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Synthesis of branched tetranuclear alkynylplatinum(II) terpyridine complexes and their photophysical properties

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ABSTRACT

Herein we report the synthesis of two luminescent branched tetranuclear alkynylplatinum(II) complexes $\{[Pt(tBu_3\text{-}tpy)]_2[Ar(C{\equiv}C)_4][Pt(tBu_3\text{-}tpy)]\}_2(PF_6)_4$ (**I** and **II**; tBu_3-tpy = 4,4′,4″-tri-tertbutyl-2,2′:6′,2″-terpyridine; Ar = $[(C_6H_4)_2(C{\equiv}C{-}C{\equiv}C)]$). Two terminal alkyne ligands were synthesized by oxidative coupling in the air, and subsequently reacted with a chloroplatinum(II) terpyridine complex. Their photophysical properties have been studied by both steady-state spectroscopy and transient spectroscopy. The final two platinum(II) complexes were found to show long-lived excited states in solution at room temperature. The longest lifetime of ~17 μs for the twisted branched molecule was observed in toluene at room temperature. Application of the two complexes as a light-harvesting chromophore in photocatalytic hydrogen production was further examined.

Introduction

The rich luminescent behaviors in functional organic and organometallic molecules have attracted great interest over the past few decades. Photoactive organometallic complexes represent one class of such molecules, showing intriguing photochemical and photophysical properties.[1,2] The main potential applications of these complexes include organic light-emitting devices, luminescent sensors, nonlinear optical devices, photovoltaic cells, and solar energy conversion.[1b,3] Although a large number of linear multinuclear alkynylplatinum(II) complexes have been synthesized and their optical properties have been studied, the research on branched molecules based on alkynylplatinum(II) moiety has barely been explored. In 2011, Yam and co-workers[4] and Yang and co-workers,[5] respectively reported a series of tetranuclear alkynylplatinum(II) phosphine complexes and found that tetra- and hexanuclear platinum(II) complexes showed better two-photon absorption and two-photon induced luminescent properties than their di- and trinuclear analogues. The branched alkynyl ligands, which directly coordinated to the metallic centers, could also play a critical role in luminescence properties of the platinum(II) complexes. Herein we report the synthesis, characterization, and photophysical properties of two branched tetranuclear alkynylplatinum(II) terpyridyl complexes linking by rigid conjugated tetrayne backbones, which may be potentially utilized as photoactive organometallic materials.

Branched tetranuclear complexes **I** and **II** are designed and shown in Scheme 1. We envisage that the steric effect between the terpyridine part and alkyne part could greatly affect the photophysical properties. Therefore, as an isomeric analogue of complex **I**, more sterically hindered compound **II** was designed to examine how the square-planar or distorted square-planar coordination geometry changes the photophysical properties of these two platinum(II) complexes. After investigating the luminescent properties of **I** and **II** in different organic solvents, it was found that the twisted complex **II** in toluene has the longest lifetimes. Furthermore, complexes **I** and **II** have been examined for the application of photocatalytic hydrogen production.

Results and discussion

Starting from the commercially available 2,6-dibromo-4-nitroaniline **3**, compound **4** was prepared by removal of the amino group according to the literature procedures,[6] followed by hydrogenation of the nitro group by Raney nickel in ethanol at room temperature (Scheme 2). Aniline **4** was transformed to iodide **5** by diazotization and iodination. Then, conversion of iodide **5** to compound **7** was achieved by Sonogashira coupling with trimethylsilylacetylene (TMSA) and (triisopropylsilyl)acetylene (TIPSA), successively. Selective desilylation of compound **7** gave terminal alkyne **8**. The branched tetrayne precursor **1**[7] was finally

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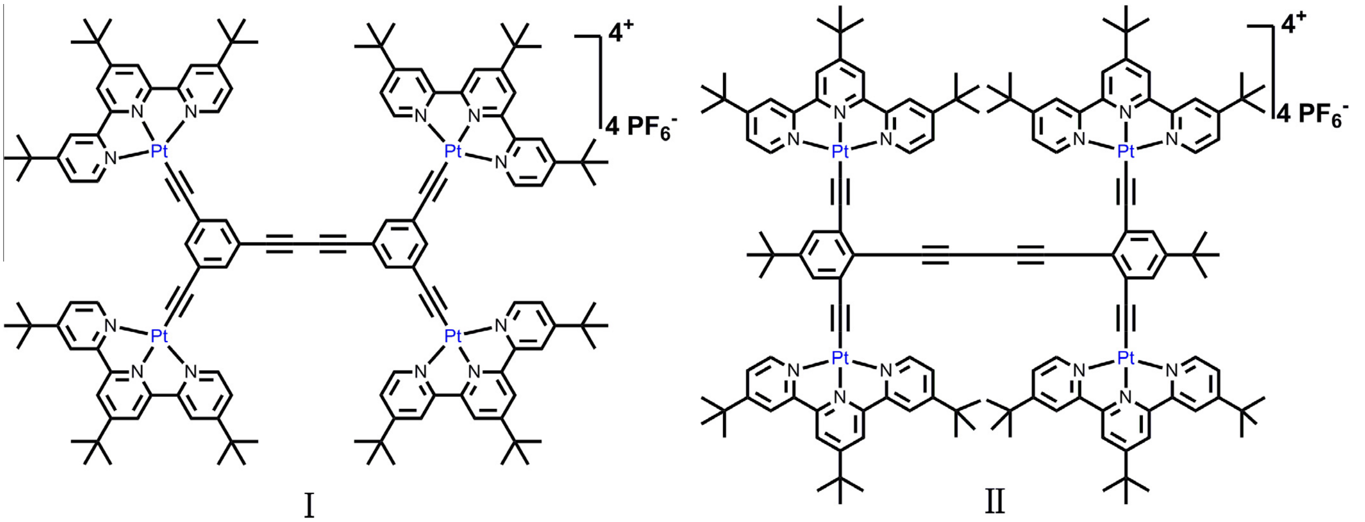
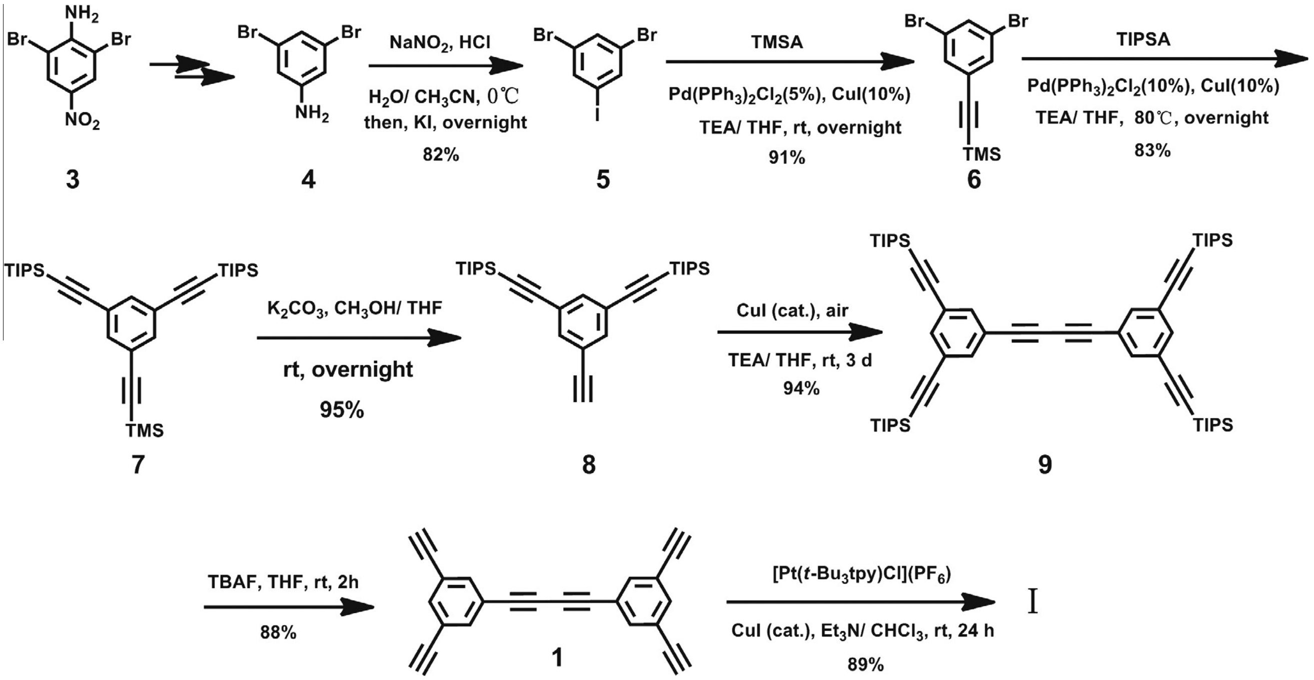


Scheme 1. Molecular structures of tetranuclear complexes **I** and **II**.



Scheme 2. Synthesis of tetrayne **1** and platinum(II) complex **I**.

synthesized by oxidative coupling[8] of alkyne **8** catalyzed by CuI in the air, followed by desilylation using tetrabutylammonium fluoride (TBAF) in THF promoted by a small amount of CH_3OH.

Starting from 4-(*tert*-butyl)aniline **10**, compound **11** was prepared by the literature procedures[9] (Scheme 3). Removal of the TMS group of compound **11** provided the terminal alkyne **12**.[10] Further oxidative coupling of **12** afforded halogenated butadiyne **13**.[11] Compound **13** was converted to tetrayne **2** by a continuous operation of Sonogashira coupling and desilylation.[12] By a modified procedure of the related platinum(II) terpyridyl complexes,[4,5] upon the reaction between terminal alkynes **1** or **2** and chloroplatinum(II) complex [Pt(*t*Bu_3-tpy)Cl](PF_6), the branched tetranuclear alkynylplatinum(II) complexes **I** and **II** were finally obtained in 89% and 84% yields, respectively.[13] Both of these two complexes have been successfully characterized by ^1H NMR, FT-IR, mass spectra, and elemental analysis.

The UV–vis absorption spectra and emission spectra of **I** and **II** were studied in acetonitrile. Both of their electronic absorption spectra show high-energy absorption bands in the range of 300–350 nm, which are assigned as the internal ligand (IL) π–π^* [(ArC≡C)$_n$] and π–π^* (*t*Bu_3-tpy) transitions (Fig. 1). The characteristic low energy absorption band of platinum(II) complex **I** is in the range of 360–500 nm (maximized at 418 nm with $\varepsilon = 22831$ dm^3 mol^{-1} cm^{-1} for **I** and 453 nm with $\varepsilon = 19453$ dm^3 mol^{-1} cm^{-1} for **II**), which could be tentatively assigned to be the metal-to-ligand [dπ(Pt)–π^*(*t*Bu_3-tpy)] charge transfer (MLCT) character, probably mixing with ligand-to-ligand (alkynyl-to-terpyridine) charge transfer (LLCT) transition.[14] However, the MLCT/LLCT transition of distorted complex **II** shifts to lower energy, a significant redshift occurred. This could be ascribed that the twisted configuration of complex **II** raised the dπ(Pt) orbital energy, and thus gave rise to a lower MLCT/LLCT absorption energy.[15]

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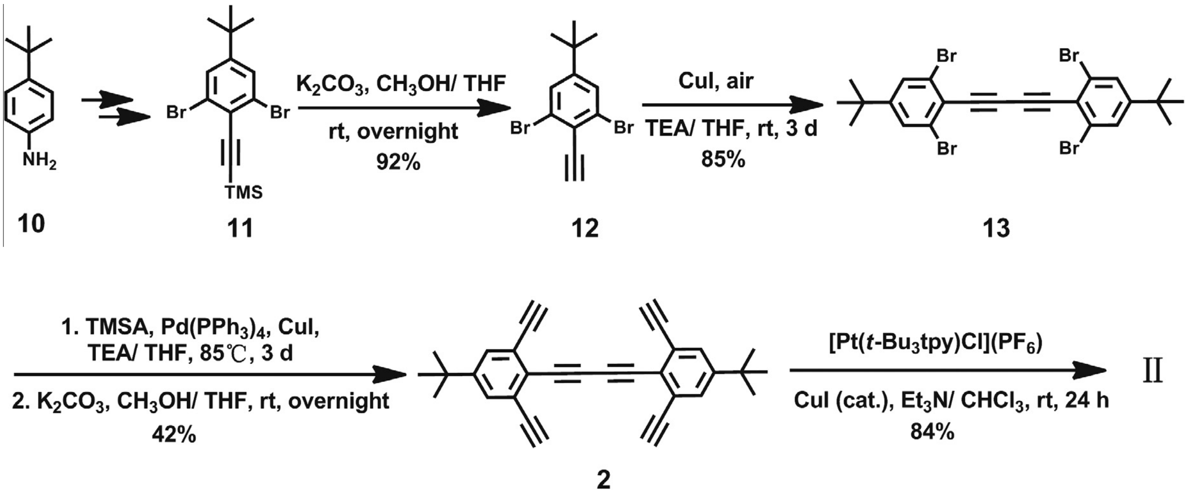

Scheme 3. Synthesis of tetrayne **2** and platinum(II) complex **II**.

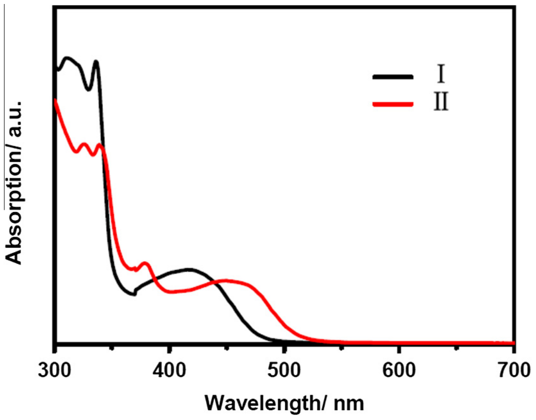

Figure 1. UV–vis spectra of complexes **I** and **II** in acetonitrile with a concentration of 1×10^{-5} M.

Excitation of complex **I** at 450 nm in acetonitrile leads to an emission band at 475–850 nm, maximized at 568 nm with $\Phi_{em} = 6.3 \times 10^{-3}$, which is tentatively assigned to be derived from ^{3}MLCT [dπ(Pt)–π^*(*t*Bu$_3$-tpy)] character (Fig. 2).[14] The photoluminescence quantum yields (Φ_{em}) were determined by using a degassed CH$_3$CN solution of [Ru(bpy)$_3$](PF$_6$)$_2$ as the reference (Table 1).[16] In contrast, the spectrum of **II** shows the emission band between 500 and 850 nm, maximized at 578 nm with Φ_{em} = 6.6

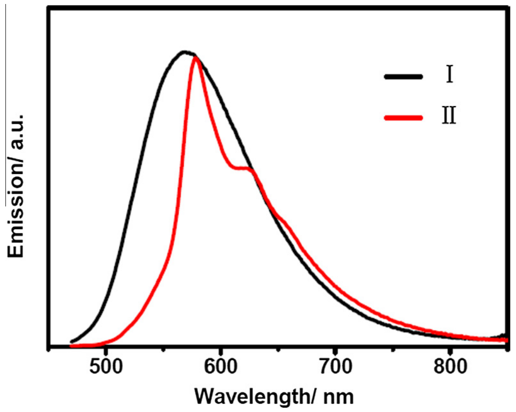

Figure 2. Normalized emission spectra for complexes **I** and **II** in acetonitrile with a concentration of 1×10^{-5} M at 298 K. The excitation wavelength is 450 nm.

Table 1
Emission and lifetimes[a] of complexes **I** and **II** in different solutions at 298 K

	I		II	
	λ_{em} (nm)	τ (μs)	λ_{em} (nm)	τ (μs)
CH$_3$CN	568	0.24	578	1.46
Acetone	570	0.43	578	2.32
CH$_2$Cl$_2$	520	4.6	578	2.02
Toluene	600	0.24	600	17
ϕ ($\times 10^{-3}$)[b]	6.29		6.61	

[a] Concentration = 1×10^{-5} M.
[b] In acetonitrile.

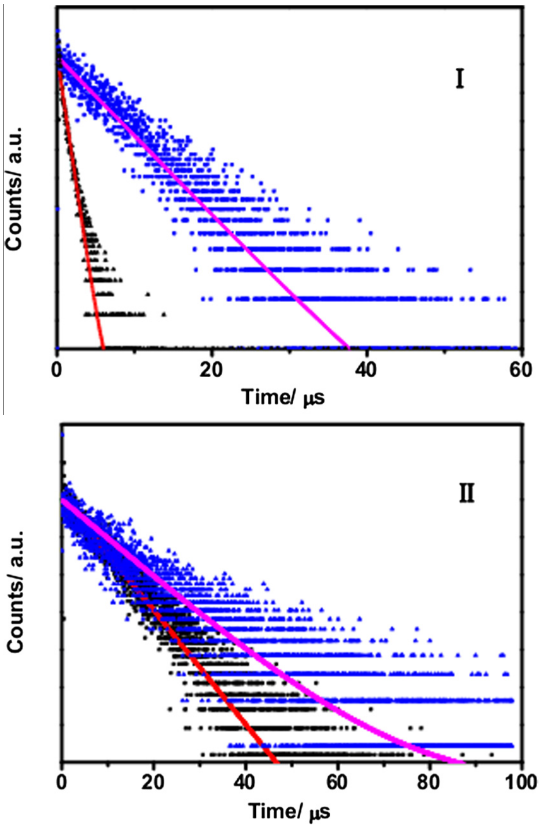

Figure 3. Luminescent decays of complexes **I** and **II** in acetonitrile (red line) and toluene (magenta line) solution at 298 K.

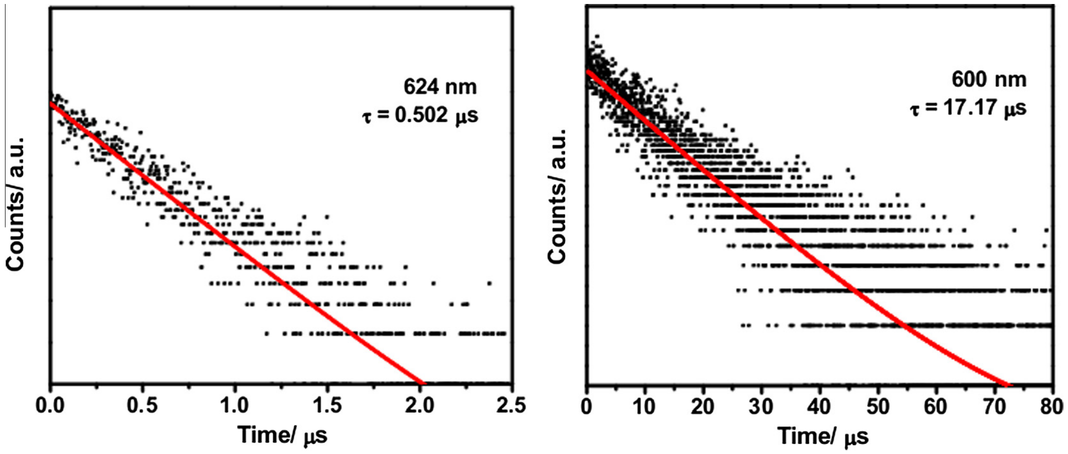

Figure 4. Luminescent decay profiles of complex **II** in nitrobenzene (left) and toluene (right) solution at 298 K.

$\times 10^{-3}$. Interestingly, a new low-energy shoulder at ca. 630 nm appeared, which could be predominantly assigned to be derived from IL transitions and/or ^{3}LLCT transition character.[1b]

Upon excitation at 450 nm in deaerated solution, both **I** and **II** show long excited-state lifetimes, which are in the range of microseconds in various solvents, such as acetonitrile and toluene. The data are shown in Figure 3 and Table 1. The lifetime of complex **II** is longer than complex **I**. Interestingly, for distorted complex **II**, the longest lifetime of ~17 μs was observed in toluene, which is much higher than the lifetimes obtained in other solvents. This observation may be attributed to the electronic effects of the solvents, which significantly affected the electron transfer between the excited state of complex **II** and solvent molecules. We compared the luminescent decay profiles of complex **II** in nitrobenzene and toluene (Fig. 4). As seen from the data, the lifetimes follow the order of toluene > nitrobenzene, which is consistent with the order of the electron accepting ability of the solvents. On the other hand, complex **II** has a longer lifetime than complex **I** because the twisted configuration raises the dπ(Pt) orbital based HOMO, as evidenced by the absorption spectra in Figure 1. The nonradiative deactivation (resulting in short lifetimes) via d–d states pathway decreases and the energy difference between the MLCT and the d–d states increases.[1,3] As a result, complex **II** shows longer lifetimes than complex **I**.

Further application of these two complexes as a light-harvesting chromophore was examined for photocatalytic generation of hydrogen. The system consists of the chromophore **I** or **II** (1.11×10^{-5} M) for visible light harvesting, TEOA (1.61×10^{-2} M) as the sacrificial electron donor, and Co(dmgH)$_2$PyCl (1.99×10^{-4} M) as the catalyst for hydrogen production in a CH$_3$CN/water mixture (3:2, v/v).[17] As shown in Figure 5, the photocatalytic activity for H$_2$ generation under visible light irradiation ($\lambda > 420$ nm) was remarkably enhanced by adding complex **II**, the corresponding H$_2$ evolution rate is 23 mol h^{-1}, which is about 52 times higher than that of complex **I**. Therefore, complex **II** largely improved the photocatalytic activity of the hydrogen evolution from water, probably due to its long lifetimes in solution.

In conclusion, two branched tetranuclear alkynylplatinum(II) complexes **I** and **II** were synthesized via the reaction between the corresponding terminal alkynes and chloroplatinum(II) complex [Pt(tBu$_3$-tpy)Cl](PF$_6$), which were fully characterized by ^{1}H NMR, FT-IR, mass spectra, and elemental analysis. Their photophysical properties have also been investigated. It was found that twisted complex **II** shows longer emission lifetimes than its planar counterpart in various solvents. The longest lifetime of ~17 μs has been observed, which could be used for potential applications in various photocatalytic reactions, such as photocatalytic generation of hydrogen.

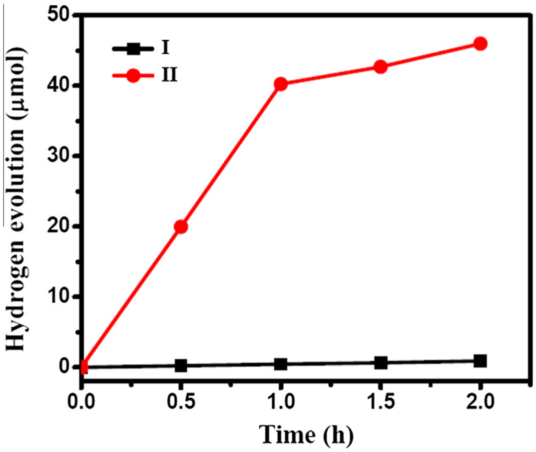

Figure 5. Comparison of hydrogen production under the conditions of 1.61×10^{-2} M TEOA, 1.11×10^{-5} M photosensitizer **I** and **II**, and 1.99×10^{-4} M Co(dmgH)$_2$PyCl (dmgH = dimethylglyoxime, py = pyridine) in a mixture of CH$_3$CN:water (3:2, v/v) at pH = 8.5.

Acknowledgments

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7. *1,4-Bis(3,5-diethynylphenyl)buta-1,3-diyne* (**1**): Desilylation was conducted in TBAF/THF at room temperature. ESI-MS (m/z) calcd for C$_{24}$H$_{10}$ [M−H]$^-$ 297.08;

found 297.42. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.13 (4H, s), 7.59 (6H, s). IR (ATR): ν_{max} 3290, 3068, 2959, 2925, 2855, 2150, 1579, 1412, 1259, 934, 883 cm^{-1}.

8. *1,4-Bis(3,5-bis((triisopropylsilyl)ethynyl)phenyl)buta-1,3-diyne (**9**):* To a stirred solution of **8** (0.46 g, 1.0 mmol) in Et_3N (2 mL), MeOH (4 mL) and THF (6 mL) was added CuI (20 mg, 0.1 mmol) in one portion at room temperature. The reaction was stirred for 3 days in the air until the starting material was not detectable by TLC. The reaction was quenched by addition of H_2O. The organic layer was removed and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous $MgSO_4$. Followed by filtration and concentration on vacuum, flash chromatography (PE/DCM) afforded compound **9** (0.43 g) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (84H, s), 7.52 (2H, m), 7.54 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.4, 18.8, 74.7, 80.4, 92.9, 105.0, 122.2, 124.5, 135.6, 135.7. IR (ATR): ν_{max} 2944, 2891, 2866, 2754, 2723, 2159, 2063, 1578, 1463, 1409, 1383, 1366, 1276, 1162, 1073, 1017, 996, 980, 995, 919, 882 cm^{-1}.
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10. *1,3-Dibromo-5-(tert-butyl)-2-ethynylbenzene (**12**):* Desilylation was conducted in MeOH/THF using K_2CO_3 at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (9H, s), 3.61 (1H, s), 7.55 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.0, 35.2, 81.1, 85.7, 123.2, 126.5, 128.9, 154.7.
11. *1,4-Bis(2,6-dibromo-4-(tert-butyl)phenyl)buta-1,3-diyne (**13**):* ESI-MS (m/z) calcd for $[M+Na]^+$ 649.85; found 649.83. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (18H, s), 7.55 (4H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.9, 35.3, 81.2, 81.3, 123.1, 127.2, 129.0, 155.2. IR (ATR): ν_{max} 3069, 2963, 2904, 2868, 1584, 1530, 1514, 1470, 1442, 1387, 1373, 1363, 1261, 1209, 1194, 1128, 873, 745 cm^{-1}.
12. *1,4-Bis(4-(tert-butyl)-2,6-diethynylphenyl)buta-1,3-diyne (**2**):* Compound **7** was transformed to corresponding alkyne by Sonogashira coupling in a sealed tube at 85 °C for 3 days. Desilylation was conducted in MeOH/THF using K_2CO_3 at room temperature. ESI-MS (m/z) calcd for $[M+Na]^+$ 433.20; found, 433.50. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (18H, s), 3.36 (4H, s), 7.52 (4H, s). IR (ATR): ν_{max} 3291, 3053, 2967, 2932, 2901, 2867, 2105, 1582, 1543, 1460, 1437, 1399, 1365, 1276, 1261, 1224, 1205, 1026, 942, 886, 806, 765 cm^{-1}.
13. (**I**) To a degassed solution of tetrayne **1** (4.2 mg, 0.014 mmol) and $[Pt(tBu_3tpy)Cl](PF_6)$ (49 mg, 0.063 mmol) in $CHCl_3$ (25 mL) and Et_3N (5 mL) was added CuI (cat.). The resulting mixture was degassed for another 5 min and stirred for 24 h at room temperature under Ar atmosphere. Solvent was removed in vacuo and the residue was dispersed in MeOH. Then NH_4PF_6 (9.2 mg, 0.056 mmol) in deionized water (20 mL) was added into the solution, which was sonicated for 10 min. Finally, the precipitate was filtered out and washed by water and ethyl ether to afford **I** (41 mg) as a yellowish-brown solid. ^{1}H NMR (400 MHz, CD_3CN): δ 1.45 (106H, m), 7.66 (14H, s), 8.21 (16H, m), 9.04 (8H, s). IR (ATR): ν_{max} 3113, 3082, 2967, 2915, 2881, 2110, 1616, 1568, 1480, 1422, 1404, 1371, 1254, 1175, 1084, 1035, 837 cm^{-1}. Mass Spec. Calcd (MALDI-TOF-MS) for $[M-PF_6^-]^+$: 3113.93; Found $[M-PF_6^-]^+$: 3113.77. Anal. Calcd (%) for $C_{132}H_{146}F_{24}N_{12}P_4Pt_4{\cdot}MeOH$: C, 48.51; H, 4.59; N, 5.15; found: C, 48.86; H, 4.92; N, 5.04.

    (**II**) Similar procedures in **I** were adopted to obtain a reddish brown solid. ^{1}H NMR (400 MHz, CD_3CN): δ 1.40 (126H, s), 7.48 (4H, s), 8.03 (24H, m), 9.21 (8H, s). IR (ATR): ν_{max} 3110, 3079, 2962, 2909, 2874, 2113, 1615, 1553, 1531, 1479, 1423, 1398, 1371, 1253, 1174, 1123, 1025, 843 cm^{-1}. Mass Spec. Calcd (MALDI-TOF-MS) for $[M-PF_6^-]^+$ 3226.06; Found $[M-PF_6^-]^+$ 3225.90. Anal. Calcd (%) for $C_{140}H_{162}F_{24}N_{12}P_4Pt_4$: C, 49.85; H, 4.84; N, 4.98; found: C, 49.77; H, 4.70; N, 5.12.
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