Inorganic Chemistry

Article

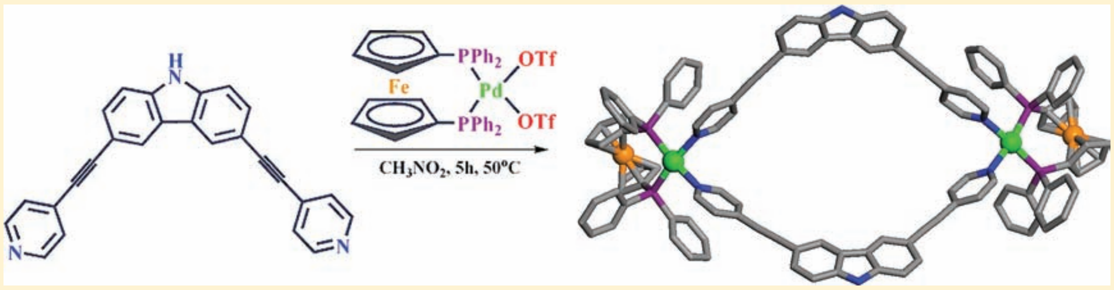
pubs.acs.org/IC

Coordination-Driven Self-Assembly of 2D-Metallamacrocycles Using a New Carbazole-Based Dipyridyl Donor: Synthesis, Characterization, and C_{60} Binding Study

Sankarasekaran Shanmugaraju,[†] Vaishali Vajpayee,[‡] Sunmi Lee,[‡] Ki-Whan Chi,*,[‡] Peter J. Stang,*,[§] and Partha Sarathi Mukherjee*,[†]

[†]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India
[‡]Department of Chemistry, University of Ulsan, Ulsan 680-749 Republic of Korea
[§]Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112, United States

Supporting Information



ABSTRACT: A new carbazole-based 90° dipyridyl donor 3,6-di(4-pyridylethynyl)carbazole (**L**) containing carbazole-ethynyl functionality is synthesized in reasonable yield using the Sonagashira coupling reaction. Multinuclear NMR, electrospray ionization-mass spectrometry (ESI-MS), including single crystal X-ray diffraction analysis characterized this 90° building unit. The stoichiometry combination of **L** with several Pd(II)/Pt(II)-based 90° acceptors (**1a**−**1d**) yielded [2 + 2] self-assembled metallacycles (**2a**−**2d**) under mild conditions in quantitative yields [**1a** = *cis*-(dppf)Pd$(OTf)_2$; **1b** = *cis*-(dppf)Pt$(OTf)_2$; **1c** = *cis*-(tmen)Pd$(NO_3)_2$; **1d** = 3,6-bis{*trans*-Pt(C≡C)$(PEt_3)_2(NO_3)$}carbazole]. All these macrocycles were characterized by various spectroscopic techniques, and the molecular structure of **2a** was unambiguously determined by single crystal X-ray diffraction analysis. Incorporation of ethynyl functionality to the carbazole backbone causes the resulted macrocycles (**2a**−**2d**) to be π-electron rich and thereby exhibit strong emission characteristics. The macrocycle **2a** has a large internal concave aromatic surface. The fluorescence quenching study suggests that **2a** forms a ∼1:1 complex with C_{60} with a high association constant of $K_{sv} = 1.0 \times 10^5\ M^{-1}$.

■ INTRODUCTION

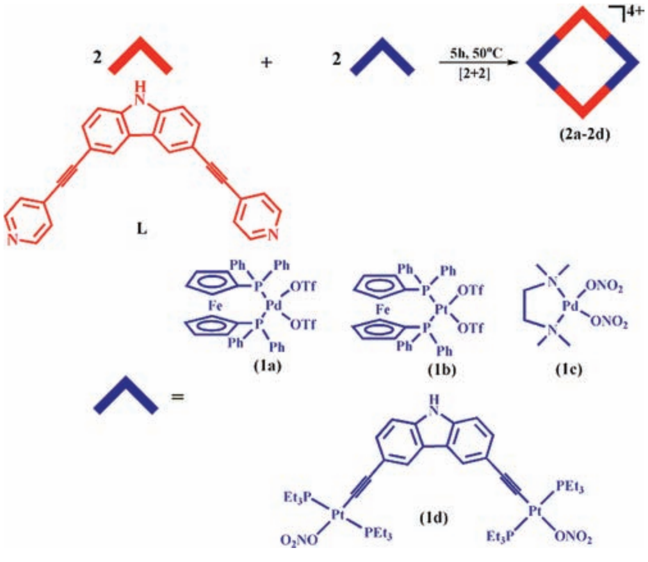
In recent times, abiological self-assembly of molecular architectures of well-defined shapes and sizes has progressed tremendously due to their structural diversity and potential for applications as chemosensors, catalysts, and molecular containers.[1] Of the various protocols, metal−ligand coordination self-assembly is especially appealing for achieving such assemblies.[2] In this context, Pt(II) and Pd(II)-based molecular building units have long been used to engineer 2D- and 3D supramolecular structures.[3] Cis-blocked 90° corner units have been widely used because of commercial availability and their easy synthesis. Over the years we, Stang et al. and others have constructed several molecular architectures such as rectangle, square, hexagon, pentagon, and dodecahedron using several π-electron-rich shape-selective di/multinuclear Pt(II)/Pd(II) linkers.[4] In light of this, we have recently reported a carbazole-based shape-selective diplatinum 90° acceptor, and its [2 + 2] self-assembly with various dipyridyl donors resulted in efficient formation of two-dimensional molecular architectures.[5] In continuation of our ongoing interests, here we report a complementary shape-selective carbazole dipyridyl donor having bite angle of 90°. Furthermore, the exploitation of luminescent conjugate organic or organic−inorganic hybrid materials is of considerable interest because of their intrinsic applications in the field of optoelectronics.[6] Among several moieties, unsaturated ethynyl group in the backbone helps the assemblies to be π-electron-rich and also gives an additional strength to keep the architectures intact.[4,5]

Herein, we report the synthesis of four new [2 + 2] self-assembled metallamacrocycles (**2a** −**2d**) via coordination-driven self-assembly of a shape-selective 90° dipyridyl donor (**L**) and several Pd(II)/Pt(II)-based 90° ditopic acceptors (**1a**−**1d**) (Scheme 1). All four macrocycles were characterized by various spectroscopic techniques like IR, NMR [^{1}H and $^{31}P\{^1H\}$], and ESI-MS spectrometric analyses including X-ray

Received: January 27, 2012
Published: April 2, 2012

dx.doi.org/10.1021/ic300199j | *Inorg. Chem.* 2012, 51, 4817−4823

Scheme 1. [2 + 2] Self-Assembly of Metallamacrocycles 2a–2d via a New Carbazole-Based 90° Ditopic Donor L and Several Pd(II)/Pt(II) Based 90° Acceptors (1a–1d)



diffraction. Macrocycle **2a** has bowl-type geometry with a large internal concave aromatic surface and it is luminescent. **2a** was tested as a macrocyclic receptor for a convex guest C_{60} in solution. The solution state initial emission intensity of **2a** was quenched efficiently upon gradual addition of C_{60} and thereby demonstrates its potential as a receptor.

EXPERIMENTAL SECTION

Materials and Methods. The 90° dipyridyl donor **L** was synthesized under dry nitrogen atmosphere using a standard Schlenk technique. Solvents were dried and distilled according to the standard literature procedures. 3,6-Dibromocarbazole and 4-ethynylpyridine hydrochloride were purchased from various commercial sources and were used without further purification. *cis*-(dppf)Pd(OTf)$_2$ (**1a**), *cis*-(dppf)Pt(OTf)$_2$ (**1b**), *cis*-(tmen)Pd(NO$_3$)$_2$ (**1c**), and 3,6-bis[*trans*-Pt(C≡C)(PEt$_3$)$_2$(NO$_3$)]carbazole (**1d**) were synthesized following the reported procedures.[5,7] NMR spectra were recorded on a Bruker 400 or 300 MHz spectrometer. The chemical shifts (δ) in ^{1}H NMR spectra are reported in ppm relative to tetramethylsilane (Me$_4$Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the NMR solvents: CD$_3$NO$_2$ (4.33) or CDCl$_3$ (7.26) or DMSO-d_6 (2.50).^{31}P NMR were recorded at 121 MHz, and the chemical shifts (δ) are reported in ppm relative to external 85% H$_3$PO$_4$ at 0.00 ppm. Mass-spectral analyses of the self-assembled macrocycles were recorded on an ESI-MS spectrometer using standard spectroscopic grade solvents. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 750 UV–visible spectrophotometer. Fluorescence emission studies were carried out on a Horiba Jobin Yvon Fluoromax-4 spectrometer.

Synthesis of 3,6-Di(4-pyridylethynyl)carbazole (L). A mixture of 3,6-dibromocarbazole (0.635 mmol), 4-ethynylpyridine·HCl (1.78 mmol), *t*-butylphosphine (0.079 mmol), CuI (0.026 mmol), Pd-(PhCN)$_2$Cl$_2$ (0.038 mmol), diisopropyl amine (4.91 mmol), and 1,4-dioxane (2–3 mL) was taken in a flame-dried 100 mL Schlenk flask and stirred at 50 °C for 48 h. After completion of the reaction (as judged by thin layer chromatography (TLC)), the mixture was diluted with ethyl acetate (50 mL) and filtered through Celite. The ethyl acetate solution was washed with 10% aqueous ethylenediamine, brine solution, dried over anhydrous Na$_2$SO$_4$, and concentrated. The crude product was purified by column chromatography (silica) using CHCl$_3$/CH$_3$OH (96:4) and 2 mL of triethylamine as eluents to give light yellow solid compound in 60% isolated yield. Anal. Calcd for C$_{26}$H$_{15}$N$_3$: C, 84.53; H, 4.09; N, 11.37. Found: C, 84.22; H, 4.31; N, 10.99. Melting point > 250 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.96 (s, NH), 8.64 (d, 4H, J = 5.6 Hz, H$_\alpha$-pyridyl), 8.54 (s, 2H, H$_1$-carbazole), 7.69 (d, 2H, J = 8.4 Hz, H$_2$-carbazole), 7.62 (d, 2H, J = 8.4 Hz, H$_3$-carbazole), 7.55 (d, 4H, J = 5.6 Hz, H$_\beta$-pyridyl). ^{13}C NMR (DMSO-d_6, 400 MHz): δ 150.8 (4C, C$_1$-pyridyl), 131.7 (2C, C$_9$-carbazole), 130.8 (2C, C$_3$-pyridyl), 126.1 (4C, C$_2$-pyridyl), 125.7 (2C, C$_7$-carbazole), 123.0 (2C, C$_{11}$-carbazole), 112.8 (2C, C$_8$-carbazole), 112.5 (2C, C$_6$-carbazole), 96.5 (2C, C$_{10}$-carbazole), 86.1 (2C, C$_4$-ethynyl), 80.2 (2C, C$_5$-ethynyl). ESI-MS (m/z): 370.4 [**L** + H]$^+$. IR (KBr): ν (cm^{-1}) = 2211.1 for ethynyl group.

Synthesis of the Macrocycle 2a. To a clear nitromethane solution (0.5 mL) of the acceptor **1a** (2.7 mg, 0.003 mmol) was added a clear nitromethane solution (0.5 mL) of the ligand **L** (1.1 mg, 0.003 mmol) drop-by-drop with continuous stirring. After stirring the reaction mixture at 50 °C for 5 h in a closed glass vial, the clear dark red solution was concentrated. Pure **2a** was isolated as brown solid upon addition of cold diethyl ether into the concentrated solution. Isolated yield: 91%. Anal. Calcd for C$_{124}$H$_{86}$F$_{12}$Fe$_2$N$_6$O$_{12}$P$_4$Pd$_2$S$_4$: C, 56.06; H, 3.26; N, 3.16. Found: C, 56.32; H, 3.44; N, 3.30. Melting point > 250 °C. ^{1}H NMR (300 MHz, CD$_3$NO$_2$): δ 9.67 (s, 2H, NH), 8.60 (d, J = 6.0 Hz, 8H, H$_\alpha$-pyridyl), 8.24 (s, 4H, H$_1$-carbazole), 8.24 (br, 4H, H$_2$-carbazole), 8.04–7.78 (m, 40H, H-phenyl), 7.54 (br, 4H, H$_3$-carbazole), 7.20 (d, J = 6.0 Hz, 8H, H$_\beta$-pyridyl), 4.77–4.84 (d, 16H, H-Cp). ^{31}P {^{1}H} NMR (121 MHz, CD$_3$NO$_2$): δ 34.9 (s). IR: ν (cm^{-1}) = 2205.4 and 1243.6 for C≡C and C–F (OTf), respectively.

Synthesis of the Macrocycle 2b. This was prepared in an analogous way as used for **2a** using **1b** (4.2 mg, 0.004 mmol) and **L** (1.4 mg, 0.004 mmol). Isolated yield: 88%. Anal. Calcd for C$_{124}$H$_{86}$F$_{12}$Fe$_2$N$_6$O$_{12}$P$_4$Pt$_2$S$_4$: C, 52.55; H, 3.06; N, 2.97. Found: C, 52.81; H, 3.28; N, 3.11. Melting point >250 °C. ^{1}H NMR (300 MHz, CD$_3$NO$_2$): δ 9.69 (s, 2H, NH), 8.27 (d, J = 6.0 Hz, 8H, H$_\alpha$-pyridyl), 8.02 (br, 4H, H$_2$-carbazole), 7.77 (br, 4H, H$_3$-carbazole), 7.70 (m, 40H, H-phenyl), 7.55 (s, 4H, H$_1$-carbazole), 7.24 (d, J = 6.0 Hz, 8H, H$_\beta$-pyridyl) 4.74–4.83 (d, 16H, H-Cp). ^{31}P {^{1}H} NMR (121 MHz, CD$_3$NO$_2$): δ 3.73(s). IR: ν (cm^{-1}) = 2179.9 and 1243.6 for C≡C and C–F (OTf), respectively. ESI-MS (m/z): 795.67 [**2b** − 3O$_3$SCF$_3^-$]$^{3+}$, 559.51 [**2b** − 4O$_3$SCF$_3^-$]$^{4+}$.

Synthesis of the Macrocycle 2c. To a stirred suspension of dipyridyl donor **L** (1.8 mg, 0.005 mmol) in 0.5 mL of acetone was added a clear aqueous solution (0.5 mL) of **1c** (1.7 mg, 0.005 mmol) drop-by-drop with continuous stirring. After stirring the reaction mixture at 50 °C for 5 h in a closed glass vial, the clear yellow solution was vacuum-dried to isolate the expected macrocycle **2c** in pure form as yellow solid. Isolated yield: 85%. Anal. Calcd for C$_{64}$H$_{62}$N$_{14}$O$_{12}$Pd$_2$: C, 53.68; H, 4.36; N, 13.69. Found: C, 53.95; H, 4.60; N, 13.87. Melting point > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.94 (s, 2H, NH), 8.64 (d, J = 6.0 Hz, 8H, H$_\alpha$-pyridyl), 8.54 (s, 4H, H$_1$-carbazole), 7.68 (d, J = 8.5 Hz, 4H, H$_3$-carbazole), 7.61 (d, J = 8.4 Hz, 4H, H$_2$-carbazole), 7.54 (d, J = 6.0 Hz, 8H, H$_\beta$-pyridyl) 2.64 (s, 8H, H–CH$_2$), 2.51 (s, 24H, H–CH$_3$). IR: ν (cm^{-1}) = 2171.4 for ethynyl group. ESI-MS (m/z): 654.05 [**2c** − 2NO$_3^-$]$^{2+}$, 296.02 [**2c** − 4NO$_3^-$]$^{4+}$.

Synthesis of the Macrocycle 2d. To a stirred suspension of dipyridyl donor **L** (1.8 mg, 0.005 mmol) in 0.5 mL of methanol was added a clear chloroform solution (0.5 mL) of **1d** (6.0 mg, 0.005 mmol) drop-by-drop with continuous stirring. After stirring the reaction mixture at 50 °C for a further 5 h in a closed glass vial, the clear pale yellow solution was concentrated and treated with cold diethylether to isolate **2d** in pure form as an off-white solid. Isolated yield: 91%. Anal. Calcd for C$_{132}$H$_{164}$N$_{12}$O$_{12}$P$_8$Pt$_4$: C, 50.51; H, 5.27; N, 5.35. Found: C, 50.67; H, 5.44; N, 5.54. Melting point > 250 °C. ^{1}H NMR (CDCl$_3$/CD$_3$OD, 400 MHz): δ 8.71 (d, J = 5.2 Hz, 8H, H$_\alpha$-pyridyl), 8.52 (s, 4H, H$_1$-carbazole), 8.41 (m, 4H, H$_2$-carbazole), 8.34 (s, 2H, NH), 7.96 (s, 4H, H$_4$-carbazole), 7.94 (s, 2H, NH), 7.78 (d, J = 6.0 Hz, 8H, H$_\beta$-pyridyl), 7.55 (m, 4H, H$_3$-carbazole), 7.35 (m, 4H, H$_{5,6}$-carbazole), 1.91 (m, 24H, CH$_2$-ethyl), 1.26 (m, 36H, CH$_3$-ethyl). ^{31}P NMR (CDCl$_3$/CD$_3$OD, 121 MHz): δ 16.00 (s, $^1J_{\text{Pt-P}}$ = 1750.0 Hz). IR: υ (cm^{-1}) = 2170.0 for ethynyl group. ESI-MS (m/z): 984.30

[**2d** − 3NO_3^-]$^{3+}$, 905.60 [**2d** − 3NO_3^- − 2PEt_3]$^{3+}$, 722.72 [**2d** − 4NO_3^-]$^{4+}$.

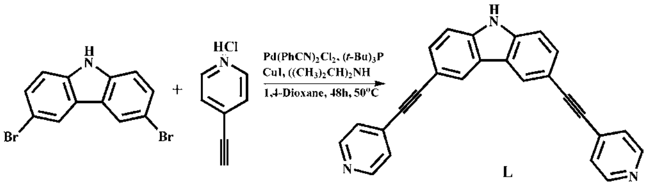
X-ray Data Collection and Structure Refinements. The diffraction data of **2a** were collected with synchrotron radiation (λ = 0.699 98 Å) using wiggler beamline 4A at the Pohang Accelerator Laboratory. This multipole wiggler has 28 magnet poles with 2.02 T and its periodic length and gap size are 14 cm and 14 mm, respectively. A fast speed CCD is installed for multiwavelength anomalous diffraction (MAD) experiments in the energy range of 6−18 keV. Crystal data for **L** were collected on a Bruker Smart Apex CCD diffractometer using the SMART/SAINT software.[8] X-ray quality crystals were mounted on a glass fiber with traces of viscous oil. Intensity data were collected using graphite monochromatic Mo−Kα radiation (0.7107 Å) at 150 K. The structures were solved by direct methods using SHELX-97[9] incorporated in WinGX.[10] Empirical absorption corrections were applied with SADABS.[11] All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U (C-methyl), and their coordinates were allowed to ride on their respective carbons. Structures were drawn using DIMOND.[12,13]

C_{60} Binding Study. Stock solutions (1 mM) of C_{60} (1.0 × 10^{-3} M) in tetrachloroethane and that of **2a** (1.0 × 10^{-4} M) in acetonitrile were prepared. A volume of 2 mL of stock solution of **2a** (1.0 × 10^{-5} M) was placed in a quartz cell of 1 cm width and C_{60} solution (1.0 × 10^{-3} M) was added in an incremental fashion and their corresponding fluorescence spectra were recorded at 298 K. Each titration was repeated at least three times to get a consistent value. For all measurements λ_{exc} = 410 nm and the emission wavelength was monitored from λ_{em} = 420 nm onward. Both excitation and emission slit widths were kept at 1 nm. There was no change in shape of the emission spectra of **2a** except gradual quenching of the initial fluorescence emission intensity upon gradual addition of C_{60} solution. Analysis of the normalized fluorescence intensity (I_0/I) as a function of increasing C_{60} concentration ([G]) was well described by the Stern−Volmer equation $I_0/I = 1 + K_{SV}[G]$. The K_{SV} was obtained from the slope of the linear Stern−Volmer plot.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of the 90° Dipyridyl Donor (L). As illustrated in Scheme 2, the 90° dipyridyl donor [**L**, 3,6-di(4-pyridylethynyl)carbazole], is synthesized via a Sonagashira coupling reaction of 3,6-dibromocarbazole with 4-ethynylpyridinehydrochloride using Pd(II)- catalyst in reasonable yield (~60%). The linker **L** was fully characterized by various spectroscopic techniques such as IR, NMR {^{1}H and ^{13}C}, and ESI-MS.

Scheme 2. Schematic Representation of the Synthesis of 3,6-Di(4-pyridylethynyl)carbazole (L) from 3,6-Dibromocarbazole and 4-Ethynylpyridinehydrochloride



The IR spectrum of **L** showed an intense peak at υ = 2211.1 cm^{-1} corresponding to the presence of an ethynyl (C≡C) functional group (Figure S1 in the Supporting Information). The ^{1}H NMR spectrum of **L** exhibited characteristic peaks in the range δ = 11.96−7.60 ppm for carbazole protons (two singlets and two doublets) and two sharp doublets at δ = 8.64 ppm and δ = 7.55 ppm corresponding to the H_α- and H_β-protons of 4-pyridyl units, respectively (Figure S2 in the Supporting Information). The ^{13}C NMR spectrum of **L** exhibited all the characteristics resonance corresponding to carbazole, pyridyl, and ethynyl units in the aromatic region in the range of δ = 150.8−80.2 ppm (Figure S3 in the Supporting Information). Electrospray ionization mass-spectrometric (ESI-MS) analysis of **L** showed a peak at m/z = 370.40, corresponding to the molecular ion [**L** + H]$^+$ (Figure S4 in the Supporting Information).

Finally, the molecular structure of the 90° building unit (**L**) was unequivocally determined by X-ray diffraction analysis. The diffraction quality single crystals of **L** were obtained by slow evaporation of a concentrated clear solution of **L** in DMSO at room temperature. The dipyridyl donor **L** crystallized in the $P2_1/n$ space group with four formula units per asymmetric units. A ball and stick representation of the structure of **L** (Figure 1) shows that the N3−NH−N2 angle being approximately 95°. Crystallographic data and refinement parameters are summarized in Table S1 in the Supporting Information, while selected bond lengths and angles are assembled in Table S2 in the Supporting Information. Notably, the pyridyl donor (N2) makes a dihedral angle of 11.6° with the carbazole moiety, whereas the other arm (N3) adopts a dihedral angle of 92.5°. One of the pyridyl donors and carbazole unit almost lie in the same plane, while the other pyridyl donor (N3) is perpendicular to the plane of carbazole. The average C≡C bond distance (1.17 Å) is in good agreement with other reported ethynyl compounds.[4−6] Interestingly, the pyridyl unit perpendicular to carbazole plane forms an intermolecular hydrogen bonding interaction (2.12 Å) with carbazole-NH of the adjacent molecule; thereby it forms a supramolecular 1D-chain in the solid-state (Figure S5 in the Supporting Information).

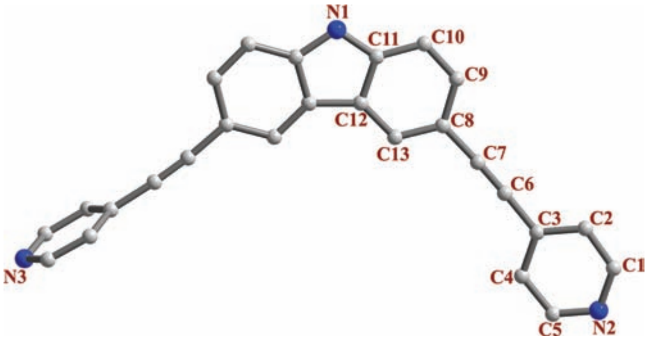


Figure 1. Molecular structure of dipyridyl donor **L** with atom labeling (color codes: blue = N, gray = carbon).

Synthesis and Characterization of the Macrocycles 2a−2d. The dipyridyl donor **L** was treated separately with four different Pd(II)/ Pt(II) based 90° acceptors (**1a**−**1d**) [**1a** = *cis*-(dppf)Pd(OTf)$_2$; **1b** = *cis*-(dppf)Pt(OTf)$_2$; **1c** = *cis*-(tmen)Pd-(NO$_3$)$_2$; **1d** = 3,6-bis{*trans*-Pt(PEt$_3$)$_2$(NO$_3$)(C≡C)}-carbazole] in a 1:1 molar ratio to obtain the [2 + 2] self-assembled macrocycles (**2a**−**2d**) after 5 h of stirring at 50 °C (Scheme 1). The resulting macrocycles are highly soluble in common organic solvents and were fully characterized using various spectroscopic techniques like IR, multinuclear {^{1}H and ^{31}P} NMR, as well as ESI-MS. The multinuclear NMR spectra of the assemblies (**2a**−**2d**) were consistent with the formation of a single and symmetrical product (Figures S6−S12 in the Supporting Information).

The ^{31}P NMR spectra of assemblies **2a**, **2b**, and **2d** exhibited sharp singlets [34.9 (**2a**), 3.73 (**2b**), 16.00 (**2d**)], which are significantly upfield shifted with respect to the starting 90° acceptor units (**1a**, **1b**, **1d**) (Supporting Information). The upfield shifts of the phosphorus peaks indicated the ligand to metal electron donation due to ligand−metal coordination. Moreover, a decrease in coupling of the observed flanking ^{195}Pt satellites of assemblies **2b** (ΔJ = −2373.6 Hz) and **2d** (ΔJ = −1750.0 Hz) were consistent with the back-donation from Pt(II) metal centers. In the ^{1}H NMR spectrum of all the resulted assemblies (**2a**−**2d**), hydrogen atoms of the pyridine rings exhibited a downfield shift due to the loss of electron density upon coordination of pyridine-N to Pd(II)/Pt(II) centers (Supporting Information). A strong band in IR spectra of the assemblies [υ (cm^{-1}) = 2205.4 (**2a**), 2179.9 (**2b**), 2171.4 (**2c**), 2170.0 (**2d**)] supported the presence of a C≡C ethynyl bond in the resulting macrocycles (Figure S1 in the Supporting Information).

Although the initial characterization of these assemblies using multinuclear (^{1}H and ^{31}P) NMR spectroscopy suggested ligand to metal coordination, it does not furnish any information about the exact composition and nuclearity of the resulting macrocycles. ESI-mass spectrometry is a well accepted soft-ionization technique to determine the composition of the charged species in solution.[14] Formation of [2 + 2] self-assembled macrocycles **2b**−**2d** was supported by the appearance of peaks in the ESI-MS spectra corresponding to multiple charged fragments (Figure 2 and Figures S13 and S14 in the Supporting Information). The multiple charged molecular ions for **2b** at m/z = 795.67 [**2b** − $3O_3SCF_3^-$]$^{3+}$, 559.51 [**2b** − $4O_3SCF_3^-$]$^{4+}$; for **2c** at m/z = 654.05 [**2c** − $2NO_3^-$]$^{2+}$, 296.02 [**2c** − $4NO_3^-$]$^{4+}$; for **2d** at m/z = 984.30 [**2d** − $3NO_3^-$]$^{3+}$, 905.60 [**2d** − $3NO_3^-$ − $2PEt_3$]$^{3+}$, 722. 72 [**2d** − $4NO_3^-$]$^{4+}$ were observed. The experimentally observed isotopic distributions of the peaks corresponding to [**2b** − $3O_3SCF_3^-$]$^{3+}$, [**2b** − $4O_3SCF_3^-$]$^{4+}$, [**2c** − $2NO_3^-$]$^{2+}$, and [**2d** − $3NO_3^-$]$^{3+}$ fragments were consistent with their charge state (Figure 2 and Figures S13 and S14 in the Supporting Information).

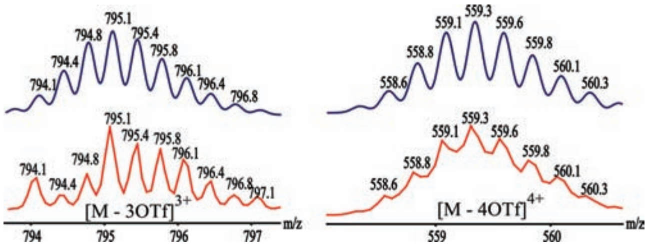


Figure 2. Calculated (blue) and experimentally (red) observed ESI-MS spectra of [**2b** − $3O_3SCF_3^-$]$^{3+}$ and [**2b** − $4O_3SCF_3^-$]$^{4+}$ fragments.

Crystal Structure of the Macrocycle 2a. The structure of **2a** was determined unambiguously by single crystal X-ray diffraction analysis. The diffraction quality single crystals of **2a** were grown by slow vapor diffusion of diethylether into a concentrated nitromethane/methanol (1:1) solution at room temperature. Diffraction analysis of **2a** demonstrated the formation of a tetranuclear heterometallic Fe_2Pd_2 bowl-shaped macrocycle, where two pyridine units of **L** linked with two *cis*-(dppf)Pd$(OTf)_2$ building blocks (Figure 3). Each Pd center is coordinated to two P atoms of dppf moiety and two pyridyl nitrogen of **L**, resulting in a distorted square-planar geometry around each Pd(II) metal center. The average Pd−N and P−Pd bond distances are 2.09 Å and 2.29 Å, respectively. The average N−Pd−N and P−Pd−P bite angles are 84.74° and 99.74°, respectively. Interestingly, though one of the pyridyl (N3) ligating sites in **L** is almost perpendicular to the plane of carbazole-moiety, in **2a** both the pyridyl donors (N2 and N3) lie in the same plane. Overall, **2a** has a bowl-shape structure with a large internal concave aromatic surface.

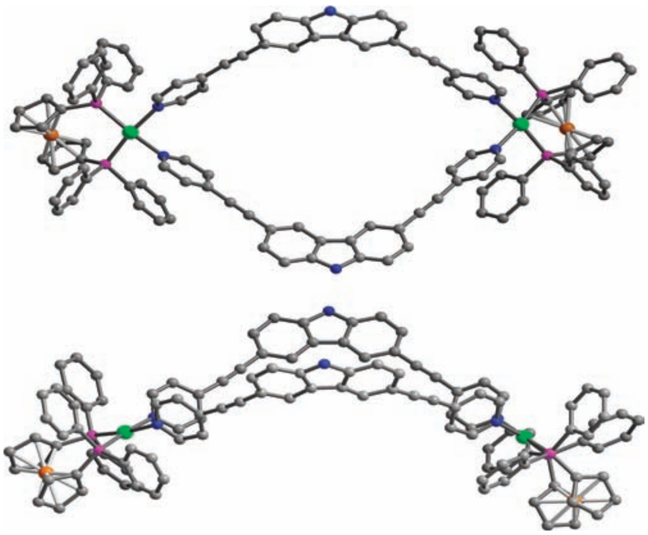


Figure 3. Top view (above) and side view (below) of X-ray crystal structure of macrocycle **2a** (green = Pd, orange = Fe, purple = P, blue = N, red = O, black C). Counter anions, hydrogen atoms, and located solvents are omitted for the sake of clarity.

Carbazole-units of two different **L** are oriented in the same direction, and the distance between opposite NH of carbazole units is 14.71 Å. The solid state packing diagram of **2a** through the crystallographic *b* axis shows a loop type of channel occupied with two triflate (OTf$^-$) counteranions and a diethylether solvent molecule (Figure S15 in the Supporting Information).

Unfortunately, all attempts to obtain X-ray diffraction quality single crystals of the macrocycles **2b**, **2c**, and **2d** were unsuccessful. However, the analysis of multinuclear NMR (^{1}H and ^{31}P) in concurrence with ESI-MS spectroscopic studies supported the formation of [2 + 2] self-assembled macrocycles. Because of the almost similar nature of the acceptor units **1a**−**1c**, macrocycles **2b** and **2c** are expected to have a similar bowl-shaped structure. In order to gain further insight into the structural nature of macrocycle **2d** which is designed using a shape-selective Pt^{II}_2 90° building unit, the energy minimized structure was obtained using molecular mechanics universal force field simulation (MMUFF).[15] A perspective view of the energy minimized structures of **2d** is depicted in Figure 4.

The optimized structure of the macrocycle **2d** suggests that the formation of a rather square type of structure (different from **2a**) with overall dimensions of 2.19 nm ×2.19 nm. To the best of our knowledge, complex **2d** represents the first example of a [2 + 2] self-assembled Pt_4 molecular square.

UV−Visible Absorption and Fluorescence Studies of the Macrocycles. Photophysical data of the macrocycles (**2a**−**2d**) are summarized in Table 1. The absorption spectra of the macrocycles **2a**−**2d** in CH_3CN (1.0×10^{-5} M) show peaks at λ = 309, 345, and 384(sh) nm for **2a**; λ = 310, 345 and 384 (sh) nm for **2b**; λ = 310, 346, and 385(sh) nm for **2c**; λ = 245, 316,

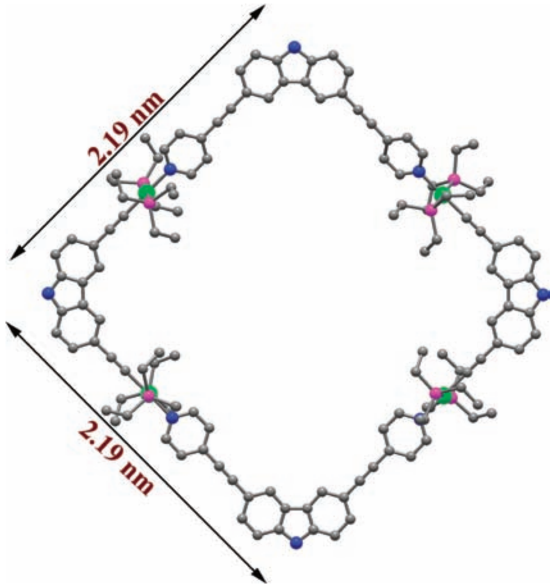


Figure 4. A view of the optimized structure of **2d** (green = Pt, pink = P, blue = N, black = C).

Table 1. Photophysical Data of the Macrocycles 2a −2d in Aerated CH_3CN Solution[a]

macrocycles	absorption maxima λ_{max} (nm)	Molar extinction coefficient 10^3 ε M^{-1} cm^{-1} [λ_{max}(nm)]	fluorescence emission maxima at 298 K λ_{max}(nm)
2a	**309**, 345, 384(sh)	309 (82)	**372**
2b	**310**, 345, 384(sh)	310 (73)	**372**
2c	**310**, 346, 385(sh)	310 (121)	**371**
2d	245, **316**, 342, 383 (sh)	316 (43)	**373**

[a] Values in bold in columns 2 and 4 represent the highest absorption (λ_{abs}) and emission (λ_{em}) maxima, respectively.

342, and 383 nm for **2d** (Figure 5). The peaks in the range of 310−346 nm are tentatively assigned to MLCT, whereas the peaks in the range of 245−310 nm are ascribed to the intra/intermolecular $\pi-\pi^*$ transitions. The observed low-energy band at λ = 384 nm for macrocycles **2a** and **2b** is attributed to the weak d−d transitions.

All the four macrocycles show high fluorescence characteristics in CH_3CN solution, and their high luminescence behavior is basically ascribed to the presence of unsaturated Pt-ethynyl and extended π-conjugation (Figure 5).

Supramolecular Complexation of Macrocycle 2a with C_{60}. Design and synthesis of artificial receptors with the ability of forming a stable inclusion complex with a specific guest has been an important area of current research in materials chemistry.[16] Since the first isolation of fullerene C_{60}, several artificial π-electron rich supramolecular receptors have been synthesized in the context of selective separation of C_{60} from the fullerite composites containing other large analogues such as C_{70} and C_{120}. It has been concluded in the reported literature that a bowl-shaped host is considered to be an ideal host to embrace the curved-surface of C_{60} through concave−convex, "ball-and-socket" $\pi-\pi$ interactions, or C−H−π interactions.[17] Inspection of the molecular structure of **2a** shows a bowl-shaped conformation with a large π-conjugated concave aromatic surface and the internal diameter of 14.71 Å, which is larger than the van der Waals radius (~10 Å) of C_{60}. Accordingly, we anticipated that the macrocycle **2a** would be a potential host to form a stable inclusion complex with C_{60} through a $\pi-\pi$ interaction.

The primary computational molecular modeling study of macrocycle **2a** with C_{60} suggested that C_{60} perfectly fits within the concave aromatic cleft of **2a** by a distance of 3.32 Å, which is in the required range for $\pi-\pi$ interaction between host and guest (Figure 6). On the basis of the information obtained from this modeling study, we performed a fluorescence titration experiment of **2a** with C_{60} in acetonitrile−tetrachloroethane solution at 298 K. As mentioned earlier, macrocycle **2a** shows emission maxima at λ_{em} = 372 nm and the initial emission intensity depleted rapidly upon gradual addition of C_{60} (Figure 7). Such a change in the emission intensity could be due to the formation of charge-transfer inclusion complex between the

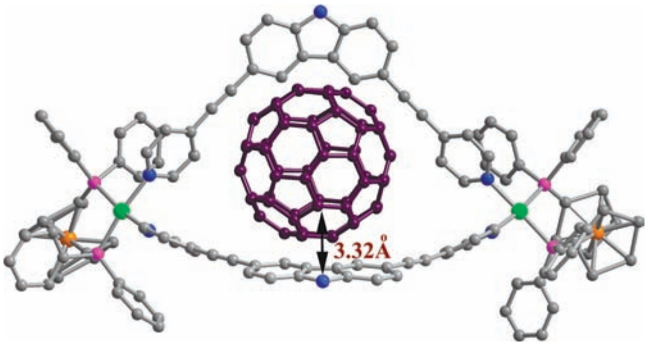


Figure 6. Simulated structure of the host−guest complex **$2a\subset C_{60}$**.

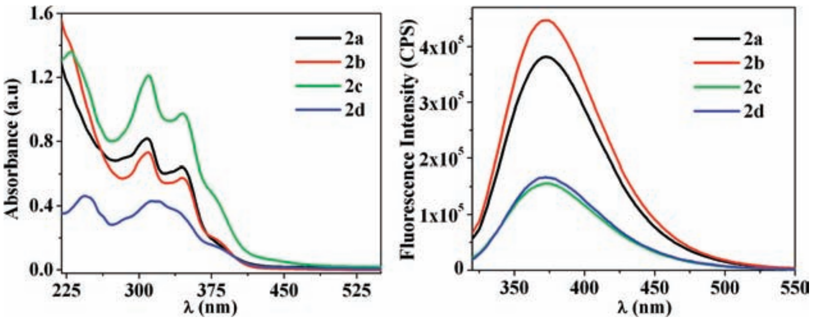


Figure 5. UV−visible (left) and fluorescence (right) spectra of macrocycles **2a**−**2d** obtained using CH_3CN solution (1.0×10^{-5} M).

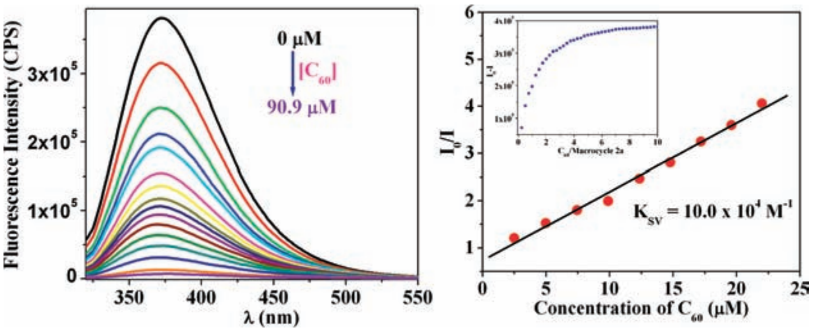


Figure 7. Reduction in the emission intensity of macrocycle **2a** (left) upon the gradual addition of C_{60} and its corresponding Stern−Volmer plot (right). Inset: stoichiometry plot.

bowl-shaped host **2a** and convex guest C_{60}. The stoichiometry plot analysis of the fluorescence titration profile suggested a ∼1:1 complex formation of **2a** with C_{60} and the estimated Stern−Volmer binding constant is 1.0×10^5 M^{-1} (Figure 7). The high value of binding constant (K_{SV}) indicated the propensity of **2a** to form a stable complex with C_{60}.[18]

■ CONCLUSION

We report here the use of a shape-selective 90° dipyridyl donor (**L**) to construct several [2 + 2] self-assembled Pd(II)/Pt(II) cationic macrocycles (**2a−2d**) in good yields under mild reaction conditions. Formation of macrocycles (**2a−2d**) was established by various spectroscopic techniques and the molecular structure of **2a** was determined by single crystal X-ray diffraction analysis. Despite the possibility of formation of open chain oligomers, we established here the self-assembly of discrete macrocycles incorporating carbazole-ethynyl functionality. Complex **2d** represents an interesting example of a [2 + 2] self-assembled Pt_4 molecular square obtained from a Pt_2 building unit. Though large number of two-dimensional metallamacrocycles using cis-blocked 90° Pd(II) or Pt(II) based 90° acceptors are known, the present paper reports few two-dimensional macrocycles from a shape-selective 90° dipyridyl donor (complementary approach). Because of the large internal concave pocket and π-electron rich nature, macrocycle **2a** was examined as a potential macrocyclic receptor for a large spherical guest C_{60} in solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

IR, NMR (^1H and ^{31}P), and ESI-MS spectra of **L** and the macrocycles (**2b−2d**) and crystallographic details of **L** and **2a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kwchi@ulsan.ac.kr (K.-W.C.); stang@chem.utah.edu (P.J.S.); psm@ipc.iisc.ernet.in (P.S.M). Partha Sarathi Mukherjee: fax, 91-80-2360-1552; phone, 91-80-2293-3352.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.S. gratefully acknowledges the Council of Scientific and Industrial Research (CSIR), New Delhi, for the research fellowship. P.S.M. thanks the Department of Science and Technology (DST) and CSIR, India, for financial support. K.-W.C. thanks the World Class University Program (Grant R33-2008-000-10003) and the Priority Research Center Program (Grant 2009-0093818) funded by the Korea Ministry of Education, Science and Technology. P.S.M. is grateful to Johnson Matthey Pvt. Ltd. U.K. for supplying K_2PtCl_4 as a loan. P.J.S. thanks the NSF (CHE-0820955) for financial support

■ REFERENCES

(1) (a) Northrop, B. H.; Yang, H.-B.; Stang, P. J. *Chem. Commun.* **2008**, *45*, 5896. (b) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. (c) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (d) Inokuma, Y.; Kawano, M.; Fujita, M. *Nat. Chem* **2011**, *3*, 349. (e) Klosterman, J. K.; Yamauchi, Y.; Fujita, M. *Chem. Soc. Rev.* **2009**, *38*, 1714. (f) Zangrando, E.; Casanova, M.; Alessio, E. *Chem. Rev.* **2008**, *108*, 4979. (g) Ward, M. D. *Chem. Commun.* **2009**, 4487. (h) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975. (i) Saalfrank, R. W.; Maid, H.; Scheurer, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8794. (j) Albrecht, M.; Fröhlich, R. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 797. (k) Mahata, K.; Saha, M. L.; Schmittel, M. *J. Am. Chem. Soc.* **2010**, *132*, 15933. (l) Rajendran, T.; Manimaran, B.; Liao, R.-T.; Lin, R.-J.; Thanasekaran, P.; Lee, G.-H.; Peng, S.-M.; Liu, Y.-H.; Chang, I.-J.; Rajagopal, S.; Lu, K.-L. *Inorg. Chem.* **2003**, *42*, 6388. (m) Wang, J.- L.; Li, X.; Lu, X.; Hsieh, I.-F.; Cao, Y.; Moorefield, C. N.; Wesdemiotis, C.; Cheng, S. Z. D.; Newkome, G. R. *J. Am. Chem. Soc.* **2011**, *133*, 11450.

(2) (a) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (b) Ruben, M.; Lehn, J.-M.; Muller, P. *Chem. Soc. Rev* **2006**, *35*, 1056. (c) MacGillivray, L. R.; Atwood, J. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1018. (d) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. (e) Philp, D.; Stoddart, J. F. *Angew. Chem. Int. Ed* **1996**, *35*, 1154. (f) Breiner, B.; Clegg, J. K.; Nitschke, J. R. *Chem. Sci* **2011**, *2*, 51. (g) Dinolfo, P. H.; Coropceanu, V.; Brédas, J.-L.; Hupp, J. T. *J. Am. Chem. Soc.* **2006**, *128*, 12592. (h) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810. (i) Shanmugaraju, S.; Bar, A. K.; Mukherjee, P. S. *Inorg. Chem.* **2010**, *49*, 10235. (j) Johnson, A. M.; Hooley, R. J. *Inorg. Chem.* **2011**, *50*, 4671.

(3) (a) Wang, M.; Lan, W.-J.; Zheng, Y.-R.; Cook, T. R.; White, H. S.; Stang, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 10752. (b) Wang, M.; Zheng, Y.-R.; Ghosh, K.; Stang, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 6282. (c) Kikuchi, T.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 15930. (d) Kamiya, N.; Tominaga, M.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2007**, *129*, 3816. (e) Ghosh, S.; Mukherjee, P. S. *Inorg. Chem.* **2009**, *48*, 2605. (f) Ghosh, S.; Mukherjee, P. S. *Dalton Trans* **2007**, 2542. (g) Wang, M.; Vajpayee, V.; Shanmugaraju, S.; Zheng, Y.-R.; Zhao, Z.; Kim, H.; Mukherjee, P. S.; Chi, K.-W.; Stang, P. J. *Inorg. Chem.* **2011**, *50*, 1506. (h) Shanmugaraju, S.; Bar, A. K.; Joshi, S. A.; Patil, Y. P.; Mukherjee, P. S. *Organometallics* **2011**, *30*, 1951.

(4) (a) Bar, A. K.; Mostafa, G.; Mukherjee, P. S. *Inorg. Chem.* **2010**, *49*, 7647. (b) Shanmugaraju, S.; Samanta, D.; Gole, B.; Mukherjee, P. S. *Dalton Trans* **2011**, *40*, 12333. (c) Ghosh, S.; Chakrabarty, R.; Mukherjee, P. S. *Inorg. Chem.* **2009**, *48*, 549. (d) Ghosh, S.;

Mukherjee, P. S. *Organometallics* **2008**, *27*, 316. (e) Mukherjee, P. S.; Das, N.; Stang, P. J. *J. Org. Chem.* **2004**, *69*, 3526. (f) Vajpayee, V.; Kim, H.; Mishra, A.; Mukherjee, P. S.; Stang, P. J.; Lee, M. H.; Kim, H. K.; Chi, K.-W. *Dalton Trans* **2011**, *40*, 3112. (g) Bar, A. K.; Shanmugaraju, S.; Chi, K.-W.; Mukherjee, P. S. *Dalton Trans* **2011**, *40*, 2257. (h) Shanmugaraju, S.; Joshi, S. A.; Mukherjee, P. S. *Inorg. Chem.* **2011**, *50*, 11736. (i) Liao, P.; Langloss, B. W.; Johnson, A. M.; Knudsen, E. R.; Tham, F. S.; Julian, R. R.; Hooley, R. J. *Chem. Commun.* **2010**, *46*, 4932. (j) Suzuki, K.; Tominaga, M.; Kawano, M.; Fujita, M. *Chem. Commun.* **2009**, 1638.

(5) Shanmugaraju, S.; Bar, A. K.; Chi, K.-W.; Mukherjee, P. S. *Organometallics* **2010**, *29*, 2971.

(6) (a) Yam, V. W.-W.; Tao, C.-H.; Zhang, L.; Wong, K. M.-C.; Cheung, K.-K. *Organometallics* **2001**, *20*, 453. (b) Sacksteder, L.; Baralt, E.; DeGraff, B. A.; Lukehart, C. M.; Demas, J. N. *Inorg. Chem.* **1991**, *30*, 2468. (c) Yam, V. W.-W.; Chan, L. P.; Lai, T. F. *Organometallics* **1993**, *12*, 2197. (d) Yam, V.W.-W.; Yeung, P. K.-Y.; Chan, L.-P.; Kwok, W.-M.; Phillips, D. L.; Yu, K.-L.; Wong, R. W.-K.; Yan, H.; Meng, Q.-J. *Organometallics* **1998**, *17*, 2590. (e) Yam, V.W.-W.; Yu, K.-L.; Cheung, K.-K. *J. Chem. Soc., Dalton Trans.* **1999**, 2913. (f) Choi, C. L.; Cheng, Y. F.; Yip, C.; Phillips, D. L.; Yam, V.W.-W. *Organometallics* **2000**, *19*, 3192. (g) Chan, C.-W.; Cheng, L.-K.; Che, C.-M. *Coord. Chem. Rev.* **1994**, *132*, 87. (h) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447. (i) Khan, M. S.; Kakkar, A. K.; Long, N. J.; Lewis, J.; Raithby, P.; Nguyen, P.; Marder, T. B.; Wittmann, F.; Friend, R. H. *J. Mater. Chem.* **1994**, *4*, 1227. (j) Chawdhury, N.; Köhler, A.; Friend, R. H.; Younus, M.; Long, N. J.; Raithby, P. R.; Lewis, J. *Macromolecules* **1998**, *32*, 722. (k) Chawdhury, N.; Köhler, A.; Friend, R. H.; Wong, W.-Y.; Lewis, J.; Younus, M.; Raithby, P. R.; Corcoran, T. C.; Al-Mandhary, M. R. A.; Khan, M. S. *J. Chem. Phys.* **1999**, *110*, 4963. (l) Grosshenny, V.; Harriman, A.; Hissler, M.; Ziessel, R. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2223. (m) Ziessel, R.; Hissler, M.; El-ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *178–180*, 1251. (n) Li, Z.; Kishi, N.; Hasegaw, K.; Akitaa, M.; Yoshizawa, M. *Chem. Commun.* **2011**, *47*, 8605. (o) Shanmugaraju, S.; Joshi, S. A.; Mukherjee, P. S. *J. Mater. Chem.* **2011**, *21*, 9130.

(7) (a) Bar, A. K.; Chakrabarty, R.; Mukherjee, P. S. *Organometallics* **2008**, *27*, 3806. (b) Bar, A. K.; Chakrabarty, R.; Chi, K.-W.; Batten, S. R.; Mukherjee, P. S. *Dalton Trans* **2009**, 3222. (c) Bar, A. K.; Chakrabarty, R.; Mukherjee, P. S. *Inorg. Chem.* **2009**, *48*, 10880.

(8) *SMART/SAINT*; Bruker AXS, Inc.: Madison, WI, 2004.

(9) Sheldrick, G. M. *SHELX-97, Program for the Solution and Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1998.

(10) Farrugia, L. J. *WinGX: An Integrated System of Windows Programs for the Solution, Refinement and Analysis for Single Crystal X-ray Diffraction Data*, version 1.65.04; Department of Chemistry: University of Glasgow: Glasgow, Scotland, 2003. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(11) Sheldrick, G. M. *SADABS, Bruker Nonius Area Detector Scaling and Absorption Correction*, version 2.05; University of Göttingen: Göttingen, Germany, 1999.

(12) Farrugia, L. J. *ORTEP-3 for Windows*, version 1.08; University of Glasgow: Glasgow, Scotland, 1997. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(13) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(14) (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. (c) Schalley, C. A.; Müller, T.; Linnartz, P.; Witt, M.; Schäfar, M.; Lützen, A. *Chem.—Eur. J.* **2002**, *8*, 3538. (d) Jeong, K. S.; Kim, S. Y.; Shin, U.-S.; Kogej, M.; Hai, N. T. M.; Broekmann, P.; Jeong, N.; Kirchner, B.; Reither, M.; Schalley, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 17672. (e) Mukherjee, P. S.; Das, N.; Stang, P. J. *J. Org. Chem.* **2004**, *69*, 3526. (f) Schweiger, M.; Seidel, S. R.; Schmitz, M.; Stang, P. J. *Org. Lett.* **2000**, *2*, 1255. (g) Fujita, M.; Yu, S. Y.; Kusukawa, T.; Funaki, H.; Ogura, K.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 2082. (h) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *Chem. Commun.* **1996**, 1535.

(15) Thompson, M. A. *ArgusLab 4.0*; Planaria Software LLC: Seattle, WA, http://www.arguslab.com.

(16) Atwood, J. L.; Steed, J. W. *Encyclopedia of Supramolecular Chemistry*; Marcel Dekker: New York, 2004; Vols. *1–2*.

(17) (a) Klärner, F.-G.; Kahlert, B. *Acc. Chem. Res.* **2003**, *36*, 919. (b) Harmata, M. *Acc. Chem. Res.* **2004**, 37, 862. (c) Kawase, T.; Kurata, H. *Chem. Rev.* **2006**, *106*, 5250. (d) Kishi, N.; Li, Z.; Yoza, K.; Akita, M.; Yoshizawa, M. *J. Am. Chem. Soc.* **2011**, *133*, 11438. (e) Samanta, D.; Shanmugaraju, S.; Joshi, S. A.; Patil, Y. P.; Nethaji, M.; Mukherjee, P. S. *Chem. Commun.* **2012**, *48*, 2298.

(18) (a) Sygula, A.; Fronczek, F. R.; Sygula, R.; Rabideau, P. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 3842. (b) Grimm, B.; Santos, J.; Illescas, B. M.; Muñoz, A.; Guldi, D. M.; Martín, N. *J. Am. Chem. Soc.* **2010**, *132*, 17387. (c) Pérez, E. M.; Sánchez, L.; Fernández, G.; Martín, N. *J. Am. Chem. Soc.* **2006**, *128*, 7172. (d) Gil-Ramírez, G.; Karlen, S. D.; Shundo, A.; Porfyrakis, K.; Ito, Y.; Briggs, G. A. D.; Morton, J. J. L.; Anderson, H. L. *Org. Lett.* **2010**, *12*, 3544. (e) Hosseini, A.; Taylor, S.; Accorsi, G.; Armaroli, N.; Reed, Christopher, A.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2006**, *128*, 15903. (f) Hosseini, A.; Hodgson, M. C.; Tham, F. S.; Reed, C. A.; Boyd, P. D. W. *Cryst. Growth Des.* **2006**, *6*, 397. (g) Boyd, P. D. W.; Reed, C. A. *Acc. Chem. Res.* **2005**, *38*, 235. (h) Yang, H.; Jin, H.; Hong, B.; Liu, Z.; Beavers, C. M.; Zhen, H.; Wang, Z.; Mercado, B. Q.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2011**, *133*, 16911. (i) Zuo, T.; Olmstead, M. M.; Beavers, C. M.; Balch, A. L.; Wang, G.; Yee, G. T.; Shu, C.; Xu, L.; Elliott, B.; Echegoyen, L.; Duchamp, J. C.; Dorn, H. C. *Inorg. Chem.* **2008**, *47*, 5234. Pirondini, L.; Bonifazi, D.; Braiuca, P.; Compagnolo, M.; Zorzi, R. D.; Geremia, S.; Diederich, F.; Dalcanale, E. *Tetrahedron* **2006**, *62*, 2008. Canevet, D.; Perez, E. M.; Martin, N. *Angew. Chem., Int. Ed.* **2011**, *50*, 9248.