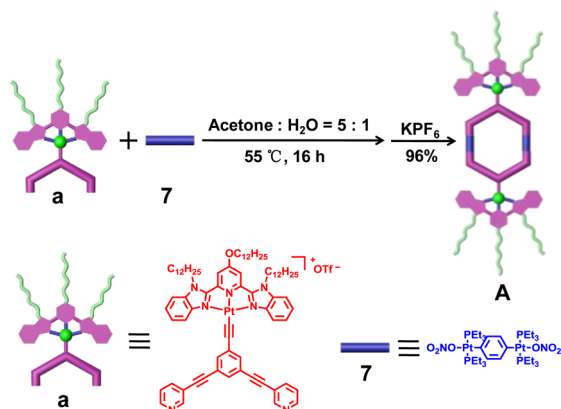
Here we present a new alkynyl-Pt(II)-functionalized supramolecular metallacycle that undergoes a color change from yellow to red in the solid state when exposed to CH₂Cl₂ vapor. Surprisingly, compared to the many known vapochromic systems, the resultant red solid sample was highly stable, maintaining its color in air for several months at room temperature or even under vacuum for >1 week. Our study of the mechanism revealed that such highly stable vapochromic behavior benefited from the chair conformation of the metallacyclic scaffold at the core, favoring close molecular stacking through intermolecular Pt···Pt and π - π stacking interactions, induced by the sorption of the CH₂Cl₂ vapor molecules. The close molecular stacking was highly stable and remained unchanged even after removal of the CH₂Cl₂ vapor molecules from the complexes. Further investigation revealed that, upon simple mechanical grinding, the red sample could revert to the original yellow species, thus exhibiting reversible color change behavior.

The synthesis procedure for the alkynyl-Pt(II)-containing dipyrindine donor **a** is described in the [Supporting Information \(SI\)](#), [Scheme S1](#). Functionalized metallacycle **A**, containing two alkynyl-Pt(II) bzimpy moieties, was then prepared by simply mixing the donor ligand **a** with the corresponding di-Pt(II) acceptor **7** in 1:1 ratio in a mixed solvent of acetone and water at 55 °C ([Scheme 1](#)). The structure of **A** was well characterized by multinuclear (¹H and ³¹P) NMR spectroscopy, which revealed

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Scheme 1. Self-Assembly of Dipyridyl Donor **a with the Corresponding Diplatinum(II) Acceptor **7** into Supramolecular Metallacycle **A****



discrete and highly symmetric species (SI, Figures S1 and S2). Its structure was further confirmed by ESI-TOF-MS, showing three peaks corresponding to different charge states resulting from the loss of PF_6^- counterions, $[\text{M} - 3\text{PF}_6^-]^{3+}$, $[\text{M} - 4\text{PF}_6^-]^{4+}$, and $[\text{M} - 5\text{PF}_6^-]^{5+}$, where M represents the intact assembly (SI, Figure S32). Further investigation revealed that the isotope pattern of each of these peaks agreed well with the corresponding simulated result.

All attempts to grow X-ray-quality single crystals of metallacycle **A** were unsuccessful. Thus, the PM6 semiempirical molecular orbital method was employed to optimize the molecular geometry of **A**. Unexpectedly, the metallacyclic scaffold at the core featured the chair conformation rather than the planar conformation in the optimized structure of **A** (Figure 1a). To further confirm the chair conformation of **A**, the model metallacycle **B** without the alkynyl-Pt(II) bzimpy moiety was designed and prepared (SI, Scheme S4). Fortunately, through the slow evaporation of a concentrated solution of **B** in CH_2Cl_2 , a white single crystal suitable for X-ray diffraction was obtained. X-ray crystallographic analysis revealed that the model **B** adopted a chair conformation in the solid state as well, which was in good agreement with the geometric structure of **A** obtained from molecular simulation (Figure 1b). The dihedral angle between the dipyridine donor and the di-Pt(II) acceptor was observed to be 149.7° .

The dried PF_6^- salt of **A** was obtained as a yellow solid (referred to as *Y-form*), which exhibited intense orange-yellow luminescence under irradiation at 365 nm at room temperature (SI, Figure S9). Surprisingly, exposing the *Y-form* sample to CH_2Cl_2 vapor

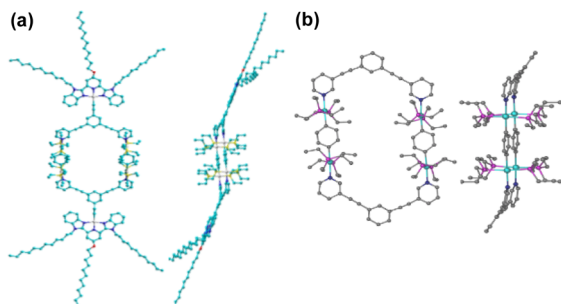


Figure 1. (a) Geometric structure of **A** optimized by the PM6 semiempirical molecular orbital method. (b) Single-crystal structure of **B** shown from different perspectives. H-atoms and hexafluorophosphate are omitted for clarity.

resulted in a distinct change of color from yellow to red within only 1 min (Figure 2a). Remarkably, the obtained red solid (referred to as *R-form*) was extremely stable, and the color remained almost unchanged in air for several months at room temperature. Notably, even after the removal of CH_2Cl_2 vapor molecules under vacuum for 1 week, the red color persisted without any obvious change. This property clearly differed from the properties reported for many known vapochromic systems, which usually recover their original color quickly when the absorbed organic vapors are removed in air or under vacuum.

To investigate the existence of CH_2Cl_2 vapor molecules in the red solid, we performed thermogravimetric analysis (TGA) experiments. As shown in Figure 2b, the TGA curves reveal that the *R-form* sample lost $\sim 3\%$ of its weight between 25 and 150°C , whereas the *Y-form* sample did not lose any weight until 200°C . The weight loss of the *R-form* sample between 25 and 150°C was attributed to the loss of CH_2Cl_2 molecules, and the molar ratio (dichloromethane (DCM):**A**) was determined to be 2:1. Note that the *R-form* sample dried under vacuum for 3 h (referred to as *R1-form*), which retained its red color, did not exhibit any weight loss between 25 and 200°C , indicating complete removal of the CH_2Cl_2 molecules from the *R-form* under vacuum. These results indicate that the vapochromic metallacycle was so stable that the red color of the *R-form* sample remained unchanged, even after complete removal of the CH_2Cl_2 molecules.

Subsequently, diffuse reflectance spectra and solid-state emission spectra of **A** in different forms were recorded at room temperature to compare their optical properties. As shown in Figure 2c, the main absorption of the original *Y-form* species was observed at 300–500 nm; this absorption was attributed to an admixture of the metal-to-ligand charge-transfer (MLCT) $[\text{d}\pi(\text{Pt}) \rightarrow \pi^*(\text{bzimpy})]$ and alkynyl-to-bzimpy ligand-to-ligand charge-transfer (LLCT) $[\pi(\text{alkynyl}) \rightarrow \pi^*(\text{bzimpy})]$ transitions.^{8c} However, in the case of both *R-form* and *R1-form*, the absorption bands at 300–500 nm decreased in intensity, with a concomitant increase in intensity of the absorption bands at $\lambda > 500$ nm. The latter absorption bands were assignable to the metal–metal-to-ligand charge-transfer (MMLCT) $[\text{d}\sigma^*(\text{Pt}) \rightarrow \pi^*(\text{bzimpy})]$ transition associated with formation of inter-

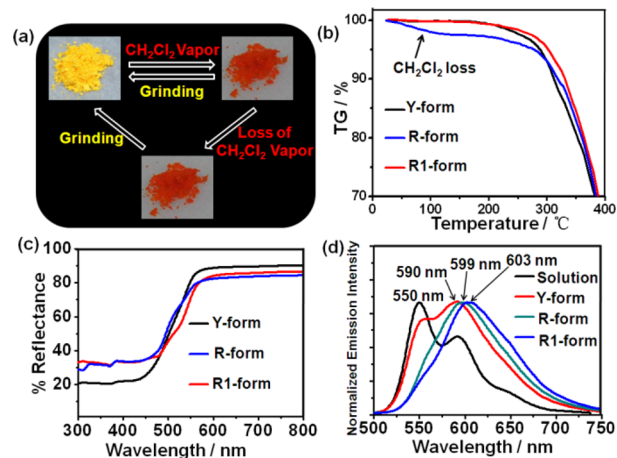


Figure 2. (a) Photographs showing the dynamic color changes under ambient light for the reversible vapochromic phenomenon of **A**. (b) TGA traces of **A** in different forms. (c) Diffuse reflectance spectra of **A** in different forms at room temperature. (d) Emission spectra of **A** in different forms and as a solution in DCM at room temperature ($\lambda_{\text{ex}} = 380$ nm).

molecular Pt...Pt and π - π stacking interactions. In addition, upon photoexcitation at 380 nm, the Y-form was observed to give an intense emission band at 590 nm with a shoulder peak at 550 nm in the solid state, similar to the emission band of the Y-form in a dilute solution of DCM (Figure 2d). Note that the emission band at 550 nm is usually ascribed to the monomeric species of alkynyl-Pt(II) bzimpy complexes.^{8c} In the case of the R-form sample, the disappearance of the shoulder peak at 550 nm was observed to be accompanied by a 9.0 nm red-shift of the emission maximum, which indicates a decrease in the monomeric species and the formation of ordered aggregates driven by intermolecular Pt...Pt and π - π stacking interactions. Moreover, the fluorescence quantum yield was observed to decrease from 24.86% for Y-form to 4.77% for R1-form, consistent with the aggregation-caused quenching (ACQ) of the light emissions in the solid state. Notably, the R1-form showed an emission band similar to that of the R-form (Figure 2d), differing by only a slight red-shift (4 nm). All these results suggest that both the R-form and R1-form feature similar physicochemical properties.

Particularly, the vapochromic response of metallacycle **A** was highly selective. When the Y-form sample was exposed to different solvent vapors at room temperature, including vapors of tetrahydrofuran, ethyl acetate, methanol, ethanol, toluene, *n*-hexanes, and triethylamine, the yellow color did not change (Figure 3). Surprisingly, even with exposure to chloroform or carbon tetrachloride, which have structures similar to that of DCM, no obvious color change was observed. These results suggest that **A** is more sensitive to CH₂Cl₂ vapor than to other solvent vapors.

Although the obtained vapochromic system is very stable, the reverse color transformation was induced through mechanical force. For instance, when the R-form or R1-form sample was mechanically ground in a mortar using a pestle, the red-colored sample recovered its original yellow color. Upon further exposure of the resulting yellow powder to CH₂Cl₂ vapor, the red solid was re-formed. This reversible color change could be repeated at least three times without a discernible change in behavior (Figure 2a). The ¹H and ³¹P NMR spectra of the yellow powder obtained from the mechanical grinding process confirmed that the structure of functionalized metallacycle **A** remained intact during the mechanochromism cycle (SI, Figures S10 and S11).

To study the molecular packing mode, we analyzed both the Y-form and R1-form samples using powder X-ray diffraction (PXRD) (SI, Figure S12). The PXRD pattern of the initial yellow powder exhibited very broad diffraction signals. By contrast, after the yellow powder was exposed to CH₂Cl₂ vapor, the PXRD pattern of the resulting red powder exhibited intense and sharp reflection peaks, indicating an ordered aggregate structure. Furthermore, the morphology of **A** in different forms was studied by using scanning electron microscopy (SEM) and transmission

electron microscopy (TEM). As shown in SI, Figures S13–S18, the SEM and TEM images of the Y-form showed sphere-like structures (~2.0 μ m) with a relatively uniform distribution. However, in the R-form, a blocky morphology was observed. Along with the PXRD study, the SEM and TEM results imply that **A** features different packing patterns in its Y-form and R-form, resulting in the occurrence of different colors. Moreover, the R1-form sample possessed a morphology similar to that of the R-form sample, indicating that the packing pattern of the red solid was unchanged even after the complete removal of CH₂Cl₂ molecules.

To better understand the vapochromic behavior of **A**, ¹⁹⁵Pt solid-state NMR spectroscopy was investigated to provide direct information about the local environment of the Pt atoms (SI, Figures S19 and S20). The ¹⁹⁵Pt solid-state NMR spectrum of the initial yellow powder exhibited five peaks, among which peaks 1 and 2 exhibited substantial changes in intensity after the sample was exposed to CH₂Cl₂ vapor. We attributed these two peaks to the Pt atoms connected with the N atoms in the alkynyl-Pt(II) bzimpy moiety. The other three peaks, which displayed almost no change in intensity, are attributable to the Pt atoms connected to the triethylphosphine in acceptor **7**. To further confirm this deduction, we also analyzed the sample using ³¹P solid-state NMR spectroscopy. As shown in SI, Figure S21, the ³¹P solid-state NMR spectra of the yellow and the red samples did not exhibit any obvious difference, suggesting that the environment of the P atoms did not change after the sample was exposed to CH₂Cl₂ vapor. This finding further implies that the environment of the Pt atoms connected to the triethylphosphine should be same in both the yellow and red samples. The ¹⁹⁵Pt solid-state NMR experiments confirmed the different local environments of the Pt atoms within the alkynyl-Pt(II) bzimpy moiety in different forms, which may be related to the change in color.

With the aim of gaining further insight into the possible mechanism of the observed vapochromic behavior, DFT calculations were performed to elucidate the changes in the HOMO and LUMO energies of the alkynyl-Pt(II) bzimpy moieties in different forms (Figure 4; see details in SI). The calculation results revealed that, in the original Y-form, the alkynyl-Pt(II) bzimpy moieties were stacked in loose proximity, with an average Pt...Pt separation of 3.67 Å and a large HOMO–LUMO energy gap of 2.817 eV, indicating that the intermolecular π - π interaction in the Y-form was weak. However, upon exposure of the Y-form to CH₂Cl₂ vapor, the CH₂Cl₂ molecules could enter the crystal lattice of metallacycle, mainly driven by C–H(CH₂Cl₂)... π interactions between CH₂Cl₂ molecules and the alkynyl-Pt(II) bzimpy moieties,^{2c} inducing a change in the nature of the HOMO. With the CH₂Cl₂ molecules in the crystal lattice, a

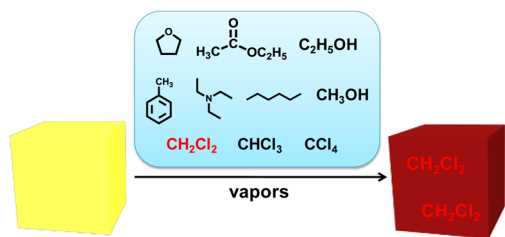


Figure 3. Selective vapochromic response of metallacycle **A** to CH₂Cl₂ vapor.

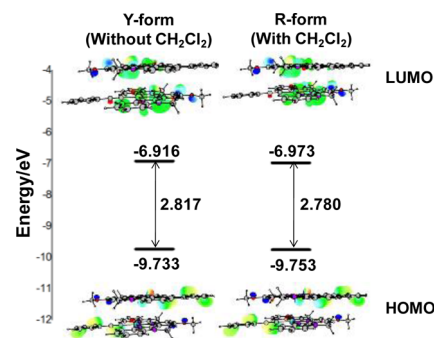


Figure 4. Frontier orbital energy levels and electron density of HOMO and LUMO for the alkynyl-Pt(II) bzimpy moieties in different forms.

decrease in the Pt...Pt distance (3.47 Å) and a lowering of the HOMO–LUMO energy gap (2.780 eV) were observed, indicating the enhanced intermolecular Pt...Pt and π – π stacking interactions, in good agreement with the result obtained from diffuse reflectance spectra. As a result of these changes, the loose arrangement of alkynyl-Pt(II) bzimpy moieties may transform into the close molecular stacking mode through intermolecular Pt...Pt and π – π stacking interactions, which was supported by the PXRD, SEM, and TEM studies. This alteration in the molecular packing is presumably responsible for the color change from yellow to red triggered by CH₂Cl₂ vapor.

Moreover, because of the strong intermolecular Pt...Pt and π – π stacking interactions along with the chair conformation of the metallacyclic scaffold that could avoid intermolecular steric repulsions between the alkyl chain and triethylphosphine, it was difficult to disrupt the close molecular stacking mode, which remained unchanged even after the removal of the CH₂Cl₂ vapor molecules in air or under vacuum. Thus, the obtained red sample was highly stable both in air and under vacuum. By contrast, when the red sample was mechanically ground, which provided sufficient energy to disrupt the intermolecular Pt...Pt and π – π stacking interactions, the close molecular stacking mode was destroyed, resulting in the loosened proximity and leading to the recovery of the original yellow color. Notably, no obvious color change was observed when yellow donor ligand **A** was exposed to CH₂Cl₂ vapor, indicating that the chair conformation of the metallacyclic scaffold favored the close molecular stacking through intermolecular Pt...Pt and π – π stacking interactions triggered by CH₂Cl₂ vapor molecules.

In conclusion, we demonstrated that the combination of an alkynylplatinum(II) bzimpy moiety with coordination-driven self-assembly leads to the formation of novel supramolecular metallacycle **A**, which displays a color change from yellow to red trigger upon exposure to CH₂Cl₂ vapor. The obtained vapochromic system features not only high selectivity toward CH₂Cl₂ vapor molecules but also ultra-stability. After exposure to CH₂Cl₂ vapor, **A** retained its red color in air for several months at room temperature or even under vacuum for >1 week, which is clearly different from the behaviors of many known vapochromic materials. The existence of a chair-shaped metallacycle at the core facilitates close molecular stacking through intermolecular Pt...Pt and π – π stacking interactions, thus allowing such a highly stable vapochromic system. This study not only represents one of very few examples of a vapochromic material with ultra-stability, which enriches the library of functionalized metallacycles with intriguing photophysical properties, but also provides new insight into the design of novel reversible vapochromic systems based on a well-defined discrete metallacycle as the main scaffold.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11409.

X-ray crystallographic data for **B** (CIF)

Experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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