Article

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Molecular Cage Impregnated Palladium Nanoparticles: Efficient, Additive-Free Heterogeneous Catalysts for Cyanation of Aryl Halides

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Supporting Information

ABSTRACT: Two shape-persistent covalent cages (**CC1^r** and **CC2^r**) have been devised from triphenyl amine based trialdehydes and cyclohexane diamine building blocks utilizing the dynamic imine chemistry followed by imine bond reduction. The cage compounds have been characterized by several spectroscopic techniques which suggest that **CC1^r** and **CC2^r** are [2+3] and [8+12] self-assembled architectures, respectively. These state of the art molecules have porous interior and stable aromatic backbone with multiple palladium binding sites to engineer the controlled synthesis and stabilization of ultrafine palladium nanoparticles (PdNPs). As synthesized cage embedded PdNPs have been characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD). Inductively coupled plasma optical emission spectrometry (ICP-OES) portrays that **Pd@CC1^r** and **Pd@CC2^r** have 40 and 25 wt% palladium loading, respectively. On the basis of TEM analysis, it has been estimated that as small as ~ 1.8 nm PdNPs could be stabilized inside the **CC1^r** while larger **CC2^r** could stabilize ~ 3.7 nm nanoparticles. In contrast, reduction of palladium salts in absence of the cages form structure less agglomerates. The well-dispersed cage embedded nanoparticles exhibit efficient catalytic performance in the cyanation of aryl halides under heterogeneous, additive- free condition. Moreover, these materials have excellent stability and recyclability without any agglomeration of PdNPs after several cycles.

INTRODUCTION

Over the past two decades discrete three-dimensional (3D) assemblies have attracted wide interest in many ways, either by their aesthetically elegant architectures or by their remarkable ability to act as sensors,[1] catalysts[2] and as molecular hosts.[3] To this end, numerous shape-persistent discrete assemblies have been devised mainly by articulating organic spacers with appropriate metal centers.[4,5] In contrast, construction of such architectures by using traditional covalent synthesis is undoubtedly more challenging owing to the laborious multiple synthetic steps. However, dynamic covalent synthesis[6] has emerged an efficient strategy for their easy access, which has been manifested in recently developed several cage compounds.[7] Our group has demonstrated that such an organic architecture could be constructed even from a complex reaction mixture by virtue of dynamic imine bonds.[8] The well-defined pore structures of such materials have been exploited for the gas adsorption/separation, however, they are yet to be explored in detail for the synthesis and stabilization of metal nanoparticles (MNPs).[9]

MNPs enjoy high surface-to-volume ratio with large number of available active catalytic sites per unit area, which is believed to be responsible for their high catalytic performance than their bulk metal counterparts.[10] Unfortunately during catalytic reactions such small MNPs lose their catalytic activity as a consequence of the formation of aggregates owing to their high surface energy.[11] Therefore, to deal with this difficulty a number of different solid support materials like metal oxides,[12] metal organic frameworks,[13] polymeric organic frameworks[14] and so on have been tested over the last few years.

In the case of porous architectures, the confined nano pores serve as template to synthesize NPs of different shapes and sizes. It is worth mentioning here that MNPs size, morphology and their interaction with the solid support have the paramount influence on their catalytic activity.[10f,14a]In spite of substantial progress in this field, precise control over the size of the MNPs and thus fine tuning of their catalytic activity is still a grand challenge. Though several discrete architectures of Pd(II)/Pt(II)/Ru(II)/Fe(II) have been explored in recent time for various purposes, they have not been explored as templates/supports for the synthesis of MNPs due to their high vulnerability towards reducing agents.[5i] Therefore, in this context shape-persistent organic cage compounds owing to their well-defined geometry, solution processability, structural tunability and chemical and thermal stability may bring new opportunities. We envision that

nano organic cage compounds bearing vicinal diamines could be ideal candidates for control synthesis of palladium nanoparticles (PdNPs). Moreover, such an organic cage anchored PdNPs may be amenable for heterogeneous/homogeneous catalysis.

The heterogenization of homogenous catalytic reactions is a major area of research in the pharmaceutical and fine chemical industries.[10e] Heterogeneous catalysts are often less active than their homogenous counterparts. However, they provide the easy catalyst recycling and separation from the reaction mixture, which is particularly important for industrial scale application of precious metal catalysts.

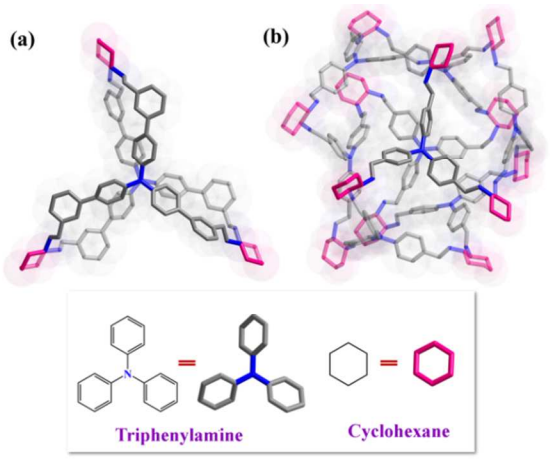


Figure 1: Shape persistent organic cage compounds (a) **CC1**^{r} and (b) **CC2**^{r}.

Herein, we report organic amine cage compounds (Figure 1) as novel platform for the size controlled synthesis of PdNPs. Furthermore, such cage anchored PdNPs have been utilized as heterogeneous catalysts and they exhibited superior catalytic performance over some well-known palladium catalysts in the cyanation of aryl halides under heterogeneous, additive-free condition.

RESULTS AND DISCUSSIONS

Synthesis and Characterization of the Cage Compounds: Purely organic trigonal-prismatic cages are relatively uncommon while they are one of the simplest possible architectures known till date. The shape-persistent prismatic **CC1**^{r} was easily obtained (~ 80% yield) via the reaction of a triphenyl amine based trialdehyde **C** with a chiral diamine **D** [(S, S)-1, 2-cyclohexanediamine]. The aldehyde building block **C** was synthesized by palladium catalyzed Suzuki-Miyaura cross coupling reaction of tris(4-bromophenyl)amine (**A**) and 3-formylphenylboronic acid (**B**) (Scheme-1). The imine based cage compound **CC1** was isolated as a pale yellow solid by treating **C** with **D** in 2: 3 stoichiometric ratio in chloroform under reflux for 48h. The dynamic nature of imine bonds ensures the formation of thermodynamically most stable product in equilibrium, which involves herein condensation between three equivalents of diamine and two equivalents of trialdehyde. Among all the possible architectures, molecular prism is enthalpically favored owing to the least angle strain, as well as entropically favored as it comprises of minimum number of building blocks.[7k] The **CC1** was transformed into more stable amine cage **CC1**^{r} by sodium borohydride reduction of the dynamic imine bonds. As synthesized **CC1**^{r} was characterized by multinuclear NMR (^{1}H, ^{13}C), ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC, FTIR and ESI-MS analyses. In ESI-MS spectrum (Figure 2), peaks at 1361.7697 and 681.3862 corresponding to $[M+H]^{+}$ and $[M+2H]^{2+}$ respectively unambiguously advocate for the formation of [2+3] assembled cage.

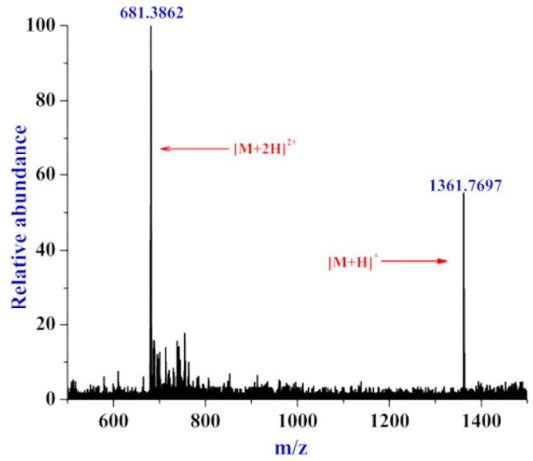
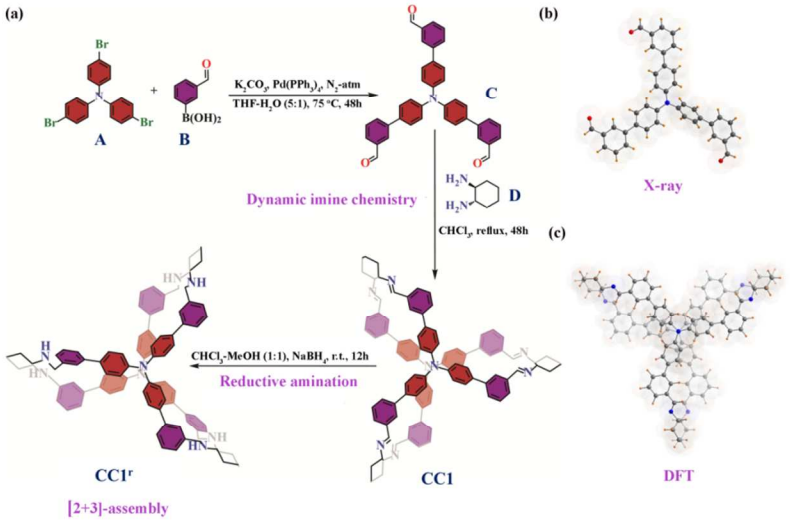


Figure 2. ESI-HRMS spectrum of **CC1**^{r} recorded in $CHCl_3$-CH_3CN (1:1; v/v).

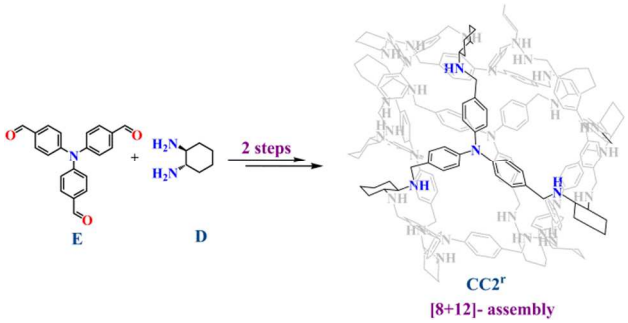
Several attempts of crystallization so far have been unsuccessful. However, gas phase DFT (B3LYP/6-31G) calculation reveals that in lowest energy conformer of **CC1**^{r}, top and bottom panels of the prism are in skew conformation, in which the distance between the nitrogen atoms of the triphenyl amine core is ~ 0.8 nm whereas the distance between the two furthest points inside the cage is ~ 2.0 nm (Figure S18).

The **CC2**^{r} has been synthesized following the same synthetic protocol as employed for **CC1**^{r}, from tris(4-formylphenyl)amine (**E**) and diamine **D** (Scheme 2 and S1). In ESI-MS spectrum peaks at m/z = 1809.4406 and 1206.7337 corresponding to $[M+2H]^{2+}$ and $[M+3H]^{3+}$ (Figure S22) respectively, bespeaks that 8 equiv. of trialdehyde and 12 equiv. of diamine condensed to form a [8+12] cage compound isomeric to what Cooper et al. obtained using (R, R)-1, 2-cyclohexanediamine.[15] Gas phase DFT calculation suggests that this distorted cubical cage compound has an internal cavity of ~ 2.4 nm with an outer diameter of ~3.0 nm.[15]

Synthesis of Cage Anchored Palladium Nanoparticles: Compounds having vicinal diamine moieties are the suitable candidates for the complexation with palladium (II) salts. Therefore, **CC1**^{r}/**CC2**^{r} furnished with secondary amine moieties could bind with Pd^{2+} ions and such a strong interaction is expected to foster controlled growth and stability of PdNPs.



Scheme 1: (a) Synthetic routes for the synthesis of trialdehyde **C** and molecular prism **CC1**^{r}. (b) X-ray crystal structure of **C** and (c) gas phase DFT (B3LYP/6-31G) optimized structure of the imine cage **CC1**.



Scheme 2. Synthesis of [8+12] assembled covalent architecture **CC2**^{r} from trialdehyde **E** and diamine **D**.

In view of this fact, **CC1**^{r} was first subjected to react with 3 equivalents (corresponding to 3 diamine clefts) of $Pd(OAc)_2$ in chloroform. A pale yellow solution of **CC1**^{r} was treated with an orange-yellow solution of $Pd(OAc)_2$ at room temperature which resulted in a sharp color change from yellow to deep brown (Figure S23), most likely due to the complexation of the diamine moieties of the cage with the Pd^{2+} ions.

This reaction mixture was subsequently reduced with a methanolic solution of sodium borohydride. The brown solution was immediately turned into black without forming any precipitates, which indicates an efficient reduction of Pd^{2+} ions into Pd^{0} and further their stabilization by the cage compound. The **Pd@CC1**^{r} was obtained as a black powder after complete removal of the solvent. Notably, this material was found to be soluble only in $CHCl_3$-MeOH solvent mixture and stable over a period of days without agglomeration and any significant color change. The palladium loading estimated by inductively coupled plasma optical emission spectrometry (ICP-OES) was found to be ~ 40 wt %, which is very high loading. In reality usually beyond 20 wt% of NPs loading leads to agglomeration of particles as manifested in preceding document.[13j] Interestingly, transmission electron microscopy (TEM) of **Pd@CC1**^{r} suggests well dispersed PdNPs with a narrow size distribution, having mean particle size of 1.8 ± 0.2 nm (Figure 3). Based on this value which matches well with the estimated internal cavity size (~ 2.0 nm) of the cage we believe that most of the nano particles are probably anchored within the cage. The scanning electron microscopy (SEM) image portrays a rough morphology composed of granular particles (Figure 3) of the material. Powder X-ray diffraction (PXRD) analysis displayed peaks at 2θ ≈ 40°, 47°, 68°, 82° and 87° which could be ascribed to (111), (200), (220), (311) and (222) lattice planes, a typical signature for Pd with a face centered cubic (fcc) structure (Figure S24). Additionally X-ray photoelectron spectroscopy (XPS) suggests that Pd is in zero oxidation state as indicated by the characteristic binding energy values 334.8 eV and 339.5 eV corresponding to two distinct spin-orbit pairs $3d_{5/2}$ and $3d_{3/2}$ respectively (Figure 3).

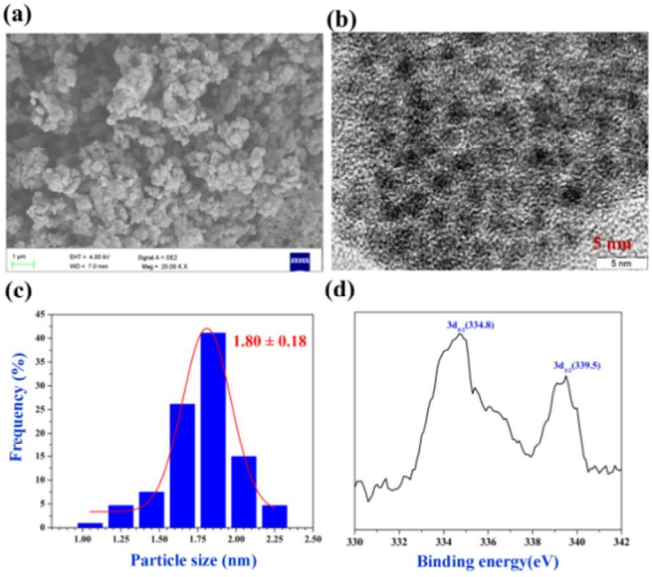


Figure 3. (a) SEM, (b) TEM, (c) particle size distribution and (d) XPS spectra of **Pd@CC1**^{r}.

In order to understand the role of structural features (size and shape) of organic cages on the growth of nanoparticles we extended our synthetic strategy for the synthesis of **Pd@CC2^r**. However, unlike previous case herein we observed an immediate formation of greenish yellow precipitate when **CC2^r** was treated with 12 equiv. (corresponds to 12 diamine clefts) of $Pd(OAc)_2$ in $CHCl_3$. To obtain the desired material the reaction mixture was treated with excess methanolic $NaBH_4$ which turned the color of the precipitate into black, indicating efficient reduction of Pd^{2+} into Pd^0 (Figure S23) . As obtained black **Pd@CC2^r** was found to be insoluble in any common organic solvent, making it a perfect candidate for heterogeneous catalysis. This material was characterized in a similar manner by TEM, SEM, PXRD, XPS and ICP-OES.

The ICP-OES estimated ~25 wt% of palladium loading. In PXRD and XPS spectra characteristic peaks corresponding to Pd^0 NPs with fcc structure were observed (Figures S25 and S26). The TEM analysis bespoke well dispersed nano particles with mean size of 3.7 ± 0.4 nm. Much larger sizes of PdNPs than the cage cavity (~ 2.4 nm) suggests that in this case most of the particles are anchored on the cage periphery where a PdNP could be stabilized by multiple cages (Scheme S2), unlike what we observed in **Pd@CC1^r**. Such a marked difference in loading and particle sizes of palladium nanoparticles with the change of cage compounds indicates the sheer role of structural features of the organic cage on NPs growth.

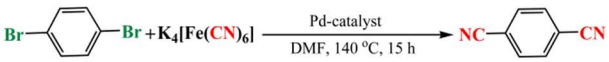
To further investigate the role of cage scaffold in PdNP synthesis we performed a controlled experiment. In that case $Pd(OAc)_2$ in chloroform was treated with excess methanolic $NaBH_4$ but in the absence of any of the cage compounds. TEM analysis of the obtained black precipitate (commonly known as palladium black) suggested the formation of structure less agglomerates (Figure S27). Such agglomeration is undoubtedly due to the lack of nucleation (i.e., Pd binding) sites, which in turn advocates the role of organic walls and diamine moieties of the cages on the control over PdNPs size.

Cyanation of Aryl Halides: From the perspective of a synthetic organic chemist, cyanide is one of the most desirable functionality as it could easily be converted into several other functional moieties like aldehyde, ketone, carboxylic acid, amine, oxime, amidine and so on. Moreover, aromatic nitriles are the key building blocks for many natural products, commercially available drugs and have extensively been used in agrochemical and dye industries.[16] The aromatic nitriles are commonly synthesized by the Sandmayer and Rosenmund–von Braun reactions.[17] However, the major concern associated with these synthetic methodologies involve use of elevated reaction temperatures (150-200 °C) and superstoichiometric amount of toxic cyanating agent CuCN, that produces equimolar amount of heavy metal wastes.

Recently transition metal catalyzed cyanation has received wide attention.[18,12e] In this context, so far several transition metals including Pd, Ni and Cu have been tested, among which Pd catalyzed cyanation found to be more beneficial considering the milder reaction condition and higher functional group tolerance.[18a] In order to address the safety concern associated with the cyanide sources non-toxic and inexpensive $K_4[Fe(CN)_6]$ has been employed recently as cyanating agent.[18e,18b] Thereafter, several palladium based catalysts involving this reagent as a cyanide source have been developed. However, most of them employ expensive ligands, additives and suffer severely due to poor recyclability of the catalysts.[18K] Therefore, a more convenient and cost effective synthetic protocol needs to be developed for this important chemical transformation.

To evaluate the catalytic activity of the cage anchored palladium nanoparticles, transformation of 1,4-dibromobenzene to 1,4-dicyanobenzene has been selected as the model reaction. For the screening of the reaction parameters, a series of experiments was carried out with varying time, temperature and catalyst loading. Reactions carried out employing **Pd@CC1^r** as catalyst suggested that best result (~ 99% product yield) could be obtained with 2 mol % Pd, 0.34 equiv of $K_4[Fe(CN)_6]$ in DMF after heating the reaction mixtures at 140 °C under inert atmosphere for 15 h (Table 1, entry 3). Variation in any one of the reaction parameters was found to have profound effect on the yield of the desired product, e.g. when the reaction was carried out at 130 °C while keeping other reaction parameters unaltered, we observed a sharp decrease in the yield (Table 1, entry 6).

Table 1. Standardization of reaction parameters for the cyanation of 1,4-dibromobenzene.[a]



entry	T (°C)	time (h)	mol % Pd		yield [%]	
			Pd@CC1^r	Pd@CC2^r	Pd@CC1^r	Pd@CC2^r
1	140	15	1	2	46	76
2	140	15	1.5	3	77	84
3	**140**	**15**	**2**	**4**	**99**	**90**
4	140	15	-	4.5	-	90
5	140	20	-	4	-	98
6	130	15	2	4	76	65
7	140	14	2	4	98	80
8	140	12	2	4	75	68

[a]Reactions were carried out using 0.34 mmol of $K_4[Fe(CN)_6]\cdot 3H_2O$.

It is a well-established fact that the catalytic activity of NPs greatly depends on their size while increase in the size leads to decrease in their catalytic activity. Therefore, a lower catalytic activity would be expected for **Pd@CC2^r** than **Pd@CC1^r**. To investigate this issue, aforementioned reaction was carried out employing **Pd@CC2^r** as catalyst. The results indicated that higher (4 mol% Pd) catalyst loading was required to achieve ~ 90% (which is lower than the yield obtained with **Pd@CC1^r**) yield under the same reaction condition (Table 1, entry 3). Furthermore, it has been observed that to achieve a comparative yield of the product as obtained with **Pd@CC1^r** catalyst a longer reaction time is required (Table 1, entry 5). These experimental results support the size-dependent catalytic activity of PdNPs in the present cases. Noticeably when the model reaction was tested in the presence of several commonly used palladium catalysts under a homogeneous/heterogeneous condition, the yields of the desired product were much less.

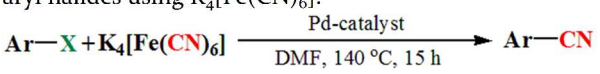
Table 2. Cynation of 1,4- dibromobenzene by different Pd catalysts.[a,b]

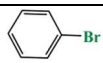
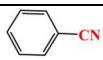
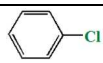
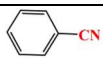
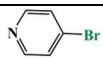
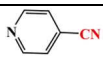
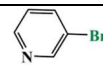
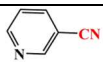
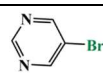
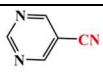
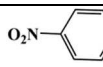
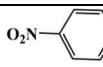
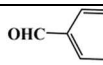
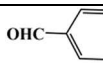
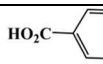
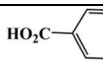
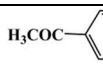
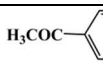
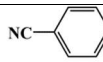
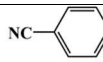
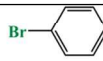
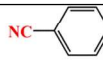
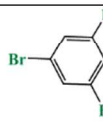
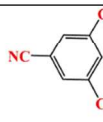
entry	Pd-catayst (4 mol %)	condition	yield [%]
1	$Pd(PPh_3)_4$	homogenous	26
2	$Pd(PPh_3)_2Cl_2$	homogenous	40
3	$Pd(OAc)_2$	homogenous	45
4	$PdCl_2$	homogenous	4
5	Pd-black	heterogeneous	2
6	Pd@C	heterogeneous	46

[a]Reaction condition: 1,4-dibromobenzene (1 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.34 mmol), 10 mL DMF, 140 °C, 15 h. [b]Yields are based on ^{1}H NMR analysis of the crude product.

To explore the generality of the catalytic systems we extended our synthetic strategy for aryl halides bearing a wide variety of diverse functionalities to produce the corresponding nitriles. As shown in Table 3 we observed quantitative yields of nitriles in most of the cases. Most importantly besides dibromobenzene these catalytic systems have great potential to convert other aromatic polyhalide like tribromobenzene to corresponding tricyanobenzene with reasonably good yield, which is generally hard to achieve under normal reaction conditions. Furthermore, less reactive chlorobenzene was cleanly converted to benzonitrile with quite high yields (Table 3, entry 2).

Table 3. Pd@CC1^r/Pd@CC2^r catalyzed cynation of various aryl halides using $K_4[Fe(CN)_6]$.[a,b]



entry	aryl halide	product	Pd@CC1^r	Pd@CC2^r
1			99	99
2			97	94
3			99	97
4			98	96
5			>99	>99
6			>99	>99
7			>99	>99
8			>99	>99
9			97	90
10			99	94
11[c]			99	90
12[d]			92	51

[a]Reaction condition: aryl halides (1 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.17 mmol), **Pd@CC1^r** (5.3 mg, 2 mol % Pd)/ **Pd@CC2^r** (17 mg, 4 mol % Pd), 10 mL DMF. [b]Yields are based on ^{1}H NMR analysis of the crude products. [c]0.34 and [d]0.51 mmol of $K_4[Fe(CN)_6]\cdot 3H_2O$ were used.

Reusability is the key issue for practical application of any heterogeneous catalyst which makes it more beneficial over its homogeneous counterpart particularly when precious metals are used. Therefore, in order to address this issue performance of both the catalytic systems was tested for the model chemical transformation (1,4-dibromobenzene to 1,4-dicyanobenzene) up to five consecutive cycles. As portrayed in the Figure 4 experimental

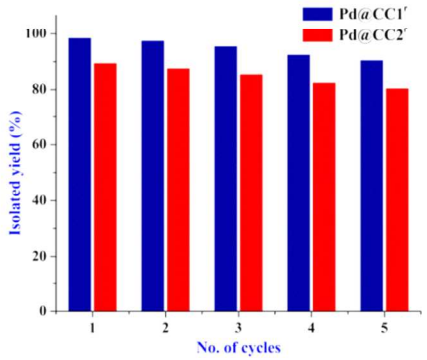


Figure 4: Recyclability of the **Pd@cage** catalysts.

results indicate a negligible decrease in their catalytic activity, while TEM images of the recovered materials after five cycles suggested no considerable change in the nanoparticle size and morphology (Figure S28). These results further support the fact that the ultrafine PdNPs are strongly bound to the cage, and such an interaction is stable even after prolonged heating of the material at high temperature.

CONCLUSIONS

In summary, we have demonstrated that shape persistent organic cage compounds having porous interior and stable aromatic backbone with multiple diamine clefts foster the control synthesis of PdNPs. The strong binding affinity of Pd^{2+} with the diamine clefts of the cage compounds is considered to be one of the governing factors during nucleation of the PdNPs whereas aromatic walls protect the newly born NPs from agglomeration. The present results demonstrate the potential of functionalized discrete organic cage compounds as novel platform for the size controlled synthesis of PdNPs. Moreover, experimental results suggest that nano-particles size distribution and their catalytic activity could be fine-tuned by changing the size of the cage compounds. It has been observed that PdNPs may anchor inside or outside the cage cavity depending on the cage architecture. As synthesized cage anchored palladium nanoparticles found to have better catalytic activity over several commercially available palladium catalysts, which offer additive-free cyanation of haloarenes under heterogeneous condition. The promising features of these catalysts include easy operational methodology, wide variety of functional group tolerance, reusability and high yield of the products.

EXPERIMENTAL SECTION

Materials and Methods: All the chemicals and solvents were purchased from commercially available sources and were used without further purification. The NMR spectra were recorded on Bruker 400 MHz instrument. The chemical shifts (δ) in the ^{1}H NMR spectra are accounted in ppm relative to tetramethylsilane (Me_4Si) as an internal standard (0.0 ppm) in $CDCl_3$ or proton resonance resulting from incomplete deuteration of the solvents. High resolution mass spectra were recorded on a Q-TOF instrument by electrospray ionization (ESI) technique using standard spectroscopic grade solvents. IR spectra were recorded on a Bruker ALPHA FTIR spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalytical diffractometer. Scanning electron microscopy (SEM) was performed on a Carl-Zeiss Ultra 55 at an operating voltage of 5-20 kV. Transmission electron microscopy (TEM) was performed on a JEOL 2100F operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra instrument. Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on a Thermo-iCAP 6000 Series instrument.

Synthesis of Aldehyde C: In a 100 mL flame dried double-neck round-bottom flask 0.96 g (2.00 mmol) of tris(4-bromophenyl)amine (**A**) and 1.40 g (9.33 mmol) of 3-formylphenylboronic acid (**B**) were taken in 50 mL THF and into that 20 mL aqueous solution of 1.40 g (10.00 mmol) K_2CO_3 was added. The resulting mixture was stirred under nitrogen atmosphere at room temperature for 10 minutes followed by addition of 0.12 g (0.10 mmol) of $Pd(PPh_3)_4$ and heated to 70 °C for 48h. After completion of the reaction THF was removed and the aqueous part was extracted with dichloromethane (50 mL × 3). Organic part was then dried over Na_2SO_4 and completely removed to obtain pale yellow solid. The resulting solid mass was purified by silica gel column chromatography in dichloromethane to get greenish yellow powder. Isolated yield: 58% (0.65 g, 1.16 mmol). Single crystals of the compound were obtained from a $CHCl_3$-EtOAc solution by slow evaporation. ^{1}H NMR (CDCl3, 400MHz): δ 10.09 (s, 3H), 8.11 (s, 3H), 7.83-7.88 (m, 6H), 7.57-7.63 (m, 9H), 7.28 (d, 6H). ^{13}C NMR (100 MHz, CDCl3): δ 192.8, 147.7, 141.9, 137.4, 134.9, 133.0, 130.0, 128.9, 128.6, 128.1, 125.1. ESI-HRMS ($CHCl_3$-CH_3CN): m/z for $C_{39}H_{27}NO_3$: $[M]^+$ 557. 1981 (calculated 557.1990). FTIR (cm^{-1}) ν: 1691 (CH=O), 1594, 1510, 1471, 1438, 1386, 1296, 1283, 1263, 1179, 1160, 900, 842, 829, 783, 738, 686, 641, 563, 531.

Synthesis of CC1: In a 250 mL round bottom flask 120 mL $CHCl_3$ solution of diamine **D** (31 mg, 0.28 mmol) was added slowly dropwise to a stirring solution of aldehyde **C** (100 mg, 0.18 mmol) dissolved in 60 mL $CHCl_3$. The resulting reaction mixture was stirred at room temperature for 48 h. After completion of the reaction solvent was removed and the obtained pale yellow solid was washed with CH_3CN several times. Isolated yield: 91% (110 mg, 0.08 mmol). ^{1}H NMR (CDCl3, 400MHz): δ 8.37(s, 6H), 7.86(s, 6H), 7.55(d, 12H), 7.36-7.40(m, 18H), 7.10(d, 12H), 3.44 (d, 6H), 1.88-1.95(m, 18H), 1.51 (m, 6H). ^{13}C NMR (100 MHz, CDCl3): δ 162.0, 147.4, 141.4, 137.5, 135.6, 129.4, 129.0, 128.4, 126.8, 126.7, 125.1, 74.1, 33.3, 25.0. ESI-HRMS ($CHCl_3$-CH_3CN): m/z for $C_{96}H_{84}N_8$: $[M+H]^+$ 1350.6999 (calculated 1350.6931), $[M+2H]^{2+}$ 675.8494 (calculated 675.8818). FTIR (cm^{-1}) ν: 2929, 2851, 1646 (CH=N), 1600, 1516, 1477, 1471, 1315, 1276, 1250, 1084, 1010, 829, 790, 686, 538.

Synthesis of CC1^r: In a 100 mL round bottom flask 100 mg (0.07 mmol) of **CC1** was taken in 60 mL $CHCl_3$-MeOH (1:1, v/v) binary solvent mixture. Into above reaction mixture, 32 mg (0.84 mmol) of $NaBH_4$ was added portion wise at room temperature and stirred for 12 h. After completion of the reaction, solvent was completely removed and the product was extracted in $CHCl_3$. Organic part was washed several times with water and dried over Na_2SO_4 followed by removal of solvent to get white solid. Isolated yield: 85% (81 mg, 0.06 mmol). ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.57 (s, 6H), 7.33-7.39 (m, 12H), 7.19-7.25(m, 18H), 6.92(d, 12H), 3.94(d, 6H), 3.62(d, 6H), 2.31(br, m, 18H), 1.78(br, s, 12H), 1.27-1.32(br, m, 6H), 1.08(br, s, 6H). ^{13}C NMR (100 MHz, CDCl3): δ 146.9, 141.7, 141.6, 135.8,

129.2, 128.1, 127.8, 127.0, 125.9, 124.9, 61.7, 51.8, 32.0, 25.6. ESI-HRMS ($CHCl_3$-CH_3CN): m/z for $C_{96}H_{96}N_8$: $[M+H]^+$ 1361.7697 (calculated 1361.7836), $[M+2H]^{2+}$ 681.3862 (calculated 681.3957). FTIR (cm^{-1}) ν: 2929, 2844, 2358, 1600, 1510, 1471, 1438, 1321, 1283, 1101, 835,790,738, 693.

Synthesis of CC2: This cage was synthesized following the same synthetic protocol as employed for **CC1**, from tris(4-formylphenyl)amine (100mg, 0.30 mmol) and **D** (50 mg, 0.45 mmol). Isolated yield: 80% (107 mg, 0.03 mmol). ^{1}H NMR ($CDCl_3$, 400MHz): 8.35 (s, 12H), 8.24 (s, 12H), 7.61-7.55 (m, 48H), 7.08-7.02 (m, 48H), 3.56-3.48 (m, 24H), 1.85 (br, 24H), 1.75 (br, 48H), 1.49 (br, 24H). ESI-HRMS ($CHCl_3$-MeOH): m/z for $C_{240}H_{240}N_{32}$: $[M+2H]^{2+}$ 1787.0146 (calculated 1786.9995), $[M+3H]^{3+}$ 1191.9636 (calculated 1191.9039).

Synthesis of CC2^r: In a 100 mL round bottom flask 71 mg (0.02 mmol) of **CC2** was taken in 60 mL $CHCl_3$-MeOH (1:1, v/v) binary solvent mixture. Into above reaction mixture 38 mg (1 mmol) of $NaBH_4$ was added portion wise at room temperature and stirred for 12 h. After completion of the reaction, solvent was completely removed and the product was extracted in $CHCl_3$. Organic part was washed several times with water and dried over sodium sulphate followed by removal of solvent to get yellow solid. Isolated yield: 77% (39 mg, 0.015 mmol). ^{1}H NMR ($CDCl_3$, 400MHz): 7.08 (d, 48H), 6.89 (d, 48H), 3.76 (d, 24H), 3.52 (d, 24H), 2.1-2.26 (br, m, 72H), 1.7 (br, d, 24H), 1.15-1.27 (br, m, 24H). ESI-HRMS ($CHCl_3$-MeOH): m/z for $C_{240}H_{288}N_{32}$: $[M+2H]^{2+}$ 1809.4375 (calculated 1809. 4406), $[M+3H]^{3+}$ 1206.7337 (calculated 1206.6763).

Synthesis of Pd@CC1^r Catalyst: In a typical synthetic protocol 40 mg (0.03 mmol) of **CC1^r** dissolved in 6 mL $CHCl_3$ was treated with 4 mL $CHCl_3$ solution of 20 mg (0.09 mmol) of $Pd(OAc)_2$ for 1 h. Into this reaction mixture a methanolic solution of $NaBH_4$ (24.3 mg, 0.18 mmol) was added dropwise at room temperature and stirred for 20 min. After the said time period the solvent was completely removed and the product was washed several times with methanol followed by drying under vacuum for overnight to obtain **Pd@CC1^r** as a black solid.

Synthesis of Pd@CC2^r Catalyst: In a typical synthetic protocol 40 mg (0.01 mmol) of **CC2^r** dissolved in 8 mL $CHCl_3$ was treated with 4 mL $CHCl_3$ solution of 29.0 mg (0.12 mmol) of $Pd(OAc)_2$ for 2h. Into this reaction mixture a methanolic solution of $NaBH_4$ (36.6 mg, 0.26 mmol) was added dropwise at room temperature and stirred for 40 min. After the said time period the precipitated black solid was filtered out and washed several times with methanol followed by drying under vacuum for overnight to obtain the desired catalyst **Pd@CC2^r**.

Sample Preparation for ICP-OES Analysis: In a typical stock solution preparation 7 mg of Pd@cage was added to a 10 mL concentrated nitric acid and stirred for overnight at room temperature. After complete dissolution of the compound the solution was filtered to remove any undissolved material. The filtrate was then diluted with deionized water to make a 100 mL stock solution.

General Experimental Procedure for Cyanation of Aryl halides: Representative procedure for the cyanation of 1, 4-dibromobenzene with $K_4[Fe(CN)_6]$: In a flame dried 50 mL round bottom flask 236 mg (1.00 mmol) of 1, 4-dibromobenzene, 73 mg (0.17 mmol) of $K_4[Fe(CN)_6]\cdot 3H_2O$ and 5.3 mg (0.02 mmol PdNPs) of **Pd@CC1^r** or 17 mg (0.04 mmol PdNPs) of **Pd@CC2^r** were taken in 10 mL DMF. The resulting reaction mixture was stirred under nitrogen atmosphere at 140 °C for 15h. After completion of the reaction the mixture was filtered to separate the solid catalyst. The filtrate was then extracted with EtOAc (3 ×10 mL). Organic part was washed with water and dried over Na_2SO_4 followed by complete removal of solvent. The resulting solid mass was purified by silica gel column chromatography in hexane/dichloromethane (1:9 v/v) to afford pure 1, 4-dicyanobenzene as white solid.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.79 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.3, 117.5, 117.2.

4-Pyridinecarbonitrile: ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.76 (d, 2H), 7.49 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 125.7, 120.8, 116.8.

3-Pyridinecarbonitrile: ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.83(s, 1H), 8.75-8.77 (m, 1H), 7.91-7.94 (m, 1H), 7.39-7.42(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 152.9, 139.7, 124.1, 117.0, 110.5.

4-Formylbenzonitrile: ^{1}H NMR ($CDCl_3$, 400MHz): δ 10.06 (s, 1H), 7.96 (d, 2H), 7.81 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 139.2, 133.4, 130.4, 118.0.

4-Cyanobenzoic acid: ^{1}H NMR (CD_3OD, 400MHz): δ 8.15 (d, 2H), 7.84 (d, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ 167.4, 135.9, 132.4, 130.3, 118.1, 116.0.

Benzonitrile: ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.58-7.63 (m, 3H), 7.45-7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.4, 132.6, 129.8, 119.4, 112.8.

4-Nitrobenzonitrile: ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.35 (d, 2H), 7.89 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 134.0, 124.8, 118.8, 117.3.

4-Acetylbenzonitrile: ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.03 (d, 2H), 7.77 (d, 2H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 140.0, 132.6, 128.8, 118.0, 116.5, 26.8.

5-Cyanopyrimidine: ^{1}H NMR ($CDCl_3$, 400MHz): δ 9.4(s, 1H), 9.0(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 159.7, 114.3, 110.5.

1, 3, 5- Tricyanobenzene: ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.17 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.2, 116.7, 114.9.

Computational Methodology: Full geometry optimizations were performed using Gaussian 09 package.[19] The hybrid B3LYP functional was used in all calculations as implemented in Gaussian 09 package, mixing the exact Hartree-Fock-type exchange with Becke's expression for the exchange functional[20] that was proposed by Lee-Yang-Parr for the correlation contribution.[21] The 6-31G basis set was used for all calculations. Frequency calculations were

carried on the optimized structures that confirmed the absence of any imaginary frequencies.

X-ray Crystal Data Collection and Structure Solution: X-ray data of the aldehyde **C** was collected on a Bruker D8 QUEST CMOS diffractometer using the SMART/SAINT[22] software, equiped with a low temperature device. The difraction quality crystal was mounted on a loop coated with traces of viscous oil. The intensity data was collected at 100(2) K using graphite monochromatic Mo-Kα radiation (0.7107 Å). The structure was solved by direct methods and refined by full-metrix least squares on F^2 employing the SHELX-97[23] incorporated in WinGX.[24] Empirical absorption corrections were applied with SADABS.[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed by using the riding models and refined isotropically.Crystallographic data and refinement parameters are provided in Table S1.

ASSOCIATED CONTENT

Syntheses and characterization data (NMR, FTIR, ESI-MS, TEM, SEM, PXRD). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Molecular Cage Impregnated Palladium Nanoparticles: Efficient, Additive-Free Heterogeneous Catalysts for Cyanation of Aryl Halides

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