pubs.acs.org/JACS

Drum-like Metallacages with Size-Dependent Fluorescence: Exploring the Photophysics of Tetraphenylethylene under Locked Conformations

Zhewen Guo,[#] Guangfeng Li,[#] Heng Wang, Jun Zhao, Yuhang Liu, Hongwei Tan, Xiaopeng Li, Peter J. Stang,* and Xuzhou Yan*



shifted fluorescence and attenuated quantum yield with the increase of their sizes. Furthermore, spectroscopic and computational studies together with a control experiment were conducted, revealing that the degree of cage tension imposed on the excited-state conformational relaxation of TPE moieties resulted in their distinct photophysical properties. The precise control of conformation holds promise as a strategy for understanding the AIE mechanism as well as optimizing the photophysical behaviors of materials on the platform of supramolecular coordination complexes.

INTRODUCTION

Fluorescent materials have gained extensive research interest in recent years due to their widespread applications in biological sensing,^{1,2} lighting devices,^{3,4} stimuli-responsive materials,^{5,6} and so on.^{7–11} However, traditional fluorophores oftentimes suffer from aggregation-caused quenching (ACQ) effects in condensed states wherein the fluorescence would be quenched precipitously because of the exciton interactions and non-radiative decays.^{12,13} This issue was subtly addressed when Tang et al. reported a completely opposite phenomenon known as aggregation-induced emission (AIE).^{14–16} In such cases, certain fluorogens that emit weakly in dilute solution become highly emissive in the aggregated state on account of the restriction of intramolecular rotation (RIR).¹⁷

Tetraphenylethylene (TPE) is an emblematic AIE fluorophore in which the initial free rotation of phenyl rings and distortion of C=C double bond would be restricted in the aggregated state.¹⁸ It is noteworthy that the TPE molecule is highly twisted, and different degrees of conformational distortion could lead to variable emissions.^{19,20} Typically, TPE fluorogens may continuously alter the resulting fluorescence, as long as the external stimulus causes the corresponding conformation change.²¹ For example, Zhou et al. reported a TPE-based metal–organic framework (MOF) exhibiting piezofluorochromic behavior due to conformational changes of the TPE linkers during the compression process.²² However, in all these cases, only the structures of the beginning and final states are known, and the details of the intermediate conformation of the TPE unit constitute a black box wherein the relationship between the distorted conformation and the accompanying fluorescence is rarely studied.

Supramolecular coordination complexes (SCCs), prepared via coordination-driven self-assembly, have been an emerging area of interest and offer a promising way to deal with the scientific question above.^{23–27} Discrete metallacages, a typical type of SCC, can be efficiently synthesized based on the spontaneous formation of labile metal–ligand bonds between ligands and metal acceptors.^{28–33} Through adjusting the angularity, directionality, and stoichiometry of the precursors, metallacages could possess well-defined sizes and shapes and

Received: April 24, 2021 **Published:** June 9, 2021



Article

pubs.acs.org/JACS

Article



Figure 1. Schematic representation of the formation of drum-like metallacages 1, 2, and 3 with different tensions and photophysics via coordination-driven self-assembly.



Figure 2. Simplified chemical structures of metallacages 1 (a), 2 (b), and 3 (c). Partial ¹H NMR spectra (400 MHz, DMSO- d_{60} 298 K) of ligand 4 (d, g, j), acceptors 5 (f), 6 (i), and 7 (l), as well as metallacages 1 (e), 2 (h), and 3 (k). ESI-TOF-MS spectra of metallacages 1 (m), 2 (n), and 3 (o).

serve as versatile platforms to explore AIE properties.^{34–38} Therefore, we expect that metallacages can be applied to

regulate the conformation of the TPE core when incorporated into such systems. It is reasonable that even subtle modulation



Figure 3. Ball-stick views of the optimized structures of metallacages 1 (a and d), 2 (b and e), and 3 (c and f). Carbon atoms are green, nitrogen atoms are blue, phosphorus atoms are brown, and platinum atoms are gray.

may have a profound influence on the photophysical properties, and thereby the structure—property relationship could be investigated in detail at the level of the molecular structure.

Herein, we designed a suite of TPE-based drum-like metallacages, 1, 2, and 3, with increasing sizes via coordination-driven self-assembly to explore the emission property of TPE in multiple locked conformations (Figure 1). In the fine structure of these metallacages, the TPE-based tetrapyridyl ligand was combined with suitable mono-, di-, and terphenyl-bridged organoplatinum(II) acceptors. The cage matrix would restrict the ligands from further distortion, thus restraining the flexibility of the TPE core and leading to the enhanced emission. The feature of our design is that, with the TPE ligands and counterpart anions being the same, different tensions of the metallacages would induce the TPE core to take different conformations, which presumably would impact the resulting fluorescent properties. In order to get rid of interference, we used the metallacycle as the comparison to exclude the conjugation effect. We expect that the conformation-locking strategy using metallacages may further contribute to a better understanding of structure-property relationships as well as offering a facile way of tuning the emission.

RESULTS AND DISCUSSION

According to the principle of coordination-driven selfassembly, the directionality and angularity of each component will determine the final structure. In this study, we combined TPE-based tetrapyridyl ligand 4 with different lengths of di-Pt(II) acceptors, 5, 6, and 7, to construct metallacages 1 (Figure 2a), 2 (Figure 2b), and 3 (Figure 2c), respectively. The mixture of ligand 4 and each di-Pt(II) acceptor in a 1:2 ratio was heated to 70 °C in deuterated DMSO and then stirred for 8 h. The three self-assembled metallacages were obtained respectively in almost quantitative yield.

The reaction mixture and ligand 4 were characterized through multinuclear 1H and $^{31}P\{^1H\}$ NMR (Figures 2e,h,k

and \$30). The results supported the formation of discrete multi-TPE metallacages. In the ¹H NMR spectrum of metallacage 1 (Figure 2e), distinct signals $H_{a-f,1}$, corresponding to coordinated structures, were assigned with downfield shifts relative to those of ligand 4 (Figure 2d,g,j) and acceptor 5 (Figure 2f). The H_a protons on the pyridine rings were split into two sets upon metal coordination, which is consistent with the previously reported SCC structures.^{39,40} Metallacages 2 and 3 also displayed a similar trend wherein all the proton signals corresponding to pyridine and phenyl rings exhibited downfield shifts and broadening (Figure 2h,i,k,l). The typical downfield shifts were due to the formation of Pt-N coordination bonds that reduced the electron density of the original moieties. 2D ¹H diffusion-ordered spectroscopy (DOSY) also suggested the formation of single products with diffusion coefficients (D) of $5.56 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for 1 (Figure S12), $5.05 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for 2 (Figure S19), and 4.24 \times 10⁻⁹ m² s⁻¹ for 3 (Figure S26). The ³¹P{¹H} NMR spectra of metallacages 1, 2, and 3 exhibited doublets (ca. 13.88 and 14.10 ppm for 1, 14.46 and 14.65 ppm for 2, as well as 14.43 and 14.62 ppm for 3) with concomitant ¹⁹⁵Pt satellites, which could be attributed to the different chemical environments of phosphorus inside and outside the metallacages. The NMR signals of metallacages 1, 2, and 3 were shifted upfield from those of Pt(II) acceptors by approximately 6.09, 6.26, and 6.23 ppm, respectively. The coupling of the flanking ¹⁹⁵Pt satellites decreased (ca. $\Delta J = -140.3$ Hz for 1, $\Delta J = -143.9$ Hz for 2, $\Delta J = -136.2$ Hz for 3) due to the electron back-donation effect of metal coordination. The well-defined signals in both the ¹H and ³¹P{¹H} spectra of these species supported the formation of such discrete structures as simplex assemblies.

Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) is a highly reliable approach to characterize the stoichiometry of the multicharged supramolecular structures. In the ESI-TOF-MS spectra (Figure 2m-o), multiple prominent peaks of $[M - x(OTf)]^{x+}$ (x = 4-11) can be found that correspond to the [3+6] assembly with charge states resulting from the loss of the OTf⁻ counterions—

pubs.acs.org/JACS



Figure 4. (a) Absorption and (b) fluorescence spectra of ligand 4 and metallacages 1-3 in CH₂Cl₂ ($\lambda_{ex} = 350$ nm, $c = 10.0 \ \mu$ M). (c) Quantum yield and Stokes shift of metallacages 1-3 in CH₂Cl₂ ($\lambda_{ex} = 350$ nm, $c = 10.0 \ \mu$ M). (d) Absorption and (e) fluorescence spectra of ligand 4 and metallacycles 9-11 in CH₂Cl₂ ($\lambda_{ex} = 350$ nm, $c = 10.0 \ \mu$ M). (f) Fluorescence decay profiles of metallacages 1-3 ($\lambda_{ex} = 365$ nm, $c = 10.0 \ \mu$ M). Insets in (b) and (e): Photographs of the metallacages/metallacycles obtained under irradiation by a 365 nm UV lamp ($c = 10.0 \ \mu$ M).

for example, peaks at m/z = 1185.6371 corresponding to $[M - 70Tf]^{7+}$ for metallacage 1 (Figure 2m), m/z = 939.9957 corresponding to $[M - 90Tf]^{9+}$ for metallacage 2 (Figure 2n), and m/z = 990.6281 corresponding to $[M - 90Tf]^{9+}$ for metallacage 3 (Figure 2o). All the dominating sets of peaks were isotopically resolved and in good agreement with their calculated theoretical distributions. Moreover, different charge states revealed by traveling wave ion mobility-mass spectrometry (TWIM-MS) of these three metallacages had narrow drift time distributions, further indicating the formation of intact structures (Figures S15, S22, and S29). On the basis of the above combined results, it was confirmed that no other assemblies were constructed at a detectable level during the self-assembly process leading to these metallacages.

Given the difficulty of growing single crystals suitable for Xray diffraction, molecular simulations were performed to obtain further insight into the architectural features of these multi-TPE metallacages 1-3 (Figure 3a-c). The geometry optimizations were performed using Gaussian09 software⁴ by a semiempirical PM6 method in C_3 symmetry, and the PEt₃ ligands on the platinum atoms were simplified as PH₃. The simulated structure of metallacage 1 possessed a well-defined drum-shaped structure with a ca. $1.2 \times 2.3 \times 1.2$ nm cavity (Figure 3d). The molecular simulations showed very similar drum-like structures for metallacages 2 and 3, with increased cavity sizes $(1.2 \times 2.5 \times 1.2 \text{ nm for } 2 \text{ and } 1.2 \times 2.7 \times 1.2 \text{ nm}$ for 3) (Figure 3e,f). The simulated structures suggested that metal coordination induced the TPE ligands to adopt the twisted conformations and further restrained their intramolecular rotation in the metallacages, which is responsible for the enhanced emission (vide infra). It is notable that, as the metallacages increase in size, they become more capacious and allow more intramolecular movement of the TPE-based ligands.

After the successful synthesis of these metallacages, their photophysical properties were studied. The normalized absorption spectra of ligand 4 and metallacages 1-3 are

shown in Figure 4a. Ligand 4 displayed two broad absorption bands with peaks at ca. 310 and 345 nm. After metal coordination, all the metallacages only displayed single absorption bands at around 315 nm. These observations indicated that the metallacages possessed similar ground-state photophysical properties on account of the similar cage scaffolds while differing from ligand 4 due to the formation of N-Pt coordination bonds. Furthermore, fluorescence spectra of ligand 4 and metallacages 1-3 were recorded (Figure 4b). Ligand 4 was weakly emissive at ca. 519 nm in CH₂Cl₂, and the lack of emission originated from the nonradiative decay through the intramolecular rotation of pyridine and benzene rings. After the TPE-based ligands were anchored into metallacages, they exhibited salient fluorescence enhancements with variable emission maxima. In the emission profile of metallacage 1, which was the smallest size and owned the highest tension, the maximum emission wavelength blueshifted to 466 nm. A trend of red-shifted emission for 2 (491 nm) and 3 (507 nm) was observed, which can be attributed to the decrease in the conformational restraint. The red shift of the emission is clearly visualized as depicted in the fluorescence images of 1-3 (inset in Figure 4b). Also, the energy differences between absorption and emission were further translated into Stokes shifts (Figure 4c). The changes in Stokes shifts are presented in the order of 1 (1.32 eV) < 2(1.44 eV) < 3 (1.52 eV). These results implied that the degree of conformational relaxation for the metallacages was in the order of 1 < 2 < 3 induced by cage tension. Given that these metallacages emitted effectively even in dilute solvent, the quantum yields $(\Phi_{\rm F})$ of 1-3 in CH₂Cl₂ solution were also recorded. The values were measured as 18.4% for 1, 12.5% for 2, and 10.2% for 3, displaying a decreasing trend. Because metallacage 1 has a smaller skeleton which may induce more restriction on the intramolecular movements of TPE units, it exhibited better fluorescent performance than those of 2 and 3.

To exclude the influence of conjugation of the phenyl groups and achieve a thorough understanding of our system, a

Journal of the American Chemical Society

control experiment was carried out in which discrete metallacycles with similar scaffolds were designed and synthesized. In this case, all the di-Pt(II) acceptors 5-7were kept unchanged except for the replacement of tetrapyridyl ligand 4 by bipyridyl ligand 8, leading to the formation of 2D metallacycles 9, 10, and 11 (Figure S31). Our design ensures that the cages and cycles have the same conjugated structure but different frameworks to constrain the TPE units. Multinuclear NMR (${}^{1}H$ and ${}^{31}P{}^{1}H$) together with ESI-TOF-MS confirmed the formation of metallacycles 9-11 with undetectable impurities (Figures S32-S40). The absorption and emission profiles were depicted in the same way as for the metallacages. As expected, the absorption spectra of metallacycles 9-11 (Figure 4d) were almost identical to those of the corresponding metallacages 1-3 on account of the same absorption groups (Figures S41-S43). However, due to the presence of freely rotating phenyl rings and C=C double bonds that led to the nonradiative decay, the fluorescence intensity of the metallacycles decreased significantly relative to the metallacages (Figure 4e). Meanwhile, all the metallacycles displayed identical emission maximum at ca. 480 nm, indicating no change of the Stokes shift with different ring sizes. Therefore, the conjugation of the phenyl groups in the acceptors had little influence on the emission behaviors of the assemblies, while the restriction of conformation played a key role.

Furthermore, the time-resolved fluorescence decay of the multi-TPE metallacages 1-3 was recorded in CH₂Cl₂ solutions (Figure 4f). Each dynamic decay was fitted well with a doubleexponential curve of τ_1 (around 10 ps) and τ_2 (around 1 ns) components (Figures S54-S59). The coefficients of the component au_1 displayed negative amplitudes, which were associated with the geometry relaxation from the Franck-Condon configuration, while the second component τ_2 represented the nonradiative decay of the excited state. The time constants τ_1 for the metallacages followed the order of 1 (10 ps) < 2 (13 ps) < 3 (14 ps), and this could be related to the cage tension at the excited state. As discussed above, the trend of the Stokes shifts, quantum yields, and the fluorescence lifetimes corresponding to the degree of conformational relaxation was unified and self-consistent, which affirmed that even subtle conformational differences could have a significant influence on the light-emitting properties of multi-TPE materials.

To obtain better insight into the structure-property relationship, a computational analysis was also performed. By comparing the structure of ligand 4 moieties in the three metallacages, we found that the size and shape of the rectangle framework formed between four nitrogen atoms were slightly different, with 12.6 \times 11.1 Å for metallacage 1, 12.3 \times 11.4 Å for metallacage 2, and 12.1×11.6 Å for metallacage 3 (Figure S64). It is plausible that these small conformational changes reflected different degrees of constraint on TPE units in these metallacages. Furthermore, such a difference in cage tension could affect the structural relaxation in the excited state. In order to study the conformational change from the ground state to the excited state, the geometry of ligand 4 in the metallacage 1 was selected and optimized via the timedependent density functional theory (TDDFT) method with the CAM-B3LYP/6-31G* basis set^{42,43} (Figure 5a). The four N atoms were fixed to mimic the coordination environment. In the excited state, we found that the change of the dihedral angle between the phenyl ring and the ethylene plane ($\angle C1-$



Potential

Excited state

Ground state

Internuclear Separation

Figure 5. (a) Structures of ligand 4 in the ground state and optimized excited state with the recorded values for the bending angle Θ_a . (b) Relative energy calculated at different Θ_a angles in metallacages 1–3. (c) Schematic illustration of the Franck–Condon effect and Stokes shift.

130

C2–C3–C4, Θ_a) was dominant,^{21,44} while other distortions were negligible. Furthermore, metallacages 1, 2, and 3 were optimized while Θ_a was fixed at 100–130° (gradually closer to the excited state). The change of energy was recorded as shown in Figure 5b. Specifically, the increased energy (ΔE) exhibited a uniform order of 1 > 2 > 3 with variable Θ_a values, indicating that metallacage 1 required the highest energy for deformation in the excited state, followed by metallacages 2 and 3. According to the principle of vertical transition (Figure 5c), lower cage tension prolonged the relaxation time of conformational adjustment at the excited state and ultimately resulted in higher Stokes shift. Therefore, metallacage 3 allows the TPE unit to have the maximum Stokes shift and fluorescent lifetime, while metallacage 1 has the minimum.

CONCLUSION

а

60

40

20

0 🚧 100

110

120

 Θ_a (°)

Relative Energy (kcal/mol)

In summary, we have synthesized and characterized three multi-TPE metallacages with increasing sizes and further used these cages as the platform to investigate the conformational influence of TPE moieties on the resulting photophysical characteristics. A TPE-based tetrapyridyl ligand and three Pt(II) acceptors of incremental length were designed and synthesized by means of metal-coordination-driven selfassembly. This strategy allows for precise control on the restriction of the intramolecular rotation of anchored TPE cores. All the metallacages were characterized by multinuclear NMR and ESI-TOF-MS to denote the molecularity of these species. Although the three metallacages shared similar absorption peaks, they exhibited varying emission peaks and quantum yields due to different cage tension. In order to exclude the conjugation effect in the acceptors, a control experiment was conducted, wherein the metallacycles corresponding to the cages were designed and synthesized for further demonstration. The computational results confirmed that a metallacage with higher tension led to a smaller Stokes

Journal of the American Chemical Society

shift. These metallacages exhibited variable yet orderly emission behaviors depending on the size, which provided a whole new understanding of the intermediate conformations of TPE moieties in the deformation processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c04288.

Experimental details and additional data, including Figures S1–S67 and Tables S1–S5 (PDF)

AUTHOR INFORMATION

Corresponding Authors

Xuzhou Yan – School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P. R. China; orcid.org/0000-0002-6114-5743; Email: xzyan@sjtu.edu.cn

Peter J. Stang – Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, United States; O orcid.org/ 0000-0002-2307-0576; Email: stang@chem.utah.edu

Authors

 Zhewen Guo – School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Guangfeng Li – School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Heng Wang – College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518055, P. R. China

Jun Zhao – School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P. R. China; © orcid.org/0000-0003-0552-4885

Yuhang Liu – School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Hongwei Tan – Department of Chemistry, Beijing Normal University, Beijing 100050, P. R. China

Xiaopeng Li – College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518055, P. R. China; © orcid.org/0000-0001-9655-9551

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.1c04288

Author Contributions

[#]Z.G. and G.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

X.Y. acknowledges the financial support of the NSFC/China (21901161 and 22071152) and Interdisciplinary Program of Shanghai Jiao Tong University (YG2019QNA16). G.L. acknowledges the China Postdoctoral Science Foundation (2020M671094).

REFERENCES

(1) Sun, C.; Li, B.; Zhao, M.; Wang, S.; Lei, Z.; Lu, L.; Zhang, H.; Feng, L.; Dou, C.; Yin, D.; Xu, H.; Cheng, Y.; Zhang, F. J-Aggregates of Cyanine Dye for NIR-II in Vivo Dynamic Vascular Imaging beyond 1500 nm. J. Am. Chem. Soc. **2019**, *141*, 19221–19225.

(2) Sepehrpour, H.; Fu, W.; Sun, Y.; Stang, P. J. Biomedically Relevant Self-Assembled Metallacycles and Metallacages. J. Am. Chem. Soc. 2019, 141, 14005–14020.

(3) Wang, Z.; Zhu, X.; Zhang, S.; Xu, L.; Zhao, Z.; He, G. Twisted Biphenyl-Diimide Derivatives with Aggregation-Induced Emission and Thermally Activated Delayed Fluorescence for High Performance OLEDs. *Adv. Opt. Mater.* **2021**, *9*, 2001764.

(4) Zhang, H.; Zhang, B.; Zhang, Y.; Xu, Z.; Wu, H.; Yin, P. A.; Wang, Z.; Zhao, Z.; Ma, D.; Tang, B. Z. A Multifunctional Blue-Emitting Material Designed via Tuning Distribution of Hybridized Excited-State for High-Performance Blue and Host-Sensitized OLEDs. *Adv. Funct. Mater.* **2020**, *30*, 2002323.

(5) Zhang, J. C.; Pan, C.; Zhu, Y. F.; Zhao, L. Z.; He, H. W.; Liu, X.; Qiu, J. Achieving Thermo-Mechano-Opto-Responsive Bitemporal Colorful Luminescence via Multiplexing of Dual Lanthanides in Piezoelectric Particles and its Multidimensional Anticounterfeiting. *Adv. Mater.* **2018**, *30*, 1804644.

(6) Wang, S.; Yang, Y.; Shi, X.; Liu, L.; Chang, W.; Li, J. Multiple Stimuli-Responsiveness Fluorescent Probe Derived from Cyclopolymers and Pyrene-Ended Ammonium Salts. *ACS Appl. Polym. Mater.* **2020**, *2*, 2246–2251.

(7) Cai, X.; Liu, B. Aggregation-Induced Emission: Recent Advances in Materials and Biomedical Applications. *Angew. Chem., Int. Ed.* **2020**, 59, 9868–9886.

(8) Smith, A. M.; Mancini, M. C.; Nie, S. Bioimaging: Second Window for in vivo Imaging. *Nat. Nanotechnol.* **2009**, *4*, 710–711.

(9) Liu, S.; Chen, R.; Zhang, J.; Li, Y.; He, M.; Fan, X.; Zhang, H.; Lu, X.; Kwok, R. T. K.; Lin, H.; Lam, J. W. Y.; Qian, J.; Tang, B. Z. Incorporation of Planar Blocks into Twisted Skeletons: Boosting Brightness of Fluorophores for Bioimaging beyond 1500 Nanometer. *ACS Nano* **2020**, *14*, 14228–14239.

(10) Li, Y.; Tang, R.; Liu, X.; Gong, J.; Zhao, Z.; Sheng, Z.; Zhang, J.; Li, X.; Niu, G.; Kwok, R. T. K.; Zheng, W.; Jiang, X.; Tang, B. Z. Bright Aggregation-Induced Emission Nanoparticles for Two-Photon Imaging and Localized Compound Therapy of Cancers. *ACS Nano* **2020**, *14*, 16840–16853.

(11) Acharyya, K.; Bhattacharyya, S.; Sepehrpour, H.; Chakraborty, S.; Lu, S.; Shi, B.; Li, X.; Mukherjee, P. S.; Stang, P. J. Self-Assembled Fluorescent Pt(II) Metallacycles as Artificial Light-Harvesting Systems. J. Am. Chem. Soc. **2019**, 141, 14565–14569.

(12) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission. Chem. Soc. Rev. 2011, 40, 5361-5388.

(13) Huang, Y.; Xing, J.; Gong, Q.; Chen, L. C.; Liu, G.; Yao, C.; Wang, Z.; Zhang, H. L.; Chen, Z.; Zhang, Q. Reducing Aggregation Caused Quenching Effect Through Co-Assembly of PAH Chromophores and Molecular Barriers. *Nat. Commun.* **2019**, *10*, 169.

(14) Luo, J.; Xie, Z.; Lam, J. W.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. Aggregation-Induced Emission of 1-Methyl-1,2,3,4,5-Pentaphenylsilole. *Chem. Commun.* 2001, 1740–1741.

(15) Mei, J.; Leung, N. L.; Kwok, R. T.; Lam, J. W.; Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **2015**, *115*, 11718–11940.

(16) Kenry; Tang, B. Z.; Liu, B. Catalyst: Aggregation-Induced Emission—How Far Have We Come, and Where Are We Going Next? *Chem.* **2020**, *6*, 1195–1198.

(17) Mei, J.; Hong, Y.; Lam, J. W.; Qin, A.; Tang, Y.; Tang, B. Z. Aggregation-Induced Emission: The Whole is More Brilliant than the Parts. *Adv. Mater.* **2014**, *26*, 5429–5479.

(18) Guan, J.; Wei, R.; Prlj, A.; Peng, J.; Lin, K. H.; Liu, J.; Han, H.; Corminboeuf, C.; Zhao, D.; Yu, Z.; Zheng, J. Direct Observation of Aggregation-Induced Emission Mechanism. *Angew. Chem., Int. Ed.* **2020**, *59*, 14903–14909.

Journal of the American Chemical Society

pubs.acs.org/JACS

(19) Xiong, J. B.; Yuan, Y. X.; Wang, L.; Sun, J. P.; Qiao, W. G.; Zhang, H. C.; Duan, M.; Han, H.; Zhang, S.; Zheng, Y. S. Evidence for Aggregation-Induced Emission from Free Rotation Restriction of Double Bond at Excited State. *Org. Lett.* **2018**, *20*, 373–376.

(20) Guo, Z.; Zhao, J.; Liu, Y.; Li, G.; Wang, H.; Hou, Y.; Zhang, M.; Li, X.; Yan, X. Conformational Effect on Fluorescence Emission of Tetraphenylethylene-based Metallacycles. *Chin. Chem. Lett.* **2021**, *32*, 1691–1695.

(21) Shustova, N. B.; Cozzolino, A. F.; Dinca, M. Conformational Locking by Design: Relating Strain Energy with Luminescence and Stability in Rigid Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2012**, *134*, 19596–19599.

(22) Zhang, Q.; Su, J.; Feng, D.; Wei, Z.; Zou, X.; Zhou, H. C. Piezofluorochromic Metal-Organic Framework: A Microscissor Lift. *J. Am. Chem. Soc.* 2015, 137, 10064–10067.

(23) Islamoglu, T.; Goswami, S.; Li, Z.; Howarth, A. J.; Farha, O. K.; Hupp, J. T. Postsynthetic Tuning of Metal-Organic Frameworks for Targeted Applications. *Acc. Chem. Res.* **2017**, *50*, 805–813.

(24) Datta, S.; Saha, M. L.; Stang, P. J. Hierarchical Assemblies of Supramolecular Coordination Complexes. *Acc. Chem. Res.* **2018**, *51*, 2047–2063.

(25) Pan, M.; Liao, W. M.; Yin, S. Y.; Sun, S. S.; Su, C. Y. Single-Phase White-Light-Emitting and Photoluminescent Color-Tuning Coordination Assemblies. *Chem. Rev.* **2018**, *118*, 8889–8935.

(26) Sun, Y.; Chen, C.; Liu, J.; Stang, P. J. Recent Developments in the Construction and Applications of Platinum-based Metallacycles and Metallacages via Coordination. *Chem. Soc. Rev.* **2020**, *49*, 3889– 3919.

(27) Zhou, Z.; Chen, D. G.; Saha, M. L.; Wang, H.; Li, X.; Chou, P. T.; Stang, P. J. Designed Conformation and Fluorescence Properties of Self-Assembled Phenazine-Cored Platinum(II) Metallacycles. *J. Am. Chem. Soc.* **2019**, *141*, 5535–5543.

(28) Chen, L.; Chen, Q.; Wu, M.; Jiang, F.; Hong, M. Controllable Coordination-driven Self-Assembly: From Discrete Metallocages to Infinite Cage-based Frameworks. *Acc. Chem. Res.* **2015**, *48*, 201–210.

(29) Wang, S.; Gao, X.; Hang, X.; Zhu, X.; Han, H.; Liao, W.; Chen, W. Ultrafine Pt Nanoclusters Confined in a Calixarene-Based {Ni24} Coordination Cage for High-Efficient Hydrogen Evolution Reaction. J. Am. Chem. Soc. **2016**, 138, 16236–16239.

(30) Hou, Y.; Zhang, Z.; Lu, S.; Yuan, J.; Zhu, Q.; Chen, W. P.; Ling, S.; Li, X.; Zheng, Y. Z.; Zhu, K.; Zhang, M. Highly Emissive Perylene Diimide-Based Metallacages and Their Host-Guest Chemistry for Information Encryption. *J. Am. Chem. Soc.* **2020**, *142*, 18763–18768.

(31) Jin, Y.; Zhang, Q.; Zhang, Y.; Duan, C. Electron Transfer in the Confined Environments of Metal–Organic Coordination Supramolecular Systems. *Chem. Soc. Rev.* **2020**, *49*, 5561–5600.

(32) Yoshizawa, M.; Catti, L. Bent Anthracene Dimers as Versatile Building Blocks for Supramolecular Capsules. *Acc. Chem. Res.* 2019, 52, 2392–2404.

(33) Rizzuto, F. J.; von Krbek, L. K. S.; Nitschke, J. R. Strategies for Binding Multiple Guests in Metal–Organic Cages. *Nat. Rev. Chem.* **2019**, 3, 204–222.

(34) Yan, X.; Cook, T. R.; Wang, P.; Huang, F.; Stang, P. J. Highly Emissive Platinum(II) Metallacages. *Nat. Chem.* **2015**, *7*, 342–348.

(35) Saha, M. L.; Yan, X.; Stang, P. J. Photophysical Properties of Organoplatinum(II) Compounds and Derived Self-Assembled Metallacycles and Metallacages: Fluorescence and its Applications. *Acc. Chem. Res.* **2016**, *49*, 2527–2539.

(36) Li, M.; Jiang, S.; Zhang, Z.; Hao, X.-Q.; Jiang, X.; Yu, H.; Wang, P.; Xu, B.; Wang, M.; Tian, W. Tetraphenylethylene-Based Emissive Supramolecular Metallacages Assembled by Terpyridine Ligands. *CCS Chem.* **2020**, *2*, 337–348.

(37) Zhang, Z.; Zhao, Z.; Wu, L.; Lu, S.; Ling, S.; Li, G.; Xu, L.; Ma, L.; Hou, Y.; Wang, X.; Li, X.; He, G.; Wang, K.; Zou, B.; Zhang, M. Emissive Platinum(II) Cages with Reverse Fluorescence Resonance Energy Transfer for Multiple Sensing. J. Am. Chem. Soc. 2020, 142, 2592–2600.

(38) Zhao, J.; Zhou, Z.; Li, G.; Stang, P. J.; Yan, X. Light-Emitting Self-Assembled Metallacages. *Nat. Sci. Rev.* **2021**, nwab045. (39) Mu, C.; Zhang, Z.; Hou, Y.; Liu, H.; Ma, L.; Li, X.; Ling, S.; He, G.; Zhang, M. Tetraphenylethylene-Based Multicomponent Emissive Metallacages as Solid-State Fluorescent Materials. *Angew. Chem., Int. Ed.* **2021**, *60*, 12293–12297.

(40) Yan, X.; Wang, H.; Hauke, C. E.; Cook, T. R.; Wang, M.; Saha, M. L.; Zhou, Z.; Zhang, M.; Li, X.; Huang, F.; Stang, P. J. A Suite of Tetraphenylethylene-Based Discrete Organoplatinum(II) Metallacycles: Controllable Structure and Stoichiometry, Aggregation-Induced Emission, and Nitroaromatics Sensing. J. Am. Chem. Soc. 2015, 137, 15276–15286.

(41) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian09, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2010.

(42) Petersson, A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. A Complete basis Set Model Chemistry. I. The Total Energies of Closed-Shell Atoms and Hydrides of the Firstrow Elements. J. Chem. Phys. **1988**, 89, 2193–2218.

(43) Petersson, G.; Al-Laham, M. A. A Complete basis Set Model Chemistry. II. Open-Shell Systems and the Total Energies of the Firstrow Atoms. J. Chem. Phys. **1991**, *94*, 6081–6090.

(44) Shustova, N. B.; Ong, T. C.; Cozzolino, A. F.; Michaelis, V. K.; Griffin, R. G.; Dinca, M. Phenyl Ring Dynamics in a Tetraphenylethylene-bridged Metal-Organic Framework: Implications for the Mechanism of Aggregation-Induced Emission. *J. Am. Chem. Soc.* **2012**, *134*, 15061–15070.

9221