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Self-Assembly of Molecular Prisms via Pt_3 Organometallic Acceptors and a Pt_2 Organometallic Clip

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The design and two-component [2 + 3] self-assembly of a series of new organometallic molecular prisms (**3a**−**d**) are described. Assemblies **3a**,**b** incorporate 4,4′,4′-tris[ethynyl-*trans*-$Pt(PEt_3)_2(NO_3)$]-triphenylamine (**1a**) containing a Pt-ethynyl functionality as tritopic planar acceptor and organic "clips" **2a** and **2b**, respectively [where **2a** = 1,3-bis(3-pyridyl)isophthalic amide; **2b** = 1,3-bis(ethynyl-3-pyridyl)benzene]. In a complementary approach an organic tritopic planar donor ligand **2c** [**2c** = 4,4′,4′-tris(4-pyridylethynyl)triphenylamine] was assembled with an organometallic "clip", 1,8-bis-[{*trans*-$Pt(PEt_3)_2(NO_3)$}ethynyl]anthracene (**1b**), to obtain prism **3c**. A new organometallic carbon-centered acceptor, 1,1,1-tris[4-{*trans*-$Pt(PEt_3)_2(NO_3)$}ethynylphenyl]ethane (**1c**), has been prepared, and its prism derivative (**3d**) using an organic "clip" is prepared. Assemblies (**3a**−**d**) were characterized by multinuclear NMR spectroscopy, electrospray ionization mass spectroscopy, and elemental analysis. **3a**−**d** showed fluorescence behavior in solution, and quenching of fluorescence intensity (**3a**, 3c−**d)** was noticed upon addition of TNT (2,4,6-trinitrotoluene), a common constituent of many commercial explosives. A thin film of the assembly **3d** made by spin coating of a solution of 3×10^{-5} M in DMF on a 1 cm^2 quartz plate showed fluorescence response to the vapor of TNT.

Introduction

Directional self-assembly of large discrete architectures driven by metal−ligand coordination bonding interaction is established as one of the most prevalent areas of modern supramolecular chemistry.[1−4] Symmetrical polypyridyl donors are the most widely used class of linkers, though in a few recent cases oxygen donor carboxylates have also been used to design neutral Pt/Pd architectures.[5] Since the properties of a molecule are guided mainly by the functional groups present, the important aspect of the coordination-driven self-assembly is the introduction of functionality into the final assemblies by choosing appropriate building units containing proper functional groups.[6] Among the several kind of linkers used to design polynuclear transition metal complexes, the ones that contain ethynyl spacers in the

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backbones have been shown to be good members to design a variety of assemblies with potential applications in optical electronics.[7] Detection of trace analyte is a central challenge in the field of chemical sensors. For security reasons attention has been paid recently to discovering suitable sensors for nitroaromatic explosives (DNT, TNT). However, polyacetylenes and other conjugated organic polymers are the commonly studied materials as sensors for these explosives. The possibility of conjugated metal−organic discrete assemblies of finite shapes and sizes as sensors for nitroaromatics needs to be explored. Recently, we have used a new Pt$_3$ organometallic acceptor, 4,4′,4″-tris[ethynyl-*trans*-Pt-(PEt$_3$)$_2$(NO$_3$)]triphenylamine (**1a**), containing Pt-ethynyl functionality to construct a fluorescent trigonal prism (**3a**) in combination with an organic “clip”.[8] Interestingly, the solution fluorescence of **3a** was quenched efficiently by adding nitroaromatics, which are the chemical signatures of many explosives. Here, we report the synthesis of a new trigonal prism (**3b**) from **1a** using an ethynyl-containing donor clip, 1,3-bis(3-pyridylethynyl)benzene[9] (**2b**) (Scheme 1). A complementary approach has also been used to prepare a prism (**3c**) from an organic tritopic planar donor, 4,4′,4″-tris(4-pyridylethynyl)triphenylamine (**2c**), in combination with an organometallic Pt$_2$-clip (**1b**) containing an ethynyl functionality (Scheme 1). In addition, we report here the synthesis of a new tripodal Pt$_3$-organometallic acceptor, 4,4′,4″-tris[ethynyl-*trans*-Pt(PEt$_3$)$_2$(NO$_3$)]triphenylethane (**1c**), and its [2 + 3] self-assembled prismatic derivative (**3d**) by assembling with a conjugated organic clip, [1,8-bis(4-pyridylethynyl)anthracene] (**2d**) (Scheme 2). All four supramolecular prisms (**3a−d**) show luminescent behavior due to the presence of a Pt-ethynyl functionality and conjugated π-electrons. The solution state fluorescence of molecular prisms **3a**, **3c**, and **3d** is gradually quenched upon addition of TNT. In the case of **3d**, a spin-cast film prepared by spin coating of a DMF solution of **3d** over quartz shows fluorescent quenching on exposure to TNT vapor.

Results and Discussion

Synthesis of the Linkers. Halogenated aromatic compounds are an adequate choice as starting materials in self-assembly because a large number of acceptors/donors can easily be synthesized starting from these compounds.[10] The acceptor **1a** was prepared from tris(4-bromophenyl)amine as a halogenated aromatic compound using the procedure discussed in our recent communication.[8] In a similar way, 1,8-dichloroanthracene was used as the starting material to obtain 1,8-diethynylanthracene followed by treatment with an excess of *trans*-Pt(PEt$_3$)$_2$I$_2$ and subsequent nitration with AgNO$_3$ to synthesize **1b**. The carbon-centered new tripodal acceptor **1c** was prepared from 1,1,1-tris(4-iodophenyl)-ethane, which was prepared according to the literature procedure.[11] Coupling of trimethylsilylacetylene (Me$_3$SiCCH) with 1,1,1-tris(4-iodophenyl)ethane followed by desilylation gives the ethynyl-incorporated compound 1,1,1-tris(4-ethynylphenyl)ethane (Scheme 3). Treatment of 1,1,1-tris(4-ethynylphenyl)ethane with 4 equiv of *trans*-(PEt$_3$)$_2$PtI$_2$ in the presence of CuI catalyst in dry Et$_2$NH medium at room temperature overnight produced the iodo derivative 1,1,1-tris [4-(*trans*-Pt(PEt$_3$)$_2$I)ethynylphenyl]ethane, which was separated by column chromatography and isolated in yellow microcrystalline form. The trinitrate derivative **1c** was synthesized from the iodide derivative upon treatment with 3 equiv of AgNO$_3$ at room temperature with an isolated yield of 88%.

The ^{1}H and ^{31}P{^{1}H} NMR spectra as shown in Figure 1 indicate the formation of a symmetric tritopic linker, **1c**. The appearance of a single peak in the ^{31}P{^{1}H} NMR along with concomitant ^{195}Pt satellites indicated the formation of a single product as well. Finally, the actual composition of **1c** was confirmed by the appearance of peaks at $m/z = 1807.5$ and 1274 in the ESI mass spectrum, corresponding to the molecular ion $[M + H^+]$ and $[M - 4PEt_3 - NO_3^-]^+$ fragment, respectively (Supporting Information).

All four donors **2a−d** were synthesized using reported procedures.[8,9,11,12] **1a** and **1b** were fully characterized by multinuclear NMR, ESI mass spectrometry, and single-crystal X-ray diffraction study.[8,6c] Several efforts to obtain good-quality single crystals of **1c** were unsuccessful, and only a very tiny amount of crystalline material was obtained. Although it was possible to determine the cell dimensions (crystal system, cubic; space group, $Pa\bar{3}$; a = 25.4754(5) Å; $\alpha = 90°$) of **1c** from a diffraction study, a full set of data could

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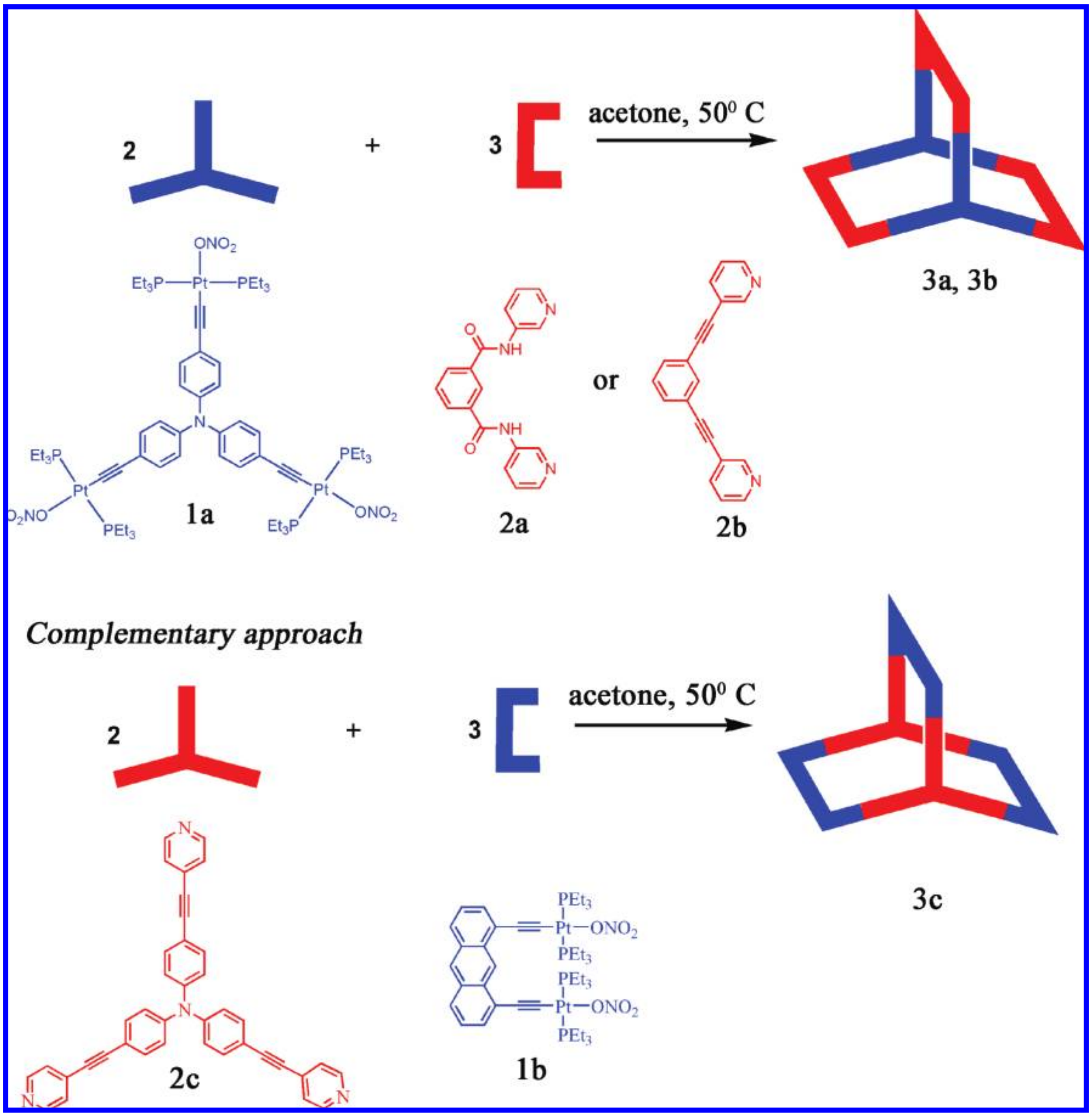
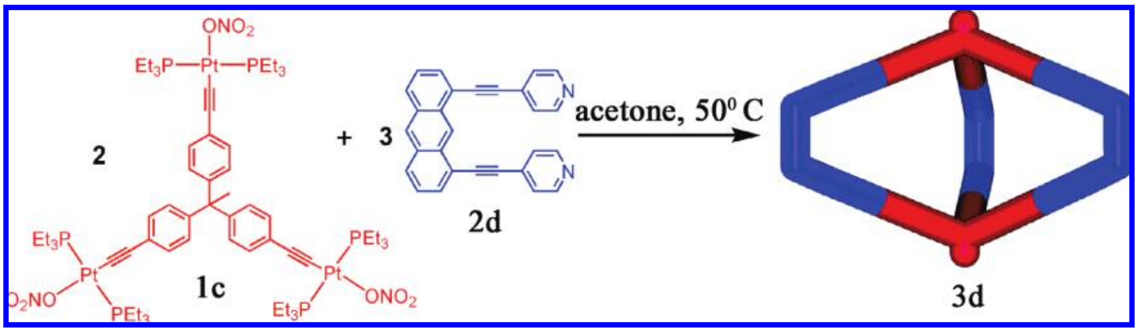
Scheme 1. Self-Assembly of Trigonal Prisms 3a−c

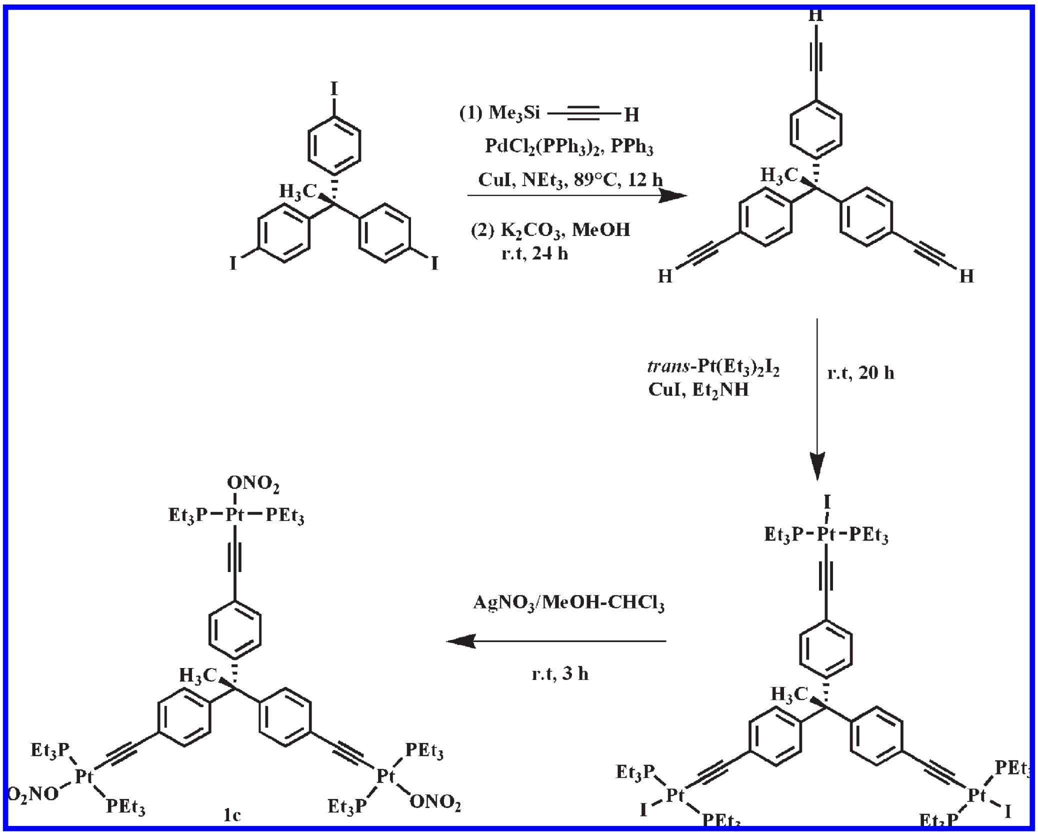


Scheme 2. Self-Assembly of the Cage 3d from the New Tripodal Pt$_3$-Organometallic Acceptor 1c and the Organic Clip 2d



not be collected. Hence, the optimization of the tripodal linker has been done by density functional theory (DFT) calculations to obtain a view of the shape of 1,1,1-tris-[4-(*trans*-Pt(PEt$_3$)$_2$I)ethynylphenyl]ethane (Figure 2). The B3LYP functional was used for the DFT calculation, which was performed with the Gaussian 03 program. Two basis sets were employed, 6-31G for lighter elements (C, H, N, and O) and LanL2DZ for heavier elements (Pt and P). The average I−C(central)−I angle in the structure is 110.97°, which is very close to a similar angle (110.53°) reported by Stang et al. from X-ray structure analysis of an analogous linker containing no ethynyl group.[11] The angles around the Pt environment vary between 86.44° and 93.11°, which is expected for a square-planar metal center.

Scheme 3. Schematic Presentation of the Synthesis of 4,4′,4″-Tris[ethynyl-*trans*-Pt(PEt_3)$_2$(NO_3)]triphenylethane (1c) from 1,1,1-Tris(4-iodophenyl)ethane



Self-Assembly of Molecular Prisms 3a–d. As per the general concept of geometry, a trigonal prism can be designed from two tritopic donors, six 90° corners, and three linear linkers by a [2 + 6 + 3] self-assembly reaction as shown in Scheme 4. The major disadvantage of three-component self-assembly is the formation of a mixture of several possible discrete assemblies (Scheme 4). Recently, Fujita's group has reported the formation of a prism including other expected closed structures using a three-component self-assembly reaction.[13] Selective formation of the prism **4** of *cis*-(en)Pt(NO_3)$_2$ was achieved only in the presence of appropriate guest, which favored the formation of a prism by host–guest interaction.[13a] To avoid the formation of unnecessary byproducts, we have utilized a [2 + 3] two-component self-assembly strategy as shown in Schemes 1 and 2.

Supramolecular prisms **3a** and **3b** were synthesized from the tritopic organometallic planar acceptor **1a** by [2 + 3] self-assembly using flexible and rigid donor clips **2a** and **2b**, respectively. When 4,4′,4″-tris[ethynyl-*trans*-Pt(PEt_3)$_2$(NO_3)]triphenylamine (**1a**)[8] acceptor was treated with 1.5 equiv of the donor ligand **2a**[14] in a mixture of methanol and dichloromethane for 30 min, the self-assembly of the cationic prism **3a** as a single product occurred. The completion of the reaction was monitored by TLC. $^{31}P\{^1H\}$ NMR analysis of the reaction solution showed the quantitative formation of a single, highly symmetrical species (**3a**) by the appearance of a sharp singlet with concomitant ^{195}Pt satellites, shifted 5 ppm upfield ($-\Delta\delta$) relative to **1a**. Finally, mass spectrometric analysis confirmed the formation of the (**1a**)$_2$(**2a**)$_3$ cage (Supporting Information).[8] In a similar way **3b** was prepared by reacting **1a** with 1.5 equiv of **2b** in acetone medium for 12 h at 50 °C. The product (**3b**) was formed as a yellow precipitate, which was washed with acetone several times. ^{31}P NMR of the product in $CDCl_3$ showed a sharp singlet at 15.6 with a change in $^1J_{P-Pt}$ (230 Hz) for the Pt satellites. An upfield shift of 4.5 ppm of the $^{31}P\{^1H\}$ NMR signal of **1a** upon reaction with **2b** and complete disappearance of the peak due to starting acceptor clearly indicate the formation of a single product. ^1H NMR shows the expected downfield shifts of the pyridyl protons and the symmetric nature (Supporting Information) of the product by the appearance of other expected signals. Supramolecular prism **3c** is an example of the scope and versatility of the directional bonding methodology, where in a complementary approach the clip type of acceptor linker **1b** with a tripodal donor **2c** forms **3c** in almost quantitative yield, as shown in Scheme 1. To a stirred suspension of the clip-type acceptor **1b** in acetone was added ligand **2c**. The suspension became transparent yellow in a few minutes after heating at 50 °C followed by the formation of the final product (**3c**) as yellow precipitate after stirring for 12 h. A sharp singlet appeared at 14 ppm in $^{31}P\{^1H\}$ NMR spectrum, which is 5 ppm upfield shifted from the $^{31}P\{^1H\}$ NMR of the starting linker **1b** (Figure S5, Supporting Information). The downfield shift of the pyridine H_α proton by 0.3 ppm and the 0.1 ppm upfield shift of the H_{10} of the clip were in strong support of the coordination of ligand **2c** to the

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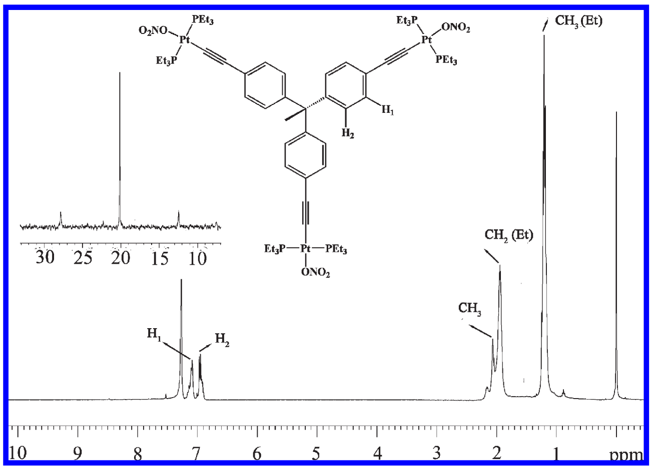

Figure 1. ^{1}H and ^{31}P{^{1}H} (inset) NMR spectra of **1c** in CDCl$_3$.

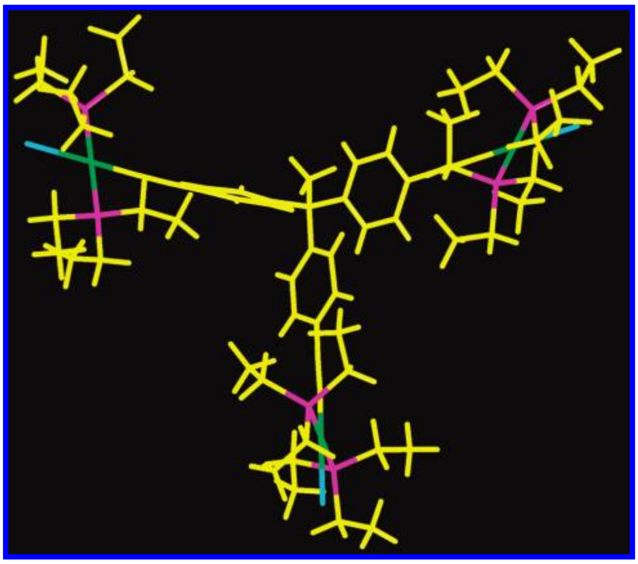

Figure 2. Calculated optimized structure of 1,1,1-tris[4-(*trans*-Pt(PEt$_3$)$_2$I)ethynylphenyl]ethane obtained using DFT.

acceptor and formation of the symmetric supramolecular prism **3c** (Supporting Information).

To expand the methodology of designing a trigonal prism by [2 + 3] self-assembly of two components, we modified the tritopic planar acceptor, replacing the central nitrogen of **1a** by $-$C(CH$_3$), and prepared a new organometallic tripodal acceptor (**1c**) containing Pt-ethynyl functionality. Reaction of this new **1c** with 1.5 equiv of the rigid organic clip **2d**[7f] in acetone at 50 °C overnight yielded **3d** as a fluorescent yellow precipitate. The expected upfield shift of the phosphorus signal of **1c** upon reaction with **2d** was observed. Similarly, the H$_\alpha$, H$_\beta$, and H$_9$ protons of the donor ligand showed the expected downfield shifts (Figure 3).

Multinuclear NMR spectroscopy provides an indication of the metal$-$ligand bonding and the formation of a single product. However, it does not provide much information about the shape of this kind of product and the actual composition. ESI mass spectrometry has proven to be a potential tool in the corroboration of structural assignments for this kind of large supramolecular assembly.[15] Mass spectrometric characterizations of **3a$-$d** were performed by ESI technique, which allowed keeping the assembly intact during the ionization process while obtaining the high resolution required for unambiguous determination of the charge states. Electrospray mass spectroscopic study confirmed a (**1a**)$_2$(**2a**)$_3$ composition for cage **3a**. The mass spectrum of **3a** (Supporting Information)[8] showed signals corresponding to the consecutive loss of nitrate counterions, $[\mathrm{M}_{3a}-3\mathrm{NO}_3]^{3+}$, $[\mathrm{M}_{3a}-4\mathrm{NO}_3]^{4+}$, and $[\mathrm{M}_{3a}-5\mathrm{NO}_3]^{5+}$. For **3a**: $[\mathrm{M}_{3a}-3\mathrm{NO}_3]^{3+}$ [m/z = 1452.00 (calcd 1451.66); M$_{3a}$ = molecular mass of **3a**]; $[\mathrm{M}_{3a}-4\mathrm{NO}_3]^{4+}$ [m/z = 1073.49 (calcd 1073.18)]; $[\mathrm{M}_{3a}-5\mathrm{NO}_3]^{5+}$ [m/z = 846.55 (calcd 845.67)].[8] The isotopic distribution pattern of the peak at m/z corresponding to $[\mathrm{M}_{3a}-3\mathrm{NO}_3]^{3+}$ matched well with the theoretical isotopic distribution pattern. In the case of **3b** the peaks at m/z corresponding to the fragments $[\mathrm{M}_{3b}-6\mathrm{NO}_3^-]^{6+}$, $[\mathrm{M}_{3b}-5\mathrm{NO}_3^-]^{5+}$, and $[\mathrm{M}_{3b}-3\mathrm{NO}_3^-]^{3+}$ were observed and the isotropic distribution pattern of the peak due to $[\mathrm{M}_{3b}-3\mathrm{NO}_3^-]^{3+}$ matched well with the theoretically expected pattern (Supporting Information). The ESI-MS spectrum of supramolecular prism **3c** gave a peak at m/z corresponding to $[\mathrm{M}_{3c}-4\mathrm{NO}_3^-]^{4+}$ along with that of $[\mathrm{M}_{3c}-4\mathrm{PEt}_3-4\mathrm{NO}_3^-]^{4+}$ and $[\mathrm{M}_{3c}-3\mathrm{PEt}_3-3\mathrm{NO}_3^-]^{3+}$ fragments. The isotropic distribution pattern of the latter established the charge state (Supporting Information). Similarly, **3d** showed signals corresponding to the consecutive loss of nitrate counterions, $[\mathrm{M}_{3d}-3\mathrm{NO}_3]^{3+}$ and $[\mathrm{M}_{3d}-5\mathrm{NO}_3]^{5+}$. For **3d**: $[\mathrm{M}_{3d}-3\mathrm{NO}_3]^{3+}$ [m/z = 1523.50 (calcd 1523.33); M$_{3d}$ = molecular mass of **3d**]; $[\mathrm{M}_{3d}-5\mathrm{NO}_3]^{5+}$ [m/z = 890.1 (calcd 889.3)]. Along with these, peaks corresponding to the fragments $[\mathrm{M}-7\mathrm{PEt}_3-4\mathrm{NO}_3^-]^{4+}$, $[\mathrm{M}-8\mathrm{PEt}_3-3\mathrm{NO}_3^-]^{3+}$, and $[\mathrm{M}-12\mathrm{PEt}_3-2\mathrm{NO}_3^-]^{2+}$ were also obtained. The isotopic distribution pattern of the peak corresponding to $[\mathrm{M}-3\mathrm{NO}_3]^{3+}$ matched well with the theoretical pattern and thus established the formation of a discrete assembly of composition (**1c**)$_2$(**2d**)$_3$. Several attempts to obtain single crystals for X-ray diffraction have failed. The proposed structure of the supramolecule **3d** obtained by energy minimization is presented in Figure 4.

Absorption and Fluorescence Studies. Absorption spectra of complexes **3b$-$d** were recorded in DMF. The spectrum of a 1.5×10^{-5} M solution of **3b** in DMF shows peaks at 283 and 365 nm (dash-dot lines in Figure 5). The peak at 365 nm is due to the metal-to-ligand (**2b**) charge transfer, whereas the peak at 283 nm is due to $\pi-\pi^*$ transition. In the case of complex **3c** the absorption spectrum of a 3×10^{-6} M solution in DMF shows peaks at 430 and 383 nm, which are originating from the anthracene moiety of **1b**, whereas the peak at 270 nm corresponds to the metal-to-ligand (**2c**) charge transfer (Figure 5, dashed line).

For complex **3d** peaks at 421 and 398 nm corresponding to the anthracene part are observed, whereas the peak at 309 nm is attributed to platinum-to-ligand (**2d**) charge transfer (Figure 5, solid line). When excited at 400 nm all complexes (**3b$-$d**) show luminescent behavior and emit between 400 and 500 nm. Fluorescence spectra of the complexes **3b$-$d** recorded in DMF solutions are assembled in Figure S10 (Supporting Information), and corresponding photophysical data are given in Table S1 (Supporting Information).

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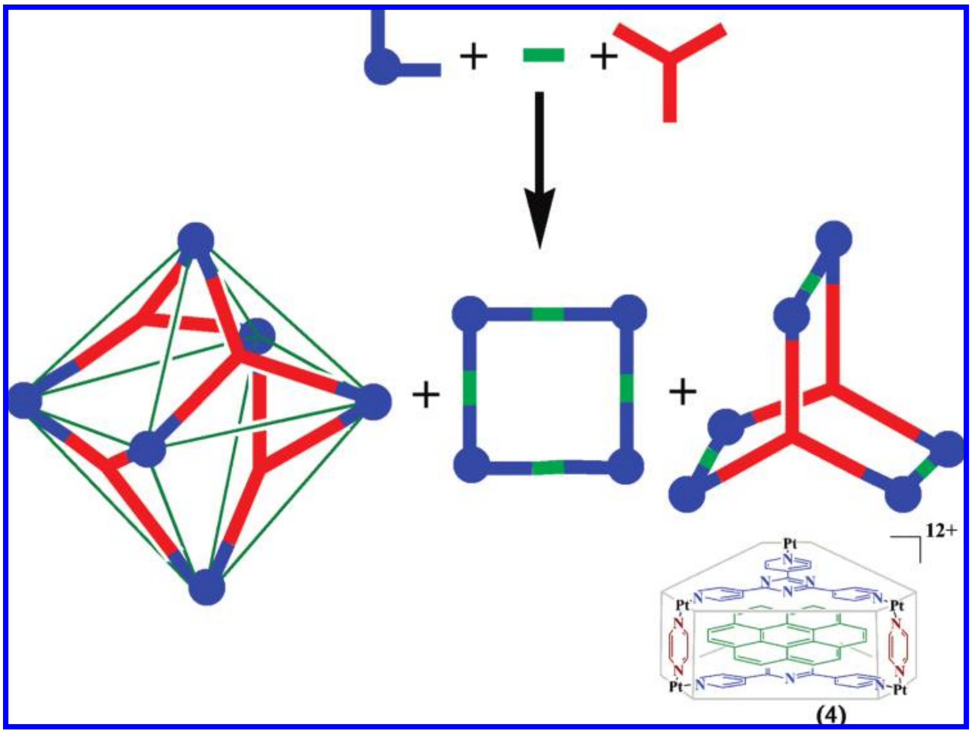
[15] (a) Jude, H.; Disteldorf, H.; Fischer, S.; Wedge, T.; Hawkridge, A. M.; Arif, A. M.; Hawthorne, M. F.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 12131. (b) Jude, H.; Sinclair, D. J.; Das, N.; Sherburn, M. S.; Stang, P. J. *J. Org. Chem.* **2006**, *71*, 4155, and references therein.

Scheme 4. Three-Component Self-Assembly of 90°, Linear, and Tritopic Planar Linkers and the Formation of the Cage 4 Using This Methodology in the Presence of Appropriate Guest



Quantum yields (Φ_F) of **3c** and **3d** are high compared to complex **3b**. Lifetimes of **3a** and **3d** were measured to be 8 and 6.2 ns.

Fluorescence Quenching Studies. Fluorescence-quenching-based detection of chemical explosives is very important because of huge applications in defense and security.[16] Conjugated polymers are proven to be efficient redox sensors for explosives, as they are electron donors.[17,16b] Porous polyethynyl compounds have been investigated as potential fluorescent sensors for nitroaromatics, which are the chemical signatures of many explosives. Porous polymers are better sensors than simple nonporous analogues since the porous nature of the polymers produces a high free volume in the structure, which imparts permeability and allows small nitroaromatic vapor to penetrate quickly into the polymer.[17,18] Nitroaromatics are electron deficient in nature, and substitution of electron-withdrawing nitro groups on the aromatic ring lowers the energy of the empty π^* orbitals, thereby making them good electron acceptors. Keeping these factors in mind, the cages **3a**−**d** were designed for the following reasons: (a) a Pt-ethynyl functionality was introduced to make the assemblies fluorescent and to make them π-electron rich; (b) open spaces in the large cages are suitable to accommodate electron-deficient small nitroaromatics; (c) bulky PEt_3 groups help to avoid intermolecular stacking and thus prevent the chance of self-quenching of fluorescence. The solution fluorescence of **3a** was quenched efficiently by adding nitroaromatics such as DNT and TNT, which are the chemical signatures of many explosives.[8] The fluorescence intensity in the solution state of both **3c** and **3d** undergoes quenching upon gradual addition of a TNT (2,4,6-trinitrotoluene) solution. In the case of prism **3c**, a 3×10^{-6} M solution in DMF was titrated with a TNT solution (Figure 6) and showed quenching of the fluorescence intensity. The Stern−Volmer plot (Figure 6) gives a quenching constant of $K_{SV} = 13.04 \pm 0.62$.

When a 1.5×10^{-6} M solution of **3d** in DMF was titrated with a TNT solution in methanol, the fluorescence intensity gradually decayed, as shown in Figure 7. The mechanism of fluorescence quenching may be due to the formation of a charge transfer complex between the excited state of

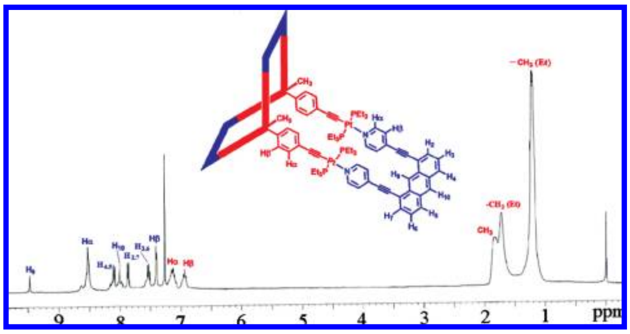


Figure 3. ^{1}H NMR spectra of **3d** in $CDCl_3$.

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(16) (a) Rouhi, A. M. *Chem. Eng. News* **1997**, *75*, 14. (b) Rose, A.; Zhu, Z.; Madigan, C. F.; Swager, T. M.; Bulovic, V. *Nature* **2005**, *434*, 876. (b) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537. (c) Yinon, J. *Anal. Chem.* **2003**, *75*, 99A. (d) Content, S.; Trogler, W. C.; Sailor, M. J. *Chem.*—*Eur. J.* **2000**, *6*, 2205. (e) Balakrishnan, K.; Datar, A.; Zhang, W.; Yang, X.; Naddo, T.; Huang, J.; Zuo, J.; Yen, M.; Moore, J. S.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 6576. (f) *Chemosensors of Ion and Molecule Recognition*; Desvergne, J. P., Czarnik, A. W., Eds.; Kluwer Academic Publishers: Boston, 1997. (g) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (h) Thomas, S. W.; Amara, J. P.; Bjork, R. E.; Swager, T. M. *Chem. Commun.* **2005**, 4572. (i) Albert, K. J.; Myrick, M. L.; Brown, S. B.; James, D. L.; Milanovich, F. P.; Walt, D. R. *Environ. Sci. Technol.* **2001**, *35*, 3193. (j) Moore, D. S. *Rev. Sci. Instrum.* **2004**, *75*, 2499. (k) Czarnik, A. W. *Nature* **1998**, *394*, 417.

(17) (a) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201. (b) Liu, Y.; Mills, R.; Boncella, J.; Schanze, K. *Langmuir* **2001**, *17*, 7452.

(18) Tsuchihara, K.; Masuda, T.; Higashima, T. *J. Am. Chem. Soc.* **1991**, *113*, 8548.

π-electron rich cage **3d** and electron-deficient oxidizing 2,4,6-trinitrotoluene (TNT). The Stern−Volmer plot (Figure 7) gives a quenching constant of K_{SV} = 173.3 ± 5.46. The high quenching constant in the case of **3d** is probably due to the presence of electron-donating $-CH_3$, which makes the cage a better host for electron-deficient TNT. TNT absorbs irradiation below 300 nm,[6g] and emissions of the supramolecules **3a−d** are far above 350 nm (Figure S10 and ref 8). The lack of overlap between the emission of supramolecular cages and the absorption of TNT ruled out the possibility of energy transfer from the excited cages to the explosives quencher. Hence the observed fluorescence quenching in the present study is presumably due to the photoinduced electron transfer from the excited state of the cages to the ground state of the TNT. This facile electron transfer is expected due to the strong oxidation potential of

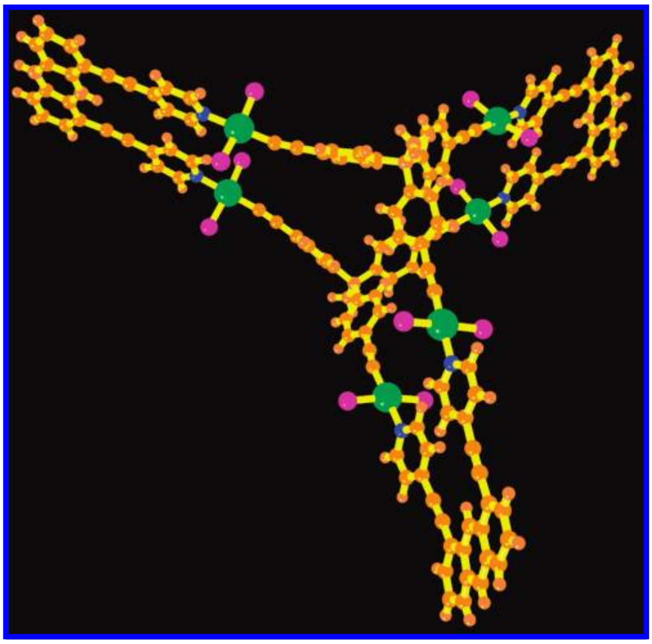

Figure 4. Proposed view of the optimized structure of **3d**. Ethyl groups are omitted for the sake of clarity. Color codes: green = Pt; pink = P; blue = N.

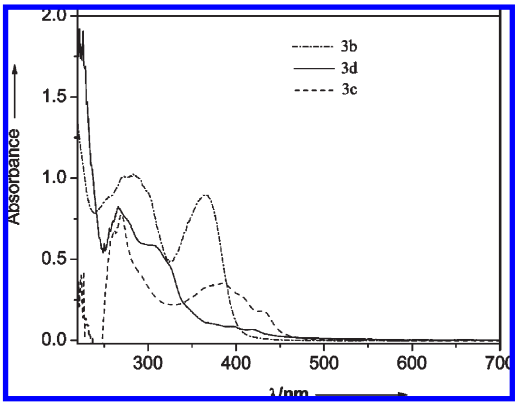

Figure 5. UV−vis spectra of **3b−d** in DMF solution.

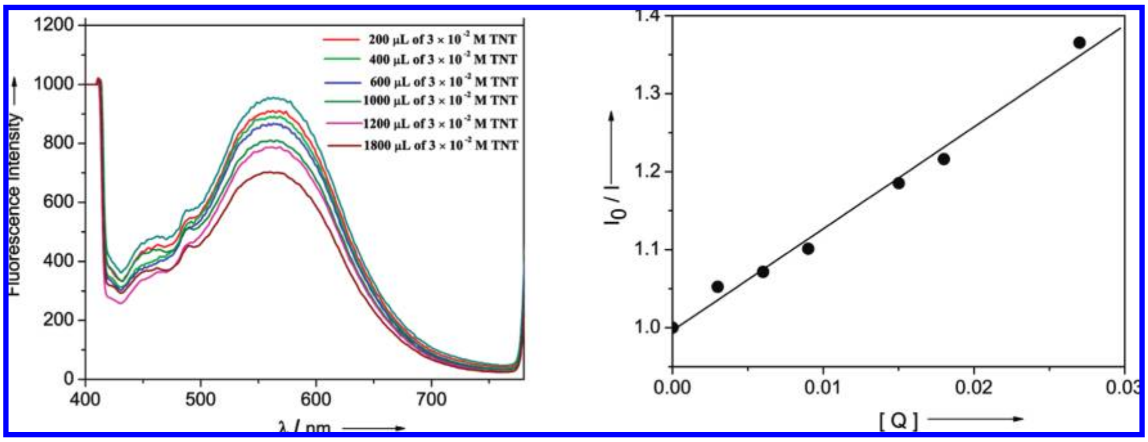

Figure 6. Quenching of fluorescence intensity of **3c** on gradual addition of TNT (left) and Stern−Volmer plot (right).

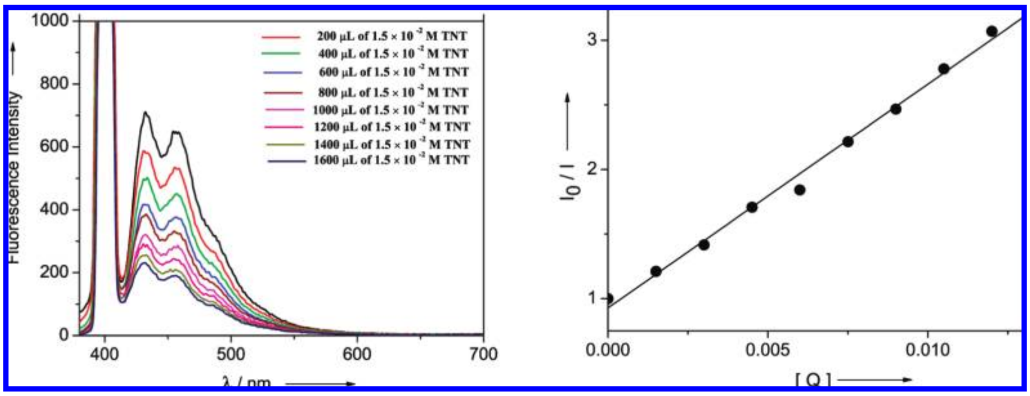

Figure 7. Quenching of fluorescence intensity of **3d** on gradual addition of TNT (left) and Stern−Volmer plot (right).

TNT and the presence of conjugated labile π-electrons in the fluorophor.

To check whether **3d** can detect the presence of trace amounts of TNT, a 1.5×10^{-5} M solution of **3d** was titrated with a $\sim 10^{-5}$ M solution of TNT (Supporting Information). Quenching of fluorescence intensity of **3d** was noticed upon addition of TNT. However, the percentage of quenching was less in this case. Interestingly, when the starting Pt_3 acceptor **1c** was titrated with TNT solution, no quenching of fluorescence intensity of **1c** was noticed. In the case of **2d** very weak quenching was noticed. These observations suggest that incorporation of the electron-deficient TNT inside the cavity of electron-rich cage **3d** and host−guest interactions among them are possible reasons for this quenching.

Solid State Fluorescence Quenching of 3d by TNT Vapor. A thin film of the prism **3d** was made by spin coating of a solution of 3×10^{-5} M of **3d** in DMF on 1 cm^2 quartz plate. The fluorescence response of this film to the vapor of TNT was ascertained by inserting the film in a sealed vial containing solid TNT and cotton gauze separating the film from direct contact with the TNT. The film was exposed to the vapor of TNT, and the fluorescence was measured between a particular time interval; it was found to be quenched gradually as shown in Figure S14 in the Supporting Information.

Conclusion

In conclusion, we herein report the synthesis and characterization of a new Pt_3 organometallic acceptor (**1c**) and a series of nanoscopic conjugated prisms (**3a**−**d**) containing a Pt-ethynyl functionality. A complementary approach has been applied using a tritopic planar donor (**2c**) and Pt_2-organometallic clip (**1b**) to establish the versatility of directional bonding to obtain a similar kind of architecture using a reverse approach. Incorporation of a Pt-ethynyl functionality makes the assemblies fluorescent in nature. Moreover, the conjugated ethynyl functionality makes the assemblies π-electron rich and possible hosts for electron-deficient nitroaromatics. All four assemblies showed fluorescent behavior in solution, and the fluorescent intensity of the cages **3a**, **3c**, and **3d** in solution was quenched upon addition of electron-deficient TNT, which is the chemical signature of many commercial explosives. Conjugated organic polyethynyl compounds have been used as potential sensors for chemical explosives.[19] However, the discrete organometallic cages **3a**−**d** presented in this article represent an interesting class of materials, which can detect the presence of TNT by fluorescence quenching study.

Experimental Section

Synthesis of 4,4′,4″-Tris[ethynyl-*trans*-Pt(PEt$_3$)$_2$(NO$_3$)]triphenylamine (1a). In a flame-dried Schlenk flask *N,N,N*-tris-(4-ethynylphenyl)amine [98.9 mg, 0.312 mmol] and *trans*-Pt-$(PEt_3)_2I_2$ [1.0 g, 1.45 mmol] were taken, and the flask was degassed and purged with nitrogen. Dry, deoxygenated toluene (25 mL) and 10 mL of dry diethylamine were added successively. After stirring for 30 min under N_2, CuI [25 mg, 0.132 mmol] was added and the mixture was stirred for 20 h under N_2. The precipitate of diethylammonium chloride (Et_2NH_2Cl) was separated, and the solvent was removed under vacuum. The residue was chromatographed using a silica gel column by a benzene/hexane (1:1) mixture to obtain 4,4′,4″-tris[ethynyl-*trans*-$Pt(PEt_3)_2(I)$]triphenylamine (MW 1989.25) (400 mg) as a pale yellow powder in 64% isolated yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.1 (d, 6H, Ph-H), 6.9 (d, 6H, Ph-H), 2.2 (q, 36H, PEt_3), 1.2 (t, 72H, PEt_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 120 MHz): δ 8.6 (s, $^1J_{P-Pt} = 2874$ Hz).

To a methanolic solution of $AgNO_3$ [5.1 mg, 0.03 mmol] was added a solution of 4,4′,4″-tris[ethynyl-*trans*-$Pt(PEt_3)_2(I)$]triphenylamine [19.9 mg, 0.01 mmol] in $CHCl_3$. After stirring for 1 h the yellowish precipitate of AgI was filtered through Celite. After removal of the solvent **1a** (MW 1794.5) [16.9 mg] was obtained in 94% isolated yield. Anal. Calcd (%): C 40.16; H 5.73; N 3.12. Found: C 40.29; H 5.60; N 3.23. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.0 (d, 6H, Ph-H), 6.9 (d, 6H, Ph-H), 1.9 (q, 36H, PEt_3), 1.2 (t, 72H, PEt_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 120 MHz): δ 20.0 (s, $^1J_{P-Pt} = 3052$ Hz).

Synthesis of 1,8-Bis[{*trans*-Pt(PEt$_3$)$_2$(NO$_3$)}ethynyl]anthracene (1b). The synthesis was carried out using a standard Schlenk technique under a N_2 atmosphere. To a 100 mL round-bottom Schlenk flask were added *trans*-$Pt(PEt_3)_2I_2$ (1198.7 mg, 1.75 mmol) and 1,8-diethynylanthracene (113.0 mg, 0.5 mmol). Dry toluene (25 mL) and 10 mL of dry diethylamine were added to the mixture. The solution was stirred for 10 min at ambient temperature before 20 mg of CuI was added in one portion under nitrogen. After 2 h of stirring at room temperature a greenish-yellow fluorescent precipitate started to appear. The solvent was removed under vacuum after 16 h to yield the crude coupled product as a greenish-yellow residue. 1,8-Bis[{*trans*-$Pt(PEt_3)_2(I)$}ethynyl]anthracene (MW 1340.85) was separated from the mixture by column chromatography on silica gel with a solvent mixture (benzene/hexane, 2:1). Yield: 60%. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.43 (s, 1H), 8.37 (s, 1H), 7.83 (d, 2H), 7.49 (d, 2H), 7.34 (d, 2H), 2.26 (q, 24H), 1.18 (t, 36H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 120 MHz): δ 8.35 (s, $^1J_{Pt-P} = 2756$ Hz).

To a stirred solution of silver nitrate (25.1 mg, 0.147 mmol) in methanol was added a solution of 1,8-bis[(*trans*-$Pt(PEt_3)_2I$)-ethynyl]anthracene (100.0 mg, 0.074 mmol) in chloroform. After stirring for 3 h the light yellow precipitate of AgI was filtered through Celite and the clear filtrate was evaporated to get **1b** (MW 1211.05) in 90% yield. Anal. Calcd (%): C 41.65; H 5.66; N 2.31. Found: C 41.44; H 5.82; N 2.01. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.27 (s, 1H), 8.35 (s, 1H), 7.82 (d, 2H), 7.42 (d, 2H), 7.35 (d, m), 2.00 (q, 24H), 1.27 (t, 36H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 120 MHz): 19.06 (s, $^1J_{Pt-P} = 3072$ Hz).

1,1,1-Tris(4-ethynylphenyl)ethane. In a flame-dried 100 mL Schlenk flask 1,1,1-tris(4-iodophenyl)ethane[14] (635.8 mg, 1.0 mmol), PPh_3 (10.0 mg, 0.038 mmol), and $PdCl_2(PPh_3)_2$ (60.0 mg, 0.085 mmol) were added, and the flask was degassed three times followed by filling with N_2. Then 40 mL of dried and degassed triethylamine was added to the flask followed by the addition of trimethylsilylacetylene (392.8 mg, 4 mmol). This mixture was stirred under N_2 for 30 min before the addition of CuI (7.0 mg, 0.036 mmol). The reaction mixture was refluxed for 12 h followed by the removal of the solvent under vacuum to yield a residue, which was dissolved in benzene and passed through a short silica gel column. Removal of the solvent gave $MeC(4\text{-}C_6H_4\text{-}CCSiMe_3)_3$ (MW 546.25). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.3 (d, 6H, Ph-H), 7.0 (d, 6H,Ph-H), 2.1 (s, 3H, CH_3), 0.26 (s, 27H, $SiMe_3$). $MeC(4\text{-}C_6H_4\text{-}CCSiMe_3)_3$ (550 mg, 0.99 mmol) was stirred overnight with K_2CO_3 (409.8 mg, 3 mmol) in methanol. Removal of methanol gave a brownish solid, and the hydrolyzed product 1,1,1-tris(4-ethynylphenyl)ethane (MW 330.14) was extracted with toluene (250 mg, 0.75 mmol) in 75% yield. Anal. Calcd (%): C 94.51; H 5.49. Found: C 94.36; H 5.77. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.4 (d, 6H, Ph-H), 7.0 (d, 6H, Ph-H), 3.0 (s, 3H, ethynyl-H), 2.1 (s, 3H, CH_3).

1,1,1-Tris[4-(*trans*-Pt(PEt$_3$)$_2$I)ethynylphenyl]ethane. In a flame-dried Schlenk flask 1,1,1-tris(4-ethynylphenyl)ethane (120 mg, 0.363 mmol) and *trans*-$Pt(PEt_3)_2I_2$ (994.6 mg, 1.45 mmol)

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[19] Toal, S. J.; Trogler, W. C. *J. Mater. Chem.* **2001**, *16*, 2871, and references therein.

were taken and degassed three times followed by purging with N_2. Dried and degassed toluene (30 mL) and 10 mL of dry diethylamine were added, and the mixture was stirred for 30 min before addition of CuI (20.0 mg, 0.105 mmol). Then this was stirred for 20 h under N_2. Solvent was removed, and the residue was chromatographed using silica gel column chromatography (1:1, benzene/hexane). After removal of solvent, 1,1,1-tris-[4-(*trans*-Pt(PEt_3)$_2$I)ethynylphenyl]ethane (MW 2002.29) (450 mg) was obtained as pale yellow powder in 61% isolated yield. Anal. Calcd (%): C 37.19; H 5.29. Found: C 37.47; H 5.56. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.1 (d, 6H, Ph-H), 6.9 (d, 6H, Ph-H), 2.2 (q, 36H, PEt_3), 2.0 (s, 3H, CH_3), 1.1 (t, 54H, PEt_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 120 MHz): δ 8.5 (s, $^1J_{P-Pt}$ = 2880 Hz).

1,1,1-Tris[4-{*trans*-Pt(PEt_3)$_2$(NO_3)}ethynylphenyl]ethane (1c). To a solution of $AgNO_3$ (28.0 mg, 0.16 mmol) in methanol was added a solution of 1,1,1-tris[4-(*trans*-Pt(PEt_3)$_2$I) ethynylphenyl]-ethane (110 mg, 0.05 mmol) in $CHCl_3$. After stirring for 1 h the yellowish-white AgI was filtered through Celite, and removal of solvent gave **1c** (MW 1807.5) (90.2 mg) in 90% yield. Anal. Calcd (%): C 41.20; H 5.85; N 2.32. Found: C 40.97; H 5.67; N 2.21. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.1 (d, 6H, Ph-H), 6.9 (d, 6H, Ph-H), 2.0 (s, 3H, CH_3), 1.9 (q, 36H, PEt_3), 1.2 (t, 54H, PEt_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 120 MHz): δ 20.1 (s, $^1J_{PPt}$ = 3072 Hz). MS (ESI): 1807.5 $[M_{1c} + H]^+$, 1274.7 $[M_{1c} - 4PEt_3 - NO_3^-]^+$. Melting point: > 270 °C, dec.

Synthesis of the Prism 3a. To a stirred solution of **1a** (12 mg, 0.006 mmol) in acetone was added a solution of **2a** (2.86 mg, 0.009 mmol) in methanol, and the resulting solution was kept under stirring at 50 °C for 12 h. The product was obtained as a light yellow powder by ether addition (MW 4542) (96% yield). Anal. Calcd (%): C 45.97; H 5.41; N 6.16. Found: C 46.26; H 5.66; N 6.21. ^1H NMR ($CDCl_3$, 400 MHz): δ 10.81 (s, 6H, −NH), 9.23 (s, 3H, ArH), 9.19 (d, 6H, Py-H), 8.79 (d, 6H, Py-H), 8.3 (m, 12H, ArH), 7.61 (m, 9H, ArH), 7.15 (d, 12H, ArH), 6.91 (d, 12H, ArH), 1.9 (q, 72H, $-CH_2$), 1.1 (t, 108H, $-CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 120 MHz): δ 15.60 (s, $^1J_{Pt-P}$ = 2872 Hz). MS (ESI) *m*/*z*: 1452 $[M_{3a} - 3NO_3^-]^{3+}$, 1073.49 $[M_{3a} - 4NO_3^-]^{4+}$.

Synthesis of the Prism 3b. To a solution of **1a** (12.0 mg, 0.006 mmol) in acetone was added a solution of **2b** (2.5 mg, 0.009 mmol). After stirring for 12 h at 50 °C the product was formed as a yellow precipitate. The final product was centrifuged and washed with acetone to obtain the supramolecular prism **3b** (MW 4430.069) (13.1 mg) in 91% yield. Anal. Calcd (%): C 48.80; H 5.46; N 4.42. Found: C 48.66; H 5.59; N 4.22. ^1H NMR (50% $CDCl_3$/ MeOH, 400 MHz): δ 9.0 (d, 6H, Py-H), 8.8 (d, 6H, Py-H), 8.2 (m, 6H, Py-H), 8.0 (d, 6H, Py-H), 7.8 (s, 3H, Ph-H), 7.7−7.5 (m, 9H, Ph-H), 7.1 (d, 12H, Ph-H), 6.9 (d, 12H, Ph-H), 1.9 (q, 72H, PEt_3), 1.2 (t, 108H, PEt_3). $^{31}P\{^1H\}$ NMR (50% $CDCl_3$/MeOH, 120 MHz): δ 15.6 (s, $^1J_{PPt}$ = 2840 Hz). ^{13}C NMR (50% $CDCl_3$/MeOH, 100 MHz): δ 155.8, 153.9, 146.5, 135.5, 134.0, 133.2, 130.8, 129.0, 124.6, 123.3, 94.4, 85.9, 61.2, 59.1, 15.0, 8.4. MS (ESI) *m*/*z*: 1413 $[M_{3b} - 3NO_3^-]^{3+}$, 823 $[M_{3b} - 5NO_3^-]^{5+}$, 675 $[M_{3b} - 6NO_3^-]^{6+}$. Melting point: > 200 °C, dec.

Synthesis of the Prism 3c. To a suspension of clip-type metal acceptor **1b** (18.1 mg, 0.015 mmol) in acetone was added a solution of the ligand **2c** (5.4 mg, 0.01 mmol) in acetone. After heating for 5 min at 50 °C a fluorescent yellow solution formed, which after stirring for more than 12 h gave a yellow precipitate. The precipitate after washing with acetone gave **3c** (MW 4730.42) (23 mg) in 93% yield. Anal. Calcd (%): C 51.80; H 5.37; N 4.15. Found: C 51.42; H 5.51; N 4.33. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.2 (s, 3H, anthra-H), 9.2 (d, 12H, Py-H_α), 8.4 (s, 3H, anthra-H), 7.8 (m, 18H, Ph-H and anthra-H), 7.5 (m, 18H, Py-H_β and anthra-H), 7.3 (m, 6H, anthra-H), 7.1 (d, 12H, Ph-H), 1.9 (q, 72H, PEt_3), 1.2 (t, 108H, PEt_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 120 MHz): δ 14.34 (s, $^1J_{PPt}$ = 2880 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.0, 148.0, 144.0, 136.0, 134.0, 132.0, 131.8, 131.0, 125.0, 122.0, 112.0, 96.0, 87.0, 63.1, 57.6, 14.8, 8.5. MS (ESI) *m*/*z*: 1396.27 $[M_{3c} - 3PEt_3 - 3NO_3^-]^{3+}$, 1122.27 $[M_{3c} - 4NO_3^-]^{4+}$, 1003.33 $[M_{3c} - 4PEt_3 - 4NO_3^-]^{4+}$. Melting point: > 180 °C, dec.

Synthesis of the Prism 3d. To a solution of **1c** (9.0 mg, 0.005 mmol) in acetone was added a suspension of ligand **2d** (2.8 mg, 0.0075 mmol) in acetone. The fluorescent yellow solution after stirring for 12 h at 50 °C gave a yellow precipitate. The precipitate was centrifuged and washed with acetone to obtain **3d** (MW 4756.48) (11.0 mg) in 92% yield. Anal. Calcd (%): C 52.52; H 5.47; N 3.53. Found: C 52.90; H 5.61; N 3.27. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.5 (s, 3H, anthra-H), 8.5 (d, 12H, Py-H_α), 8.1 (d, 6H, anthra-H), 8.0 (s, 3H, anthra-H), 7.9 (d, 6H, anthra-H), 7.5 (m, 6H, anthra-H), 7.4 (d, 12H, Py-H_β), 7.1 (d, 12H, Ph-H), 6.9 (d, 12H, Ph-H), 1.8 (s, 6H, CH_3), 1.7 (q, 72H, PEt_3), 1.2 (t, 108H, PEt_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 120 MHz): δ 14.9 (s, $^1J_{PPt}$ = 2800 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.0, 154.0, 147.0, 148.0, 135.0, 132.7, 131.6, 130.6, 129.6, 127.0, 119.8, 97.5, 92.5, 61.3, 56.1, 20.9, 15.1, 8.6. MS (ESI) *m*/*z*: 1606.7 $[M_{3d} - 12PEt_3 - 2NO_3^-]^{2+}$, 1523.5 $[M_{3d} - 3NO_3^-]^{3+}$, 1209.6 $[M_{3d} - 8PEt_3 - 3NO_3^-]^{3+}$, 921.67 $[M_{3d} - 7PEt_3 - 4NO_3^-]^{4+}$, 890.1 $[M_{3d} - 5NO_3^-]^{5+}$. Melting point: > 200 °C, dec.

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Supporting Information Available: ^1H and ^{31}P NMR spectra of linkers and cages, fluorescence quenching of **3d** using 10^{-5} M TNT, and ESI mass spectra are available free of charge via the Internet at http://pubs.acs.org.