SELF-ASSEMBLED TRIGONAL PRISMATIC ALTITUDINAL ROTORS WITH TRIPTYCENE PADDLE WHEELS

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We describe the synthesis of a trigonal prismatic molecular rotor by self-assembly from paddle-wheel carrying molecular rods and trigonal star connectors in a 3:2 ratio. The rod is 9,10-diethynyltriptycene terminated in transversely reactive $[Pt(dppp)]^+$ groups (dppp = 1,3-bis(diphenylphosphino)propane) and the connector is 1,3,5-tris[(4-pyridyl)ethynyl]benzene. The structure of the molecular rotor has been established by 2-D NMR and MS, including diffusion-ordered NMR and collision-induced dissociation.

Keywords: Molecular rotors; Molecular machines; Triptycenes; Platinum complexes; Alkynes; Pyridines; Self assembly; NMR spectroscopy; Mass spectrometry.

For some time[1–3], this laboratory has been developing a molecular assembly kit of rods[4,5] and star-shaped connectors[6–8] analogous to elements of the children's "Tinkertoy"[9] construction set for the fabrication of molecular structures on surfaces[10]. We are especially interested in the preparation of artificial molecular rotors[11], which are likely constituents of any molecular machinery. Recently, we described a gold surface-mounted molecular rotor whose dipolar rotator can be flipped by the electric field of a scanning tunnelling microscope tip[12]. Computations suggest that the application of a linearly oscillating electric field to some of the conformers of this rotor will induce unidirectional rotation at the frequency of the field or its simple fraction[12,13]. A second-generation dipolar altitudinal rotor has been synthesized[14] and is expected to have a lower barrier to rotation[15]. We would next like to find out whether surface-mounted molecular rotors can be driven by fluid flow, and ultimately, whether such rotors driven by light pulses or electric field could drive fluid flow for active applications of molecular machinery for transport on the nanoscale.

Molecular dynamics simulations suggest that it will be possible to drive propeller-shaped azimuthal rotors (axle perpendicular to surface) mounted on a grid with a flow of gas from a supersonic nozzle directed perpendicular

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to the grid[16,17]. Experimentally, it may be more desirable to use paddle-wheel-shaped altitudinal rotors (axle parallel to surface) and a flow of fluid parallel to the surface. For this purpose, it might be necessary to half-bury the rotors in a self-assembled monolayer of a height that exposes only the rotator paddle that is the most distant from the surface.

We are currently attempting to use molecular dynamics calculations to design suitable structures for such altitudinal rotors, and it begins to appear that three or four large paddles on a rotor will be desirable. This will require large structures that permit the axle to be located farther away from the surface than was the case in the first two generations of surface-mounted altitudinal rotors[12,15]. As the dimensions of the rotors increase, classical synthetic approaches based on covalent bonding, such as those used for the first two generations of altitudinal rotors, become unwieldy, and it is tempting to use assembly from rods and connectors, in the spirit of the original Tinkertoy ideas[1–3]. Molecules that define regular prisms offer an attractive choice. Two edges of the prism would be adsorbed on the surface, and one or more other edges would represent axles carrying rotators to be driven by the flow.

Coordination-driven self-assembly based on metal ions[18–24] is a particularly attractive option for the construction of such prismatic rotors, if sufficiently sturdy metal–ligand bonds can be used. Since its application to targeted synthesis of functional molecules is relatively uncommon, and since the computational search for optimally functional structures is still under way, we felt that finding suitable reaction conditions for simpler model systems would be worthwhile. Some examples of prior synthesis of self-assembled functional structures are a supramolecular optical sensor capable of Ni(II), Cd(II), and Cr(III) uptake[25], squares from Re with Zn and Mn porphyrin ligands used as epoxidation catalysts with tailored stability and selectivity[26], and a supramolecular rectangle and rhomboid with incorporated perylenecarboximide[27].

The prisms desired as our molecular rotors would be most rigid if each edge were defined by a molecular rod, but to our knowledge such structures have never been prepared. It appeared easier and possibly adequate to give up some rigidity by defining only the paddle-wheel carrying edges with molecular rods and spanning the two polygonal faces with star connectors in a face-directed manner. We chose star connectors terminated with pyridines at arms ends, and rods terminated with covalently attached platinum ions possessing laterally directed active sites.

The use of square planar platinum(II) and palladium(II) has long been popular in this area, and a wide variety of 2D and 3D architectures have been reported with these metals[28,29]. Much of this work was based on the use of simple and fairly inert building blocks that are rigid and maintain bonding directionality. Our requirement of facile rotation around the long axis of the rods complicated matters, and we were concerned about reduced predictability during self-assembly and possible formation of catenanes, helicates, or oligomers[30].

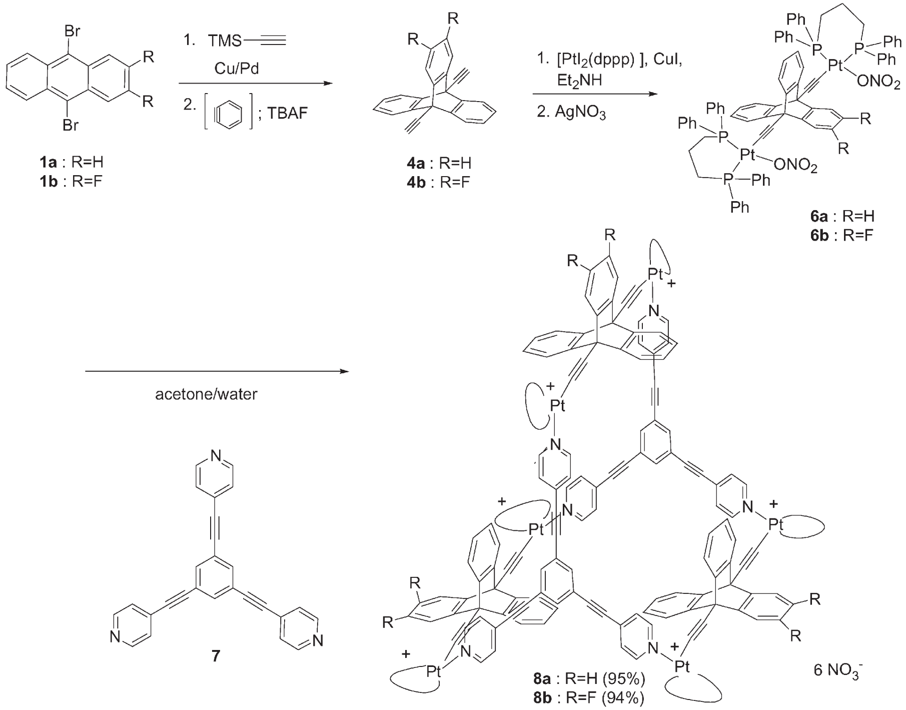
We were pleased to find that the proposed synthetic approach, based on a combination of a star connector and a rod terminated at both ends with a metal ion whose active site is laterally directed, worked well on simpler systems in which the rods carried no rotators, and that we were indeed able to prepare a rectangle ("digonal prism")[31] and a trigonal prism[32] as planned. Presently, we report the synthesis of two actual trigonal prismatic molecular rotors carrying triptycene paddle wheels, one polar and one non-polar.

RESULTS

Synthesis

The preparation of the triptycene or difluorotriptycene carrying rods followed a straightforward path (Scheme 1). 9,10-Dibromoanthracene (**1a**) or 2,3-difluoro-9,10-dibromoanthracene (**1b**) were treated with (trimethylsilyl)acetylene in the presence of Pd(0)/CuI to yield the corresponding 9,10-bis[(trimethylsilyl)ethynyl]anthracenes **2**. Addition of benzyne, prepared in situ from anthranilic acid and isoamyl nitrite, afforded the corresponding triptycenes **3**, and deprotection with K_2CO_3 in a methanol/THF mixture provided the diethynyltriptycenes **4a** and **4b**. Reaction with $[PtI_2(dppp)]$ in the presence of diethylamine converted them to the corresponding platinum iodides **5** and ligand exchange with silver nitrate led to the desired rods **6a** or **6b**. The synthesis of the star connector **7** has been already described[8].

The general procedure for the assembly of the prismatic molecular rotors **8a** and **8b** consisted of preparing a suspension of the rod **6a** or **6b** and ligand **7** in acetone/water, which slowly dissolved over the period of a few hours at room temperature (Scheme 1). We were unable to grow X-ray diffraction quality crystals of the products, but their composition, structure, and purity were determined beyond reasonable doubt by a combination of multinuclear and diffusion-ordered NMR, ESI-MS-CID, and elemental analysis.



SCHEME 1

Nuclear Magnetic Resonance

The NMR spectra of both **8a** and **8b** have been fully assigned and in each case fit the presence of a single type of square planar Pt atom carrying the dppp ligand as well as one alkyne and one pyridine ring in mutual cis orientation. Signals of only one type of triptycene rod and one type of connector arm terminating in pyridine are present, compatible with product structures consisting of bicyclic architecture of alternating diethynyltriptycenes and star connectors linked via $[Pt(dppp)]^+$ cations. Signals for only one type of ortho and one type of meta ^{1}H and ^{13}C atoms in each aromatic ring of the triptycyl and pyridyl moieties in **8a** are present and they remain sharp down to –90 °C, demonstrating both the equivalence of both ends of each rod and the equivalence of all three arms of the star connector. The results for **8b** are analogous. The absence of differentiation of triptycene paddles is attributed to nearly free rotation, which was intended.

The ^{195}Pt NMR spectra reveal a doublet of doublets for both **8a** ($J_{\text{P-Pt}}$ = 3123 and 2205 Hz) and **8b** ($J_{\text{P-Pt}}$ = 3122 and 2210 Hz), consistent with Pt satellites observed in the ^{31}P spectra. The ^{31}P{^{1}H} NMR spectrum of **8a** reveals two doublets (J_{PP} = 28 Hz), one at 0.6 ppm, cis to pyridine (as determined by NOE), with ^{195}Pt satellites (J_{PPt} = 2214 Hz), and another of equal intensity at –11.7 ppm, trans to pyridine (NOE), J_{PPt} = 3124 Hz. Similarly, ^{31}P{^{1}H} NMR spectrum of **8b** reveals two doublets (J_{PP} = 28 Hz), one at 0.4 ppm, cis to pyridine (NOE), with ^{195}Pt satellites (J_{PPt} = 2224 Hz), and another of equal intensity at –11.8 ppm, trans to pyridine (NOE), J_{PPt} = 3139 Hz. Chemical shifts and coupling constants of ^{195}Pt and ^{31}P are similar to those observed for other assemblies constructed with Pt(II)$^{+1}$ centers[31,32]. The ^{1}H NMR spectrum shows a single set of α-pyridine protons, at 8.5 ppm for **8a** and **8b**. The β-pyridine protons of **8a** and **8b** produce a single set of signals at 7.2 ppm. A single resonance from the protons of the central benzene ring of the star connectors is seen at 7.6 ppm in both **8a** and **8b**. Compared to the free star connector **7**, the pyridyl signals are shifted upfield by an average of 0.4 ppm. This is attributed to shielding by the dppp phenyl rings (Fig. 1), as has been reported for similar systems[31,32]. The ^{13}C NMR spectrum revealed one alkyne CC-Pt$_{\alpha}$ resonance as a doublet for both **8a** and **8b**, at 98.4 and 97.6 ppm ($^{2}J_{P\text{-}C}$ = 30 Hz), respectively.

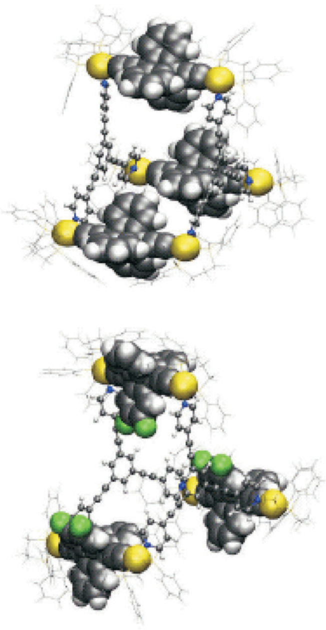


FIG. 1
Molecular mechanics optimized geometries of **8a** (top) and **8b** (bottom)

Assignments of signals were made through the use of gCOSY, gHSQC, and gHMBC experiments. A typical procedure is described for **8a**. One single-bond ^{13}C correlation to ^{1}H$_{o,triptycyl}$ was observed at 125.2 ppm and one to ^{1}H$_{m,triptycyl}$ was observed at 122.3 ppm by HSQC, allowing assignment of ^{13}C$_{o,triptycyl}$ and ^{13}C$_{m,triptycyl}$. An HMBC experiment established a ^{1}H$_{o,triptycyl}$ multiple-bond correlation to ^{13}C$_{bridgehead}$ at 52.5 ppm, and ^{13}CC-Pt$_{\beta}$ at 123.1 ppm. The CC-Pt$_{\alpha}$, at 98.4 ppm which shows $^{2}J_{P\text{-}C}$ coupling is consistent with attachment to a platinum center carrying a dppp ligand. Assignments of ^{1}H and ^{13}C NMR spectra of the pyridyl star connector **7** were made similarly. One single-bond ^{13}C correlation to ^{1}H$_{\alpha,pyr}$ was observed at 151.6 ppm and one to ^{1}H$_{\beta,pyr}$ was observed at 128.0 ppm by HSQC, allowing assignment of ^{13}C$_{\alpha,pyr}$ and ^{13}C$_{\beta,pyr}$. An HMBC experiment established a ^{1}H$_{\alpha,pyr}$ multiple-bond correlation to ^{13}C$_{p,pyr}$ at 132.3 ppm, and a ^{1}H$_{\beta,pyr}$ multiple-bond correlation to ^{13}CC$_{\alpha,pyr}$.

NOE has been used to examine group proximity. To eliminate the possible loss of NOE correlations due to rotational correlation times approaching $1/\omega_0$, the rotating frame ROESY method was used. NOE signals were observed from ^{1}H$_{\alpha,pyr}$ to ^{1}H$_{\beta,pyr}$, ^{1}H$_{o,triptycyl}$ and ^{1}H$_{o,ph}$ for both **8a** and **8b**. Also, NOE contacts are observed from ^{1}H$_{\beta,pyr}$ to ^{1}H$_{\alpha,pyr}$ and ^{1}H$_{o,triptycyl}$ for both compounds. These results support the expected cis arrangement around the metal center of the diethynyltriptycene and of the arm of the star connector **7**, and leave no doubt that the products have a molecular structure consisting of alternating triptycene and star connector units.

In synthesis by self-assembly there is always danger of forming larger aggregates than intended. We have therefore examined the size of **8a** and **8b** by diffusion-ordered NMR (DOSY) with ^{1}H detection. The observed values were compared to that found[32] for a very similar trigonal prism **9** previously formed from a biphenyl rod, $(NO_3)(dppp)Pt\text{-}C_6H_4\text{-}C_6H_4\text{-}Pt(dppp)(NO_3)$ and the same star connector **7** (Table I).

TABLE I
Radii of trigonal prisms

Compound	$D^{a} \times 10^{10}$, m^2 s^{-1}	r^{b}	R^{c}
8a	2.9	18.2	16.8
8b	3.53	15	16.8
9	2.97	17.6	20.3

[a] Diffusion coefficient obtained from DOSY measurements in CD_2Cl_2 at 298 K. [b] Radius *r* calculated from *D* and the Stokes–Einstein equation. [c] Approximate distance in Å from the prism center to the central CH_2 moiety of the dppp ligand in the UFF[39]-optimized geometry.

An approximate value of each "experimental" radius *r* was calculated from the diffusion coefficient using the Stokes–Einstein equation, $D = k_BT/6\pi r\eta$, where D is the diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of methylene chloride (0.0041 g s^{-1} cm^{-1}). The distance from prism center to the central CH_2 moiety of the dppp ligand measured on a structure optimized with the TINK[16] program was used as an approximate measure of the radius R of the smallest sphere required to enclose the prism. The sizes r found experimentally agree roughly with the calculated values R and support the postulated formation of discrete prisms composed of two star connectors and three organometallic rods for both **8a** and **8b**.

Mass Spectrometry

Although the combined NMR evidence alone is sufficient to establish the structures **8a** and **8b** beyond reasonable doubt, additional independent evidence for the structural assignments was obtained from electrospray ionization mass spectra. The spectrum of **8a** showed $[M - NO_3]^+$, $[M - 2\ NO_3]^{2+}$, $[M - 3\ NO_3]^{3+}$, $[M - 4\ NO_3]^{4+}$, and $[M - 5\ NO_3]^{5+}$ peaks at the values of *m/z* 5618.9, 2778.4, 1831.4, 1358.3, and 1074.1 respectively, expected for **8a**, with the anticipated isotopic distribution patterns (Fig. 2). Similarly, the spec-

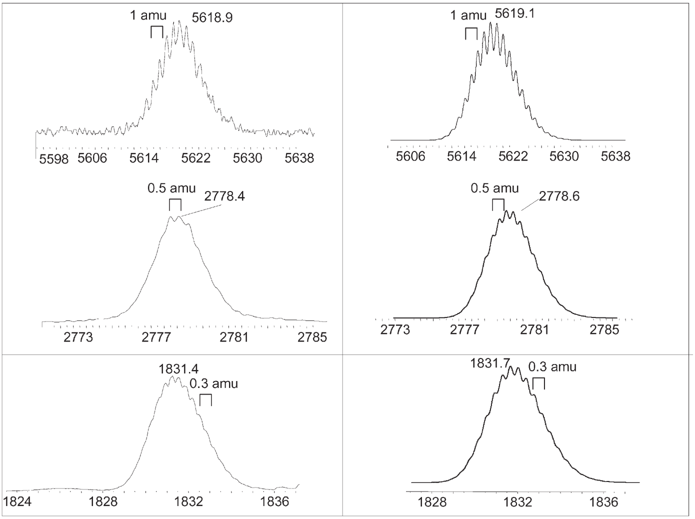


FIG. 2

Observed (left) and simulated (right) isotopic distribution patterns in the mass spectra of **8a** trum of **8b** showed $[M - NO_3]^+$, $[M - 2\ NO_3]^{2+}$, $[M - 3\ NO_3]^{3+}$, $[M - 4\ NO_3]^{4+}$, and $[M - 5\ NO_3]^{5+}$ peaks at the values of *m/z* 5727.2, 2832.8, 1867.9, 1385.4, and 1095.8 respectively, expected for **8b**, with the anticipated isotopic distribution patterns.

Collision-induced dissociation (CID) on the *m/z* 2778 ion $[M - 2\ NO_3]^{2+}$ was compatible with the structure **8a** (Fig. 3). The peak at *m/z* 1958.8, with a spacing of Δm = 0.5 amu, corresponds to the cleavage of two Pt–N bonds and the loss of one organometallic rod, the peak at *m/z* 1139.4, with a spacing of Δm = 0.5 amu, corresponds to the loss of two rods, and a peak at *m/z* 1706.3, with a spacing of Δm = 0.5 amu, corresponds to the loss of one rod and one connector. CID of the *m/z* 2832.8 ion $[M - 2\ NO_3]^{2+}$ from **8b** resulted in similar fragmentation.

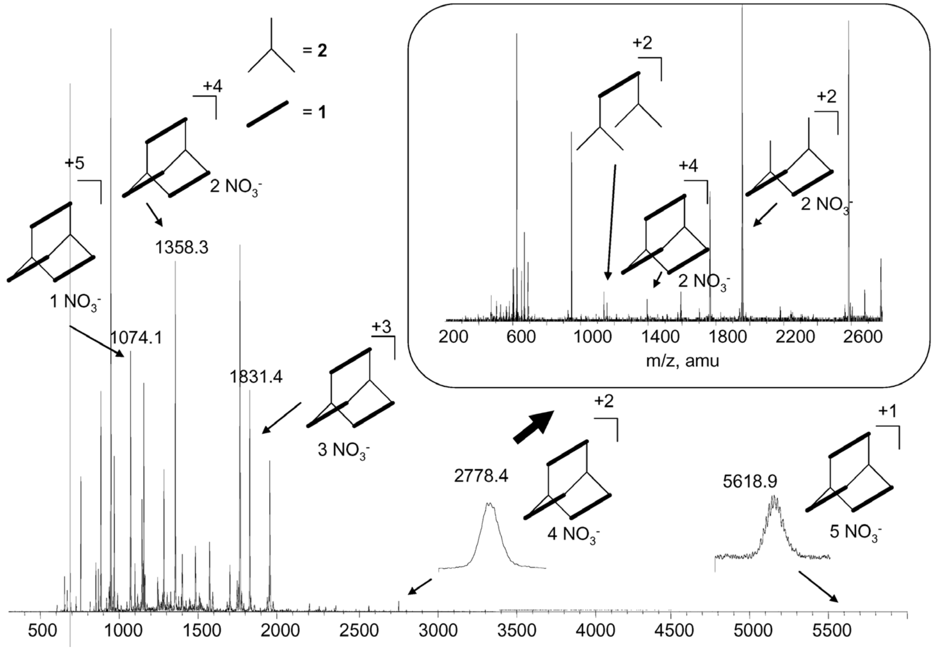


FIG. 3
ESI-MS of **8a**. Inset, CID of peak at 2778.4 *m/z*

Ultraviolet Absorption Spectroscopy

Electronic spectroscopy is not of much help in assigning the structures of **8a** and **8b**, but we expect that it will ultimately be useful if we attempt to follow rotator motion by photophysical means. Table II summarizes the UV spectra of the prisms **8a** and **8b** and their constituent parts: the rods **6a** and **6b**, and the connector **7**. The spectra are compatible with the structures assigned. The absorption of **8a** and **8b** features intense bands centered at about 305 and 322 nm, which we associate with intense π–π* transitions of **7**, red-shifted by about 20 nm due to conjugation with the attached platinum centers. Such shifts have been noted in similar Pt complexes before[33]. The spectral contributions of the benzene and acetylene chromophores in the rods **6a** and **6b** are much weaker and are assumed to be buried under the absorption bands due to the connectors **7**.

TABLE II
UV absorption maxima and absorption coefficients

Compound	λ_{max} (nm), ε_{max} (M^{-1} cm^{-1})
6a	272 (7.8 × 10^3), 286 (5.7 × 10^3)
6b	272 (7.6 × 10^3), 290 (5.5 × 10^3)
7	284 (59.6 × 10^3), 302 (58.2 × 10^3)
8a	304 (129 × 10^3), 322 (117 × 10^3)
8b	306 (135 × 10^3), 322 (126 × 10^3)

Molecular Mechanics Calculations

The results of a UFF[39] optimization of **8a** and **8b** are shown in Fig. 1. The optimized structures show that the symmetry of both prisms is very close to D_{3h}. The phenyl rings of the dppp ligand lie only about 3.7 Å from the triptycene benzene rings and about 3.3 Å from the pyridine rings.

DISCUSSION AND CONCLUSIONS

The spectral results leave no doubt in our minds that our immediate goal has been achieved and that the connectivity of the self-assembled prismatic molecular rotors **8a** and **8b** is as shown in Scheme 1. This result bodes well for the use of the same self-assembly method for the preparation of other prismatic altitudinal rotors from rotator carrying rods terminated in metal atoms with a laterally directed active site, combined with pyridine-terminated star connectors such as those that we have already synthesized. Although it is clear that both the triptycene paddle wheels and the pyridine rings are rotating rapidly on the NMR time scale, it may be useful for our purposes to use a less sterically demanding diphos ligand in the future. This will be especially appropriate if larger paddle wheels are employed.

Preliminary scanning tunnelling micrographs suggest that **8a** adsorbs on a gold surface and is not easily pushed about by the scanning tip[34], although it does not have any functionalities especially installed for adhesion to gold. It is likely that the positively charged platinum atoms are responsible for this behavior, which we intend to investigate further. In all probability, however, it will be necessary to attach suitable functional groups to assure adhesion of one of the square faces of the trigonal prism to gold surface. A differentiation of the three prism edges thus looms as an important synthetic goal. Even before this is attempted, however, we need to modify the paddle-wheel carrying rods in a way that compensates the positive charges on the platinum atoms and renders the final molecular rotor electroneutral. This would be especially important if it turns out to be impossible to remove counterions from the multiply charged surface-mounted rotor, as such loose charges would almost certainly interfere with differential barrier height imaging[12], needed to examine the rotation of the dipolar rotor on a surface under the effect of outside electric field. Other areas of future concern are the kinetic stability of the self-assembled rotors and their possibly insufficient rigidity.

EXPERIMENTAL

General Methods

Known procedures were used to prepare [PtI_2(dppp)][35], 2,3-difluoroanthracene[36], and 9,10-bis(trimethylsilylethynyl)anthracene[37]. All reagents were purchased from Aldrich and used as received. Solvents were dried by standard methods and freshly distilled before use. Deuterated solvents were used as received from Cambridge Isotope Laboratories, Andover (MA). IR spectra (in cm^{-1}) were recorded with a Nicolet Avatar 360 FT-IR spectrophotometer. UV-VIS spectra were recorded on a Hewlett–Packard 8452A spectrophotometer. NMR spectra were recorded with an Inova 400 spectrometer in deuterated acetone, $CDCl_3$, or CD_2Cl_2 solutions; all chemical shifts are given in ppm, coupling constants (*J*) in Hz. ^1H (400 MHz) and ^{13}C (101 MHz) shifts are relative to external Me_4Si. ^{31}P (162 MHz) shifts are relative to external 85% H_3PO_4. ^{195}Pt (86 MHz) shifts are relative to external Na_2PtCl_6 in D_2O. ^{19}F (377 MHz) shifts are relative to external $CFCl_3$. A Dbppste (DOSY bipolar pulse pair stimulated echo) pulse sequence[38] was used for the diffusion experiment. Data were obtained in CD_2Cl_2. Mass spectra were obtained using electrospray ionization conditions with an API QSTAR Pulsar with a TOF mass analyzer. The CID spectra were obtained at 55 eV using Ar as a collision gas. Elemental analyses were performed by Desert Analytics Laboratory, Tucson (AZ). The structures of **8a** and **8b** were optimized with UFF 1.02 (ref.[39]) using the TINK program[16].

9,10-Dibromo-2,3-difluoroanthracene (**1b**)

A solution of bromine (2.74 g, 17.1 mmol) in CCl_4 (10 ml) was slowly added to a suspension of 2,3-difluoroanthracene[36] (1.79 g, 8.35 mmol) in CCl_4 (100 ml) with a catalytic amount of ferric chloride (5 mg) at room temperature. The addition lasted for 1 h and the reaction mixture was heated at reflux for additional 2 h. After the mixture was cooled to room temperature, a saturated aqueous solution of sodium thiosulfate (100 ml) was added to quench the reaction. The organic phase was washed with water (100 ml), dried with anhydrous magnesium sulfate, and concentrated to ~10 ml. A solid precipitated, which was collected by filtration, washed with CH_2Cl_2, and dried in the air to give yellow microcrystals of **1b** (2.74 g, 88%). M.p. 232–234 °C (dec.). ^1H NMR ($CDCl_3$): 7.65 (m, 2 H, aromatic), 8.35 (t, $J_{F,H}$ = 10.1, 2 H, aromatic), 8.51 (m, 2 H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 114.3 (dd, $J_{F,C}$ = 15, 7), 122.6, 128.2, 128.4, 131.3, 132.9, 151.6 (dd, $J_{F,C}$ = 256, 19). ^{19}F NMR ($CDCl_3$): –132.8 (t, $J_{H,F}$ = 10). IR (KBr): 3067, 3030, 1650, 1529, 1494, 1455. MS (EI), *m/z*: 370 (M^+), 291 (M^+ – Br), 212 (M^+ – 2 Br). For $C_{14}H_6Br_2F_2$ (372.0) calculated: 45.20% C, 1.63% H; found: 45.03% C, 1.53% H.

2,3-Difluoro-9,10-bis[(trimethylsilyl)ethynyl]anthracene (**2b**)

A mixture of **1b** (2.53 g, 6.80 mmol), (trimethylsilyl)acetylene (2.27 g, 23.1 mmol), $[Pd(PPh_3)_4]$ (0.47 g, 0.41 mmol), and CuI (0.16 g, 0.82 mmol) in triethylamine (20 ml) and THF (20 ml) was heated at 70 °C for 16 h in the dark. After all solvent was removed under reduced pressure, the residue was partitioned in CH_2Cl_2 (50 ml) and 1 M aqueous HCl (50 ml). The organic phase was washed with water (50 ml), dried with anhydrous magnesium sulfate, and concentrated to dryness. The crude product was chromatographed on silica gel with CH_2Cl_2/hexanes (30:70) to give **2b** as a yellow solid (2.31 g, 84%). M.p. 256–258 °C (dec.). ^1H NMR ($CDCl_3$): 0.43 (s, 18 H, $SiMe_3$), 7.62 (m, 2 H, aromatic), 8.25 (t, $J_{F,H}$ = 9.8, 2 H, aromatic), 8.50 (m, 2 H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 0.3, 100.9, 109.1, 113.0 (dd, $J_{F,C}$ = 15, 7), 118.3, 127.2, 127.5, 129.6 (t, $J_{F,C}$ = 4), 132.3, 151.8 (dd, $J_{F,C}$ = 255, 19). ^{19}F NMR ($CDCl_3$): –134.3 (t, $J_{H,F}$ = 10). IR (KBr): 3063, 2960, 2900, 2148, 1642, 1567, 1495, 700, 654, 627. MS (EI), *m/z*: 406 (M^+), 391 (M^+ – Me). For $C_{24}H_{24}F_2Si_2$ (406.6) calculated: 70.89% C, 5.95% H; found: 71.24% C, 5.77% H.

9,10-Bis[(trimethylsilyl)ethynyl]triptycene (**3a**)

A solution of 9,10-bis[(trimethylsilyl)ethynyl]anthracene[37] (**2a**; 5.56 g, 15 mmol) in anhydrous DME (40 ml) was added to a 250 ml three-neck flask equipped with a condenser and two 100 ml dropping funnels. Isoamyl nitrite (10.8 ml, 9.37 g, 80 mmol) and anthranilic acid (8.23 g, 60 mmol) were dissolved in DME (40 ml) in two funnels seperately. After the reaction system was purged with nitrogen, the solution in the flask was heated to a state of gentle reflux using an oil bath at 100 °C. The two solutions in the funnels were slowly dropped into the reaction vessel at the same rate over 2 h. After the addition was complete, the reaction mixture was stirred at reflux for 3 h and was then kept at 50 °C overnight. The mixture was dried under reduced pressure. The residue was chromatographed on silica gel with petroleum ether to give crude **3a** that was further purified by crystallization from hexanes as colorless prisms (2.41 g, 36%). M.p. 219–221 °C. ^{1}H NMR ($CDCl_3$): 0.47 (s, 18 H, $SiMe_3$), 7.10 (m, 6 H, aromatic), 7.72 (m, 6 H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 0.6, 53.2, 98.3, 99.8, 122.4, 125.9, 143.5. IR (KBr): 3068, 3031, 2956, 2897, 2184, 1606, 1455, 1384, 1303, 1251, 1226, 1045, 1031, 850, 753, 638. MS (EI), *m/z*: 446 (M^+), 406 (M^+ – Me), 373 (M^+ – $SiMe_3$), 252 ($C_{14}H_8^+$). For $C_{30}H_{30}Si_2$ (446.8) calculated: 80.66% C, 6.77% H; found: 80.40% C, 6.62% H.

2,3-Difluoro-9,10-bis[(trimethylsilyl)ethynyl]triptycene (**3b**)

A solution of **2b** (1.51 g, 3.72 mmol) in DME (100 ml) was added to a 500 ml three-neck flask equipped with a condenser and two 100 ml dropping funnels. Isoamyl nitrite (2.31 g, 19.7 mmol) and anthranilic acid (2.04 g, 14.9 mmol) were dissolved in DME (50 ml) in two funnels seperately. After the reaction system was purged with nitrogen, the solution in the flask was heated to a state of gentle reflux using an oil bath at 100 °C. The two solutions in the funnels were slowly dropped into the reaction vessel at the same rate over 2 h. After the addition was complete, the reaction mixture was stirred at reflux for 16 h. The mixture was dried under reduced pressure. The residue was chromatographed twice on silica gel with petroleum ether to give a raw product of **3b** that was further purified by crystallization from hexanes as a colorless solid (395 mg, 22%). M.p. 236–237 °C. ^{1}H NMR ($CDCl_3$): 0.47 (s, 18 H, $SiMe_3$), 7.13 (m, 4 H, aromatic), 7.50 (t, $J_{F,H}$ = 8.6, 2 H, aromatic), 7.69 (m, 4 H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 0.5, 52.7, 98.9, 112.6 (dd, $J_{F,C}$ = 14, 7), 122.5, 126.2, 140.3 (t, $J_{F,H}$ = 5), 143.0, 148.0 (dd, $J_{F,C}$ = 249, 15). ^{19}F NMR ($CDCl_3$): –141.8 (t, $J_{H,F}$ = 9). IR (KBr): 3061, 3031, 2958, 2899, 2184, 1622, 1599, 1498, 1464, 1251, 851. MS (EI), *m/z*: 482 (M^+), 467 (M^+ – Me), 409 (M^+ – $SiMe_3$), 385 (M^+ – C_2SiMe_3). For $C_{30}H_{28}F_2Si_2$ (482.7) calculated: 74.65% C, 5.85% H; found: 75.11% C, 5.87% H.

9,10-Diethynyltriptycene (**4a**)

A mixture of **3a** (447 mg, 1.0 mmol), K_2CO_3 (553 mg, 4.0 mmol), methanol (20 ml), and THF (20 ml) was stirred at room temperature for 16 h. After all solvent was removed under reduced pressure, water (20 ml) was added to the residue and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic phase was dried with anhydrous $MgSO_4$ and concentrated to give a slightly tanned solid. Flash chromatography of the crude product on silica gel with diethyl ether/petroleum ether (5:95) afforded colorless microcrystals of **4a** (297 mg, 98%). M.p. 294–296 °C. ^{1}H NMR ($CDCl_3$): 3.32 (s, 2 H, CCH), 7.13 (m, 6 H, aromatic), 7.78 (m, 6 H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 52.4, 78.2, 81.2, 122.4, 126.1, 143.1. IR (KBr): 3288, 3064, 3014, 2129, 1606, 1450, 1387, 1303, 1212, 1029, 875, 747, 648. MS (EI), *m/z*: 302 (M^+), 276 (M^+ – C_2H_2), 224 (M^+ – C_6H_6). For $C_{24}H_{14}$ (302.4) calculated: 95.33% C, 4.67% H; found: 95.74% C, 4.63% H.

2,3-Difluoro-9,10-diethynyltriptycene (**4b**)

A mixture of **3b** (140 mg, 0.28 mmol), K_2CO_3 (190 mg, 1.4 mmol), methanol (10 ml), and THF (10 ml) was stirred at room temperature for 15 h. After all solvent was removed under reduced pressure, water (10 ml) was added to the residue and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 ml). The combined organic phase was dried with $MgSO_4$ and concentrated to give a slightly tanned solid. Flash chromatography of the crude product on silica gel with diethyl ether/petroleum ether (5:95) afforded **4b** as a colorless powder (87 mg, 92%). M.p. 195–196 °C. ^{1}H NMR ($CDCl_3$): 3.24 (s, 2 H, CCH), 7.14 (m, 6 H, aromatic), 7.58 (t, $J_{F,H}$ = 8.6, 2 H, aromatic), 7.75 (m, 4 H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 51.9, 81.5, 112.6 (dd, $J_{F,C}$ = 14, 7), 122.5, 126.4, 140.0 (t, $J_{F,C}$ = 5), 142.6, 148.1 (dd, $J_{F,C}$ = 249, 15). ^{19}F NMR ($CDCl_3$): –141.5 (t, $J_{H,F}$ = 9). IR (KBr): 3288, 3062, 3032, 2146, 1600, 1495, 1465, 1384, 1170, 1028, 863, 749, 630. MS (EI), *m/z*: 338 (M^+), 312 ($M^+ - C_2H_2$), 260 ($M^+ - C_6H_6$). For $C_{24}H_{12}F_2$ (338.4) calculated: 85.20% C, 3.58% H; found: 85.10% C, 3.81% H.

Triptycene-9,10-diethynylbis[cis-(dppp)iodoplatinum] (**5a**)

Diethylamine (40 ml) was added to a solution of 9,10-diethynyltriptycene (**4a**; 93 mg, 0.3 mmol) and $[PtI_2(dppp)]$ (1.0 g, 1.2 mmol) in CH_2Cl_2 (80 ml). After 1 h, CuI (16 mg, 0.08 mg) was added and the mixture was stirred in the dark at room temperature for 2 days. After all solvent was removed under reduced pressure, the remaining solids were partitioned between CH_2Cl_2 (100 ml) and water (100 ml). The aqueous layer was extracted twice more with CH_2Cl_2 (100 ml). Flash chromatography of the resulting solids on silica gel with acetonitrile/toluene (5:95) afforded white microcrystals of **5a** (300 mg, 55%). M.p. 284 °C (dec.). ^{1}H NMR: 2.01 (m, 4 H, CH_2), 2.58 (m, 8 H, CH_2P), 6.66 (m, 6 H, H_m-triptycyl), 7.25 (m, 6 H, H_o-triptycyl), 7.40 (m, 8 H, ph), 7.47 (m, 4 H, ph), 7.51 (m, 12 H, ph), 7.88 (m, 8 H, ph), 8.03 (m, 8 H, ph). $^{13}C\{^1H\}$ NMR: 19.9, 26.6 (d, CH_2P, $J_{C\text{-}P}$ = 32), 27.9 (d, CH_2P, $J_{C\text{-}P}$ = 36), 52.5, 95.0, 100.5, 101.8, 106.3, 123.0, 124.8, 129.0, 130.5, 131.1, 131.3, 131.7, 132.2, 134.5. $^{31}P\{^1H\}$ NMR: –8.9 (d, 2 P, J_{PP} = 25, J_{PPt} = 3348), –8.4 (d, 2 P, J_{PP} = 25, J_{PPt} = 2171). $^{195}Pt\{^1H\}$ NMR: –5033 (dd, J = 3356, 2184). UV-VIS (CH_2Cl_2), λ_{max} (ε): 290 (5200). IR (KBr): 3052, 2923, 2360, 1607, 1484, 1435, 1297, 1264, 1156, 1102, 741, 691, 667, 515. For $C_{78}H_{64}I_2P_4Pt_2$ (1769.3) calculated: 52.95% C, 3.65% H; found: 52.95% C, 3.80% H. MS (MALDI$^+$, dihydroxybenzoic acid): calculated *m/z* 1768.1, found *m/z* 1769.4 $(M + H^+)^+$.

2,3-Difluorotriptycene-9,10-diethynylbis[cis-(dppp)iodoplatinum] (**5b**)

Diethylamine (0.95 ml, 673 mg, 9.2 mmol) was added to a solution of 2,3-difluoro-9,10-diethynyltripycene (**4b**; 311 mg, 0.92 mmol), $[PtI_2(dppp)]$ (3.28 g, 3.8 mmol), and CuI (44 mg, 0.23 mmol) in CH_2Cl_2 (80 ml). The mixture was stirred in the dark at room temperature for 12 h. The solvent was removed under reduced pressure. The remaining solids were partitioned between CH_2Cl_2 (200 ml) and water (200 ml). The aqueous layer was extracted twice more with CH_2Cl_2 (200 ml). Flash chromatography of the resulting solids on silica gel with acetonitrile/toluene (5:95) afforded white microcrystals of **5b** (1.1 g, 66%). M.p. 290 °C (dec.). ^{1}H NMR: 2.01 (m, 4 H, CH_2), 2.59 (m, 8 H, CH_2P), 6.68 (m, 4 H, triptycyl), 7.13 (t, 2 H, $J_{H,F}$ = 9.0, triptycyl), 7.25 (m, 4 H, ph), 7.38–7.55 (m, 24 H, ph), 7.86 (m, 8 H, ph), 8.00 (m, 8 H, ph). $^{13}C\{^1H\}$ NMR: 19.8, 26.4 (d, CH_2P, $J_{C\text{-}P}$ = 15), 27.6 (d, CH_2P, $J_{C\text{-}P}$ = 16), 101.4, 102.9, 105.4, 112.6, 123.0, 125.1, 128.7, 129.6, 130.5, 131.4, 131.7, 131.9, 132.3, 134.5, 142.8, 145.7, 147.5. $^{31}P\{^1H\}$ NMR: –8.7 (d, 4 P, J_{PP} = 25, J_{PPt} = 2185), –8.7 (d, 2 P, J_{PP} = 24, J_{PPt} = 3339). $^{195}Pt\{^1H\}$ NMR: –5035 (dd, J = 3343, 2187). ^{19}F NMR: –145.1 (t, $J_{H,F}$ = 9). UV-VIS (CH_2Cl_2), λ_{max} (ε): 298 (6400). For $C_{78}H_{62}F_2I_2P_4Pt_2$ (1805.2) calculated: 51.90% C, 3.46% H; found: 51.90% C, 3.48% H.

Triptycene-9,10-diethynylbis[cis-(dppp)nitratoplatinum] (**6a**)

To a room-temperature stirred solution of **5a** (106 mg, 0.06 mml) in CH_2Cl_2 (50 ml) was added silver nitrate (21.4 mg, 0.13 mmol), all at once. The reaction mixture was stirred in the dark at room temperature for 8 h. A clear solution with a white precipitate resulted. The precipitate was filtered off, and the solvent was removed under reduced pressure. The crude white solid was suspended in 50 ml of water and sonicated for 15 min. The suspension was filtered, washed with excess water, and air-dried. The solids were redissolved in a minimal amount of CH_2Cl_2 and a layer of toluene was added, resulting in yellow crystals of **6a** (87 mg, 89%). M.p. 225 °C (dec.). ^1H NMR: 2.10 (m, 4 H, CH_2), 2.71 (m, 8 H, CH_2P), 6.80 (m, 6 H, H_m-triptycyl), 7.10 (m, 6 H, H_o-triptycyl), 7.44 (m, 24 H, ph), 7.75 (m, 8 H, ph), 7.97 (m, 8 H, ph). $^{13}C\{^1H\}$ NMR: 19.3, 24.9 (d, CH_2P, $J_{C\text{-}P}$ = 31), 26.2 (d, CH_2P, $J_{C\text{-}P}$ = 35), 52.8. $^{31}P\{^1H\}$ NMR: –10.0 (s, 2 P, J_{PPt} = 3618), 0.1 (s, J_{PPt} = 2377). $^{195}Pt\{^1H\}$ NMR: –4465 (dd, J = 3614, 2374). UV-VIS (CH_2Cl_2), λ_{max} (ε): 286 sh (5700), 272 sh (7800). IR (KBr): 3052, 2925, 2360, 1607, 1506, 1487, 1274, 1101, 989, 745, 692, 667, 561. ESI-MS: calculated *m/z* 1639.4, found *m/z* 1662.4 $(M + Na^+)^+$.

2,3-Difluorotriptycene-9,10-diethynylbis[cis-(dppp)nitratoplatinum] (**6b**)

To a room-temperature stirred solution of **5b** (147 mg, 0.08 mmol) in CH_2Cl_2 (50 ml) was added silver nitrate (30.0 mg, 0.18 mmol), all at once. The reaction mixture was stirred in the dark at room temperature for 8 h. A clear solution with a white precipitate resulted. The precipitate was filtered off, and the solvent was removed under reduced pressure. The crude white solid was suspended in 50 ml of water and sonicated for 15 min. The suspension was filtered, washed with excess water, and air-dried. The solids were redissolved in a minimal amount of CH_2Cl_2 and a layer of toluene was added, resulting in yellow crystals of **6b** (110 mg, 81%). M.p. 230 °C (dec.). ^1H NMR: 2.08 (m, 4 H, CH_2), 2.68 (m, 8 H, CH_2P), 6.75 (m, 4 H, H_m-triptycyl), 6.97 (t, 2 H, $J_{H,F}$ = 8.8, triptycyl), 7.11 (m, 4 H, H_o-triptycyl), 7.49 (m, 24 H, ph), 7.73 (m, 8 H, ph), 7.97 (m, 8 H, ph). $^{13}C\{^1H\}$ NMR: 19.5, 24.9 (d, CH_2P, $J_{C\text{-}P}$ = 35), 26.2 (d, CH_2P, $J_{C\text{-}P}$ = 33), 52.7, 102.4, 112.4, 122.6, 125.6, 129.4, 130.5, 132.3, 133.8, 141.9, 144.5, 147.8. $^{31}P\{^1H\}$ NMR: –20.3 (s, 2 P, J_{PPt} = 3673), 2.24 (s, J_{PPt} = 2229). $^{195}Pt\{^1H\}$ NMR: –4465 (dd, J = 3690, 2245). UV-VIS (CH_2Cl_2), λ_{max} (ε): 290 sh (5600), 272 sh (7900). IR (KBr): 3056, 2924, 2361, 1487, 1457, 1274, 1159, 1104, 974, 747, 693, 631, 518. ESI-MS: calculated *m/z* 1675.4, found *m/z* 1612.9 $(M - NO_3)^+$.

Bicyclo{tris[triptycene-9,10-diethynyl]bis[cis-(dppp)nitratoplatinum]-bis[1,3,5-tris(4-ethynylpyridyl)benzene]} (**8a**)

A suspension of **6a** (78.1 mg, 0.048 mmol) and **7** (13.2 mg, 0.035 mmol) in acetone (3 ml) and water (1 ml) was stirred at room temperature. Over 8 h, the white suspension gradually turned to a clear yellow solution. Diethyl ether was added, resulting in the formation of a precipitate that was collected, washed with diethyl ether, and dried under reduced pressure to yield **8a** (85 mg, 95%). M.p. 174 °C (dec.). ^1H NMR: 2.17 (m, 12 H, CH_2), 2.86 (m, 12 H, CH_2P), 3.06 (m, 12 H, CH_2P), 6.68 (m, 36 H, $H_{o,m}$-triptycyl), 7.17 (d, 12 H, β-py, J = 5.6), 7.32 (m, 24 H, ph), 7.43 (m, 12 H, ph), 7.50–7.63 (m, 66 H, ph-dppp and 1,3,5-subst. benzene), 8.07 (m, 24 H, ph), 8.51 (m, 12 H, α-py). $^{13}C\{^1H\}$ NMR: 19.6, 24.1 (d, CH_2P, $J_{C\text{-}P}$ = 34), 25.6 (d, CH_2P, $J_{C\text{-}P}$ = 35), 52.5, 87.1, 95.1, 98.4, 122.3, 123.0, 125.2, 128.0, 128.4, 128.6, 129.2, 129.6, 129.7, 129.9, 132.3, 133.4, 133.8, 136.6, 145.1, 151.6. $^{31}P\{^1H\}$ NMR: –11.7 (d, 6 P, J_{PP} = 28, J_{PPt} = 3124), 0.6 (d, 6 P, J_{PP} = 28, J_{PPt} = 2214). $^{195}Pt\{^1H\}$ NMR: –4545 (dd, J = 3123, 2205). UV-VIS (CH_2Cl_2), λ_{max} (ε): 304 (129 000), 322 (117 000). IR (KBr): 3052, 2923, 2361, 2212, 1608, 1507, 1456, 1436, 1384, 1334, 1274, 1212, 1158, 1102, 1062, 1028, 973, 881, 829, 794, 746, 693, 640, 517. ESI-MS: 5618.9 (calculated for $[M - 1\ NO_3]^+$ 5619.0), 2778.4 (calculated for $[M - 2\ NO_3]^{2+}$ 2778.6), 1831.4 (calculated for $[M - 3\ NO_3]^{3+}$ 1831.7), 1358.3 (calculated for $[M - 5\ NO_3]^{5+}$ 1074.2). For $C_{288}H_{222}N_{12}O_{18}P_{12}Pt_6$ (5681.3) calculated: 60.89% C, 3.94% H; found: 60.43 C, 3.71 H.

Bicyclo{tris[2,3-difluorotriptycene-9,10-diethynyl]bis[cis-(dppp)nitratoplatinum]-bis[1,3,5-tris(4-ethynylpyridyl)benzene]} (**8b**)

A suspension of **6b** (63.5 mg, 0.038 mmol) and **7** (9.9 mg, 0.026 mmol) in acetone (3 ml) and water (1 ml) was stirred at room temperature. Over 8 h, the white suspension gradually turned to a clear yellow solution. Diethyl ether was added, resulting in the formation a precipitate which was collected and washed with diethyl ether and dried under reduced pressure to yield **8b** (69 mg, 94%). M.p. 187 °C (dec.). ^1H NMR: 2.19 (m, 12 H, CH_2), 2.88 (m, 12 H, CH_2P), 3.09 (m, 12 H, CH_2P), 6.49 (t, 6 H, $J_{H,F}$ = 8.8, triptycyl), 6.71 (s, 24 H, triptycyl), 7.16 (12 H, β-py, J = 5.7), 7.32 (m, 24 H, ph), 7.42 (m, 12 H, ph), 7.45–7.62 (m, 66 H, ph-dppp and 1,3,5-subst. benzene), 8.05 (m, 24 H, ph), 8.52 (m, 12 H, α-py). $^{13}C\{^1H\}$ NMR: 19.5, 23.9 (d, CH_2P, $J_{C\text{-}P}$ = 34), 24.8 (d, CH_2P, $J_{C\text{-}P}$ = 35), 52.6, 87.1, 95.1, 97.6, 112.0, 122.4, 123.1, 125.5, 128.0, 128.5, 128.6, 129.2, 129.6, 129.7, 129.9, 132.4, 133.4, 133.8, 136.6, 142.0, 144.6, 146.4, 151.6. $^{31}P\{^1H\}$ NMR: –11.8 (d, 6 P, J_{PP} = 28, J_{PPt} = 3139), 0.4 (d, 6 P, J_{PP} = 28, J_{PPt} = 2224). $^{195}Pt\{^1H\}$ NMR: –4542 (dd, J = 3122, 2210). ^{19}F NMR: –143.7 (t, J = 9). UV-VIS (CH_2Cl_2), λ_{max} (ε): 306 (187 000), 322 (178 000). IR (KBr): 2360, 2212, 1652, 1610, 1558, 1488, 1384, 1334, 1103, 1062, 778, 694, 518. ESI-MS: 5727.2 (calculated for $[M - 1\ NO_3]^+$ 5727.0), 2832.8 (calculated for $[M - 2\ NO_3]^{2+}$ 2832.5), 1867.9 (calculated for $[M - 3\ NO_3]^{3+}$ 1867.7), 1385.4 (calculated for $[M - 4\ NO_3]^{4+}$ 1385.3), 1095.8 (calculated for $[M - 5\ NO_3]^{5+}$ 1095.8). For $C_{288}H_{216}F_6N_{12}O_{18}P_{12}Pt_6$ (5789.2) calculated: 59.75% C, 3.76% H; found: 59.60% C, 3.71% H.

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