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A Self-Assembled Trigonal Prismatic Molecular Vessel for Catalytic Dehydration Reactions in Water

Paramita Das,[a#] Atul Kumar,[a#] Prodip Howlader,[a] and Partha Sarathi Mukherjee[a,*]

Dedication ((optional))

Abstract: A water-soluble Pd_6 trigonal prism (**A**) was synthesized by two-component coordination-driven self-assembly of a Pd(II) 90° acceptor with a tetraimidazole donor. As the walls of the prism are constructed by three conjugated aromatic building blocks, the confined pocket of the prism is hydrophobic. In addition to the hydrophobic cavity, large product egress windows make **A** an ideal molecular vessel to catalyze otherwise challenging pseudo multicomponent dehydration reactions in its confined nanospace in aqueous medium. This study is an attempt towards selective generation of the intermediate tetraketones and xanthenes by fine-tuning the reaction conditions employing a supramolecular molecular vessel. Moreover, poor or no yield of the dehydrated products in absence of **A** under similar reaction conditions ascertains the ubiquity of the confined space of the barrel in promoting such reactions in water. Furthermore, we focussed on the rigidification of the tetraphenylethylene-based tetraimidazole unit anchored within the Pd(II) coordination architecture; enabling counter-anion dependent aggregation induced emission in presence of water.

Introduction

In the past two decades perceptible progress has been made in the self-assembly of elaborately designed diverse tectons encrypted with explicit information in specific stoichiometric ratios. Thus, preprogrammed thermodynamically favorable abiological supramolecular architectures with well-defined shapes and sizes can be afforded using appropriate building blocks.[1] This enables the construction of a suite of finite supramolecular coordination complexes (SCCs), from two-dimensional (2-D) polygons to three-dimensional (3-D) cages, prisms, bowls, tubes and capsules.[2,3] Unified under the principle of open window and easy ingress and egress of guests, distinct barrel-shaped structures by metal–ligand self-assembly remain very challenging and limited examples are reported in the literature.[4] Again non-covalent cages are of particular interest because of circumvention of tedious multistep synthesis which is obligatory for covalent analogs.[5] Furthermore, the intriguing features of an imidazole donor over a pyridyl donor[6] and the declining fame of templates[7] have appealed synthetic chemists to engineer polyimidazole-functionalized supramolecules without template. In this quest, several groups have contributed template-free supramolecular assemblies paving access to rare structures.[8] The nanoscopic confined space that is endowed with desired functionality provides the impetus for applications in selective encapsulation,[9] molecular flasks,[10] gas adsorption, sensing, separation, bioengineering and so on.[11]

Among the many potential applications of container molecules, the one which has made very attractive in the last several years is their ability to catalyze reactions of bound guests[12] in aqueous media[13] reminiscent of enzyme catalysis. Although many striking results have been reported in the field of supramolecular catalysis, the biggest challenge in establishing a catalytic cycle is product inhibition.[14] Albeit a few enticing examples are reported for cavity-induced organic transformations, but their statistics are limited in the Diels-Alder,[15] epoxidation,[16] the aza-Cope rearrangement,[17] Knoevenagel reaction,[18] Nazarov cyclization,[19] sigmatropic rearrangements, and a few others.[20] Again reversible dehydration condensation in aqueous media is a difficult transformation and remains an important challenge because the large excess of water drives the equilibrium backward.[21] While most of the examples accomplished inside molecular cavities are thermal[12e] and photochemical organic transformations,[13b,e] dehydration condensation reactions in supramolecular microenvironment are infrequent. On the contrary, enzymes can readily achieve the dehydration in water even under neutral conditions at ambient temperature which hard pressed the synthetic chemists to construct such well-furnished catalytic frameworks.

On the other hand, various applications of fluorescent chromophores[22-24] have captured much attention of the contemporary researchers motivating them to develop novel fluorophores with the aspiration to explore new smart molecular devices.[25] Conventional fluorophores recurrently display highly emissive fluorescence in dilute solutions but suffer severely from aggregation-caused quenching (ACQ) in concentrated solutions or in the condensed state owing to the formation of excimers and exciplexes that restrain their practical applications.[26] In contrast, a contrary effect known as aggregation-induced emission (AIE), wherein fluorogens that endure non-radiative decay through intramolecular rotations/vibrations at low concentrations emit intense fluorescence in the condensed state.[27] Thus, the discovery and development of AIE luminogen molecules have attracted pervasive attention.[28] Again, non-covalent self-assembled AIEgens engross special attention over covalent AIEgens.[29] In the present context, it is pertinent to mention that the “AIE phenomenon” [27] has enthralled the contemporary chemists to design such AIE-active fluorophores. Furthermore, the concept of “light-emitting tetraphenylethylene (TPE)-based architectures on SCC platforms” by Stang *et al.*[30]

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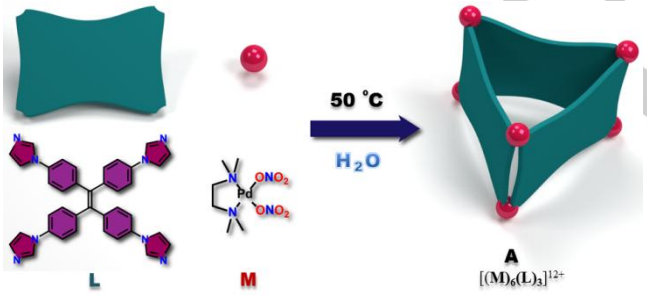
has exemplified their multifaceted applications in sensor devices, advanced optoelectronic materials and so on. Although quite a few light-emitting TPE-based discrete organoplatinum(II) metallacycles and metallacages are reported,[29] AIE active aqueous TPE-Pd-metallacage is yet to be explored. Again, Pd^{2+} is an 'open-shell' transition-metal ion and is notorious for its fluorescence quenching effect.[31] Considering this effect of Pd^{2+} in diminishing fluorosence quantum efficiency, synthesis of Pd(II) containing fluorescent metallacage is quite challenging.

Herein, we report a template-free synthesis of a water-soluble trifacial molecular barrel **A** *via* two-component self-assembly of TPE–functionalized tetraimidazole donor **L** with 90° acceptor *cis*-Pd(tmeda)$(NO_3)_2$ (**M**) [tmeda = N,N,N',N'-tetramethylethane-1,2-diamine, **L** = 1,1,2,2-tetrakis(4-(1*H*-imidazol-1-yl)phenyl)ethene] (Scheme 1). This newly engineered water-soluble molecular barrel with integrated hydrophobic pocket has shown to be suitable for otherwise difficult dehydration reactions of water-insoluble guests in aqueous medium to form xanthene derivatives. To the best of our knowledge, the nanobarrel **A** represents the first example of a discrete self-assembled molecular vessel as a catalyst for the selective generation of both tetraketone intermediates and xanthenes in a homogeneous aqueous environment under mild reaction conditions. It is worth affirming that in absence of the cage, same reactions preceded sluggishly giving either poor or no yields of the non-cyclized tetraketones or cyclized xanthenes. This defines the significance of the confined cavity in promoting such unfavorable reactions in aqueous media. Additionally, for the first time, we have explored the AIE behavior of this Pd(II) containing metallacage in aqueous medium. Rigidification of the TPE-based linker (**L**) to Pd(II) acceptors within a SCC matrix confers the counter-anion dependent AIE properties in our synthesized molecular barrel **A**.



Scheme 1. Schematic representation of the formation of 3D molecular barrel **A**.

Results and Discussion

Synthesis and Characterization

L was synthesized in two steps, starting from TPE precursor following the reported procedure.[32] It was fully characterized by IR, melting point, ^{1}H (Figure 1a), ^{13}C NMR, ESI-MS spectrometry, and its molecular structure was determined by single-crystal X-ray diffraction (XRD) analysis (CCDC 1550022) (Supporting Information).

With TPE-based donor (**L**) in hand, two-component **A** was obtained by adding an aqueous solution of *cis*-(tmen)$Pd(NO_3)_2$ (**M**) into the solid tetratopic donor **L** in 2:1 molar ratio followed by subsequent stirring at 50 °C for 6 h. The resulting clear solution was triturated with acetone to obtain self-assembled [6+3] molecular barrel **A** [$\mathbf{M_6L_3}$] as an off-white precipitate in pure form. **A** was highly soluble in water. It was characterized by ^{1}H NMR spectroscopy (Figure 1b), DOSY (Figure S3, Supporting Information), COSY (Figure S4, Supporting Information) and ESI-MS (Figure S5, Supporting Information). ^{1}H NMR analysis of **A** in D_2O exhibited sharp distinct peaks with noticeable downfield shift as compared to the ligand **L** which is expected owing to the coordination of **L** to Pd(II). The peaks of **A** were assigned with the help of the ^{1}H–^{1}H COSY spectra.

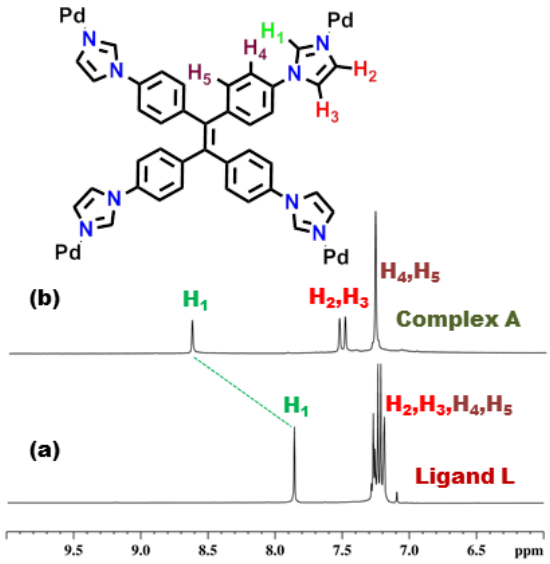


Figure 1. Partial ^{1}H NMR spectra of (**a**) ligand **L** recorded in $CDCl_3$, and (**b**) complex **A** recorded in D_2O.

Notably, diffusion-ordered NMR spectroscopy (DOSY, D_2O) corroborated the formation of a single species by the appearance of a clear single band at D = 1.5488×10^{-10} m^2/s (log D = –9.81) with a hydrodynamic radius of about 12.81 Å (Supporting Information). ESI-MS spectra of the **A** (after anion exchange with PF_6^-) in acetonitrile displayed three salient peaks at m/z = 1476.66, 1071.26 and 828.21 with isotopic distribution patterns corresponding to $[\mathbf{A}(PF_6)_9]^{3+}$, $\mathbf{A}(PF_6)_8]^{4+}$ and $[\mathbf{A}(PF_6)_7]^{5+}$ charge fragments respectively (Figure S5), attesting the formation of a $\mathbf{M_6L_3}$ species. Finally, diffraction quality single crystals were obtained by slow vapor diffusion of acetone into an aqueous solution of complex **A** at room temperature for two weeks.

Single crystal XRD analysis of complex **A** unequivocally confirmed the formation of a trifacial barrel containing open windows (Figure 2, CCDC 1550021). The vertices of the barrel were occupied by Pd(II) ions. Structural refinements revealed that the distance between the metal ions (Pd⋯Pd distance) within one equilateral triangle is about 15 Å. Two of these triangles

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were linked by the ligand **L** to construct the barrel which makes the closest distance between the metal ions (two triangles) ca. 12 Å having an approximate volume of 1169 Å^3. Molecular orientation in the crystal lattice shows the formation of a channel type of structure along the c-axis with slight interpenetration between alternative channels of barrels (Figure S6, Supporting Information). Important crystallographic data and refinement parameters of **A** are provided in Table S2 (Supporting Information).

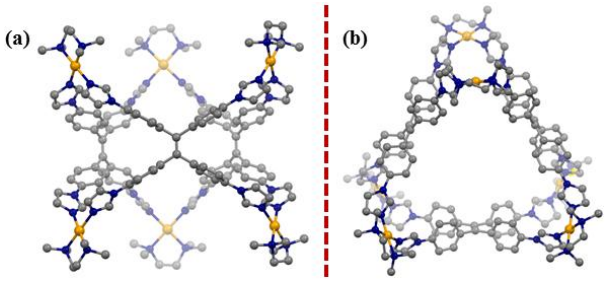


Figure 2. Single crystal XRD structure of the cage **A** (**a**) side view; and (**b**) top view. Color codes: yellow-Pd, blue-N, dark grey-C (**CCDC 1550021**). Hydrogen atoms are omitted for clarity.

Encapsulation Studies

The interior cavity of **A** has hydrophobic pocket fenced by the three aromatic walls (**L**). This enthused us to study the prospect of encapsulating water-insoluble aromatic guest in an aqueous medium. Our investigations started with 2-naphthaldehyde (**1i**) as a test sample. An excess amount of **1i** was suspended in an aqueous solution of **A** at room temperature. As anticipated, **1i** was encapsulated in **A** which was confirmed by the substantial up-field shifts of the ^{1}H NMR signals of the encapsulated guests. Notably, **1i** was not sufficiently water soluble to permit their ^{1}H NMR spectra to be recorded in D_2O in the absence of hosts. Moreover, encapsulations caused splitting of the H_4 and H_5 protons on the phenyl rings of the ligand (**L**) (hitherto at 7.27 ppm in **A**) into two doublets of equal intensity (Figure S7, Supporting Information). This is attributed to the strong CH–π interaction of the guest molecules with the walls of the cavity. The stoichiometry of cage *vs*. guest was evaluated to be 1 : 3 from the ^{1}H NMR spectra (Figure S8, Supporting Information). Again DOSY NMR exhibited identical diffusion coefficients for the guest (**1i**) and the host cage (Figure S9, Supporting Information). The peaks of the inclusion complex **1i**⊂**A** (⊂ denotes encapsulation) were assigned with the help of the ^{1}H–^{1}H COSY spectra (Figure S10, Supporting Information). Recognition of **1i**⊂**A** was further scrutinized by UV-Vis spectroscopy where additional bands along with cage peaks assigned to the guest molecule were witnessed (Figures S11 and S12, Supporting Information). Additionally 1:3 stoichiometry is obtained based on UV-Vis studies (Supporting Information). The peak at 1686 cm^{-1} in infrared spectroscopy was attributed to the stretching of aromatic CH=O bond, suggesting the encapsulation of **1i** by the host (Figure S14, Supporting Information). The host-guest (1 : 3) complex was modeled and the structure was optimized using semi-empirical method with a PM6 basis set (Figure S15, Supporting Information). As the aldehyde group is more polar than the aromatic ring of naphthaldehyde, it may lean outside the cavity. However, the naphthyl moieties are stabilized inside the hydrophobic cavity of the cage by CH–π stacking interactions with the phenyl rings of the walls (**L**) of the cavity further throwing light (specifying the reason) for the splitting of the phenyl peak in ^{1}H NMR spectra (Figure S7b). Encapsulations of the bulkier substrates were monitored by absorption spectroscopy (Figure S16-21, Supporting Information). Thus, we hypothesized that **A** would be adept to act as a molecular nanovessel to catalyze classic organic reactions in green aqueous medium.

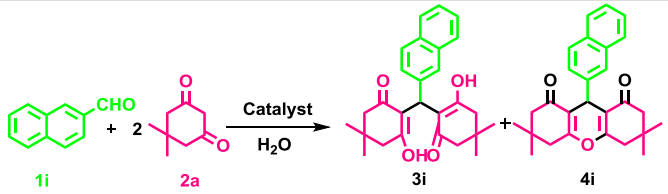
Catalytic Activity and Regulation

Xanthenes, a special branch of pyran systems are important building blocks of many natural products and possess potential applications in medicinal chemistry as well as fluorescent materials.[33] Again tetraketones and their tautomeric enol forms are the basic intermediates for the preparation of biologically relevant heterocyclic compounds and numerous acridinones as laser dyes.[34] Capitalizing the enormous applications and recognition of the aforementioned compounds and in continuation of our quest for performing dehydration reactions in aqueous media,[5c,6d] we employed water-soluble **A** as an efficient and homogeneous catalyst for the one-pot pseudo three-component synthesis of tetraketones (**3**) and their corresponding xanthenes (**4**) in water. Furthermore, the tetraketones (**3**) are prone to cyclization by the elimination of water affording the corresponding xanthenes (**4**). In some instances, the driving force of dehydration is so enhanced that the intermediate **3** cannot be isolated and the reaction affords only **4**. Conversely, the number of domino reactions for the synthesis of intermediate **3** is scarcer compared to **4**. To evade this problem, we wish to disclose the first development and implementation of a 3D nanocage as a homogeneous catalyst for the selective generation of both cyclized xanthenes (**4**) and non-cyclized tetraketone intermediates (**3**) under two different conditions.

To optimize the reaction conditions, a series of experiments was conducted with an illustrative reaction of 2-naphthaldehyde (**1i**) (0.02 mmol) and dimedone (**2a**) (0.04 mmol) with a variation of reaction parameters, such as catalyst, reaction temperature etc., and the results are summarized in Table 1. The results established that the temperature of the reaction had a significant effect on the yield of the non-cyclized product (**3i**) to cyclized product (**4i**). The initial reaction was performed in the presence of 5 mol% **A** in H_2O at room temperature (r.t.). After extraction of the reaction mixture with $CDCl_3$, the ^{1}H NMR diagnosed the formation of the non-cyclized product (**3i**). Albeit, 1 mol% catalyst afforded the desired product (**3i**) in poor yield. With 10 mol% of catalyst, no significant improvement in the yield was observed. In contrast, on repeating the same experiment at 60 °C with 5 mol% catalyst yielded only the cyclized product (**4i**) in 90% yield. This could probably be due to the ease of elimination of H_2O at a higher temperature in the hydrophobic cavity of the cage. Reducing the catalyst to 1 mol% afforded **4i** in only 19% yield with

<5% of **3i** at 60 °C. It was found that at 50 °C, 5 mol% catalyst could afford mainly non-cyclized **3i** (76%) along with the very small amount of cyclized **4i** (15%) after 24 h. In hope of higher yields, further optimizations were performed

Table 1. Optimization of Reaction Conditions for the Dehydration reactions[a]



Entry	Catalyst (mol%)	Temp (°C)	Time (in h)	% Yields Tetraketone (3i)[b]	% Yields Xanthene (4i)[b]
1	**A** (05)	r.t.	12	90	-
2	**A** (01)	r.t.	12	22	
3	**A** (10)	r.t.	12	91	
4	**A** (05)	60	12	-	90
5	**A** (01)	60	12	<5	19
6	**A** (10)	60	12	-	90
7	**A** (05)	50	48	76	15
8	**A** (05)	80	12	-	91
9	**L** (15)	r.t.	24	-	-
10	**L** (15)	60	24	-	-
11	**M** (30)	r.t.	24	-	-
12	**M** (30)	60	24	-	-
13	-	r.t.	24	-	-
14	-	60	24	-	-

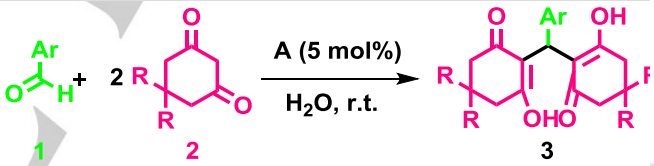
[a]: Aldehydes **1** (0.02 mmol), cyclic 1,3-diketones **2** (0.04 mmol), 1 mL water, stirring. [b]: Crude yields determined from ^{1}H NMR based on starting materials.

at 80 °C, but no improved results were obtained. Importantly, no product was observed (cyclized as well as non-cyclized) without any catalyst which further necessitates the importance of hydrophobic cavity in this transformation. Moreover, reactions did not proceed when control experiments with individual cage components like ligand **L** (15 mol%), and *cis*-(tmen)Pd(NO_3)$_2$ (**M**) (30 mol%) were performed at r.t. and 60 °C.

Temperature dependence on the yield of non-cyclized product (**3i**) to the cyclized product (**4i**) was probed with the same test reaction with 5 mol% of catalyst **A** in H_2O (1 mL) for 12 h at various temperatures with an increment of 10 °C (Figure S22, Supporting Information). Reaction results established that hydrophobic nature of the cage can assist elimination of H_2O at a sufficiently low temperature in an aqueous medium. This stands in stark juxtaposition to xanthene synthesis in bulk solution, which generally requires heating to reflux in neat or in an organic solvent.

Further, the scope of **A** as a catalyst was examined using a suite of aldehydes to synthesize the non-cyclized products (**3**) as well as cyclized products (**4**) under two different conditions and the results are presented in Tables 2 and 3, respectively. Despite the difficulty of a Knoevenagel condensation reaction with electron-rich carbonyl, the reaction occurred successfully with 4-methyl benzaldehyde, 3-methoxy benzaldehyde. The versatility of the reaction was established since aldehydes with neutral and electron-withdrawing groups at *o*-, *m*- and *p*-positions all afforded moderate to good yields in the presence of **A**. It was pleasing to find that sensitive aldehydes (containing a heteroatom, and CF_3 groups) also reacted very efficiently with no side reactions. Despite the mild conditions, even sterically bulky 1-naphthyl and 2-naphthyl aldehydes were easily transformed into the desired products in good yields. However, the relative reaction rate was decreased with bulkier 1-pyrenealdehyde as evident from the reaction completion time (48 h). This size-selective catalysis provides evidence about the involvement of cavity of **A**. The scope of the reaction was further expanded using 1,3-cyclohexadione.

Table 2. Nanobarrel "**A**" Catalyzed r.t. Synthesis of Non-cyclized Product[a]

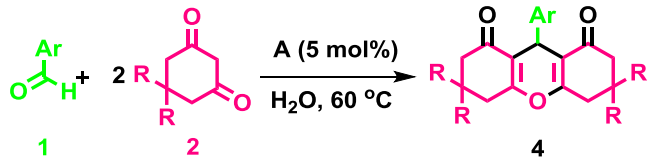


Entry	Ar (1)	R	Product (3)	Time (in h)	Product (% Yields)[b]	
					without **A**	with **A**
1	Ph	Me (**2a**)	3a	02	30	99
2	4-Me-Ph	Me (**2a**)	3b	02	22	96
3	3-OMe-Ph	Me (**2a**)	3c	02	25	98
4	4-Br-Ph	Me (**2a**)	3d	02	35	99
5	2,4-$(Cl)_2$-Ph	Me (**2a**)	3e	02	30	99
6	3-Br-Ph	Me (**2a**)	3f	02	30	98
7	4-CF_3-Ph	Me (**2a**)	3g	02	27	98
8	Py-4-al	Me (**2a**)	3h	02	30	99
9	2-naphthyl	Me (**2a**)	3i	12	-	90
10	1-naphthyl	Me (**2a**)	3j	12	-	91
11	1-pyrene	Me (**2a**)	3k	48	-	92

12	4-Cl-Ph	H (**2b**)	3l	02	35	97
13	2-naphthyl	H (**2b**)	3m	12	-	88
14	Terephthaladehyde	Me (**2a**)	3n	48	-	82

[a]: Aldehydes **1** (0.02 mmol), cyclic 1,3-diketones **2** (0.04 mmol), catalyst **A** (5 mol%), water (1 mL), r.t. stirring. [b]: Crude yields determined from ^{1}H NMR based on starting materials.

Table 3. Barrel "**A**" Catalyzed Snthesis of Xanthenes at High Temperature[a]



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Entry	Ar (1)	R	Product (4)	Time (in h)	Product (% Yields)[b]	
					without **A**	with **A**
1	Ph	Me(**2a**)	4a	02	-	99
2	4-Me-Ph	Me(**2a**)	4b	02	-	99
3	3-OMe-Ph	Me(**2a**)	4c	02	-	96
4	4-Br-Ph	Me (**2a**)	4d	02	-	98
5	2,4-$(Cl)_2$-Ph	Me(**2a**)	4e	02	-	97
6	3-Br-Ph	Me(**2a**)	4f	02	-	99
7	4-CF_3-Ph	Me(**2a**)	4g	02	-	98
8	Py-4-al	Me(**2a**)	4h	02	-	99
9	2-naphthyl	Me(**2a**)	4i	12	-	90
10	1-naphthyl	Me(**2a**)	4j	12	-	91
11	1-pyrene	Me(**2a**)	4k	48	-	88
12	4-Cl-Ph	H (**2b**)	4l	02	-	97
13	2-naphthyl	H (**2b**)	4m	12	-	89
14	1-naphthyl	H (**2b**)	4n	12	-	87
15	1-pyrene	H (2b)	4o	48	-	86
16	Terephthalaldehyde	Me (**2a**)	4p	48	-	85

[a]: Aldehydes **1** (0.02 mmol), cyclic 1,3-diketones **2** (0.04 mmol), catalyst **A** (5 mol%), water (1 mL), stirring and heating at 60 °C. [b]: Crude yields determined from ^{1}H NMR based on starting materials.

The efficiency of these processes was extra stretched to exhibit the double multicomponent processes by utilizing *bis*-1,4-aldehyde in an analogous manner to furnish the respective *bis*-systems (Table 3). This reaction efficiently resulted in the formation of six chemical bonds (4 C–C, 2 C–O) and two 4*H*-pyran units in a single operation.

All the compounds were obtained with high purity by simple filtration as evident for ^{1}H NMR spectra and column chromatography was not obligatory. The structures of compounds **3k** (CCDC 1550025) and **4j** (CCDC 1550023) were clearly determined using X-ray crystallography (Figures S23-24, Supporting Information). The most striking observation arose when 9-anthraldehyde was employed. No progress was witnessed beyond Knoevenagel condensation even after 7 days, probably because of steric reasons (Figure S25, CCDC 1550024 Supporting Information). Furthermore, under similar reaction conditions, in absence of the cage the dehydration reactions afforded poor or no yield of the non-cyclized tetraketones or cyclized xanthenes. This essentially reflects the role of hydrophobic confined space of the barrel in endorsing such unfavorable dehydration reactions in water. It is pertinent to mention that in case of the intermediate tetraketone synthesis, the poor background reaction in absence of catalyst for smaller mono benzene substituted aldehydes can be attributed to their partial solubility in water.

The recyclability of **A** was also examined in the model reaction of **1i** and **2a**. After extraction of the reaction mixture with $CDCl_3$, the addition of further aliquots of **1i** and **2a** showed that the substrate continues to react just as fast as the first cycle of the experiment, for at least four times without much loss of catalytic activity (Figure S26, Supporting Information). The recycled catalyst was characterized by IR, ESI-MS spectroscopy (Figure S27-28, Supporting Information). After abstraction of the product in $CDCl_3$, the NMR spectra showed no trace of **L**, which indicated that the **A** was not collapsed or decomposed during the reaction.

A plausible reaction cascade for the catalytic cycle is shown in Figure 3. The reaction commences with the encapsulation of the aromatic aldehyde **1** within the hydrophobic cavity of the cage (Step I). 5,5-dimethylcyclohexane-1,3-dione **2a**, which is water soluble exists in equilibrium with its enolate form (**a**) due to its low pKa (4.34).[35] Compound **a** reacts with the encapsulated aldehyde to generate oxyanion intermediate followed by rapid loss of water to generate Knoevenagel product **b** [Step II]. Again, the reaction of a subsequent molecule of **a** with **b** generates another oxyanion intermediate. This intermediate takes a proton from water to afford the non-cyclized product **3** [Step III]. The product **3** being too large to be fully encapsulated in the cavity came out of the cage [Step IV] and finally precipitated during the course of the reaction at room temperature. However, when the reaction is performed at higher temperature (60 °C), the intermediate **3** acquires sufficient activation energy to allow the prompt exclusion of water before parting the cage. This dehydration is further aided by the hydrophobic cavity of **A** to generate the dehydrated product **4** [Step V]. Owing to the bulky nature of the product, it spontaneously comes out of the cage that results in the completion of the catalytic transformation [Step VI]. We hypothesized that the anionic intermediates are stabilized by the Pd^{2+} centers located at every portal of the cage. In order to garner further mechanistic insights as well as to

determine that dehydration in Step V is facilitated inside the hydrophobic cavity, further control experiments were conducted. When the empty cage **A** was externally treated with diol **3i**, no trace of **4i** was formed even after 48 h of stirring at 60 °C. Also when **B** was externally treated with diol **3i** and stirred at room temperature for 48 h no encapsulated diol was found inside **B** in ^{1}H NMR. But when in situ reaction was performed with aldehyde **1i**, **2a** and **A** at r.t., the presence of traces of diol **3** in the resulting aqueous solution indicates its encapsulation inside the cage (Figure S29-S31, Supporting Information). These attested that (i) at r.t. once **3** is formed, it steps out of the cage and becomes benchtop stable; no hydrophobic abetted dehydration takes place, (ii) when

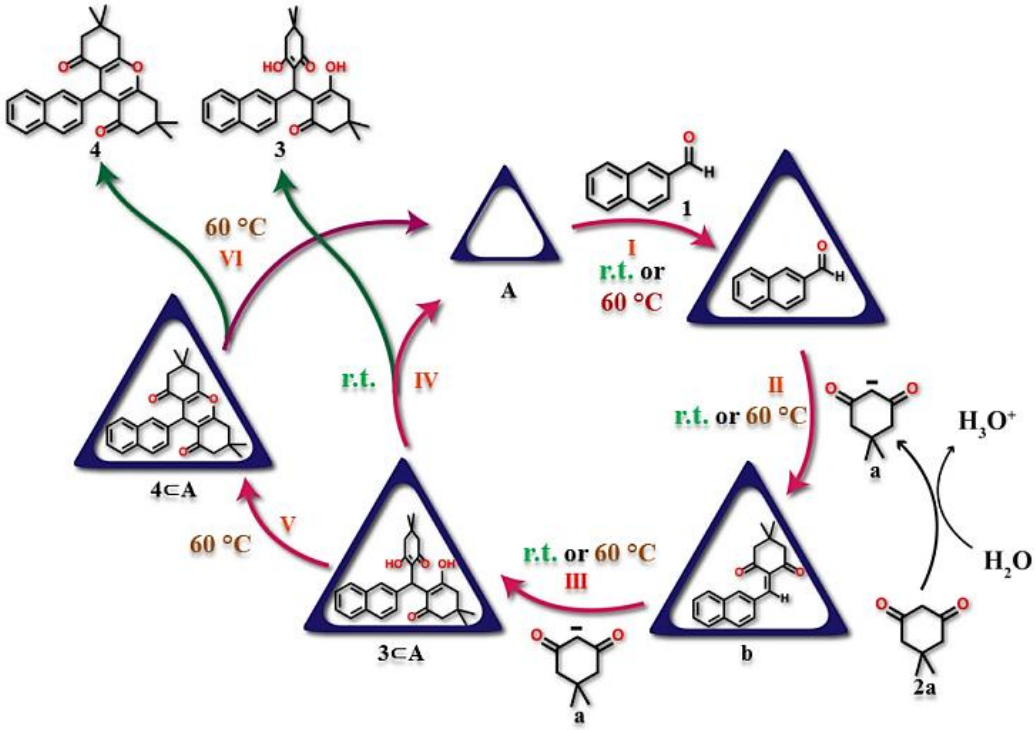

Figure 3. Probable catalytic cycle for the dehydration reactions in the presence of **A**.

reaction is carried out at 60 °C, dehydration occurs prior to exclusion of in-situ synthesized diol leading to cyclized product and (iii) that the reaction pathway leading to **4** is possible inside the cavity of **A**.

Photophysical Studies of Trigonal Barrel A

Tetraphenylethylene (TPE) is an iconic AIE fluorophore in which, restricted phenyl-ring rotation and ethylenic C=C bond twist on aggregation in the condensed state induce its fluorescence.[36] Recent studies revealed that the aggregation of TPE chromophores is not the only way to "*turn on*" the emission; these conformational changes can be accomplished by other strategies such as covalent modifications,[37] host–guest chemistry,[38] coordination,[39] hydrogen bonding,[40] π–π stacking,[41] electrostatic interactions[42] and embedding into metal–organic frameworks.[43] Although many interesting results have been reported in the field of TPE-based MOFs, in our view the area of light-emitting metal–organic materials based on SCC platforms is still in a premature stage. SCCs preserve the attractive features of MOFs, yet also afford circumvention of synthetic steps,[1a] inherent error-correction,[1d] and defect-free assembly,[1e] facile and fast formation,[2f] increased solubility. These facilitate solution-based characterizations owing to their discrete nature.[2h,44]

Our investigations into this field inaugurated with the correct selection of solvent mixtures (good solvent/poor solvent), as the duo solvent played an imperative role in observing the AIE effect. Lots of efforts were therefore made in the early stage, probing for an appropriate solvent system, and finally, acetonitrile (ACN)/water was selected as the best solvent system for such supramolecular aggregation. To this end, we prepared the hexafluorophosphate analogue of the barrel after anion exchange with PF_6^- salt [**A**(PF_6^-)] which was soluble in acetonitrile. This assembly was characterized by ^{1}H NMR spectroscopy (Figure S32, Supporting Information), DOSY (Figure S33, Supporting Information) and ESI-MS (Figure S5, Supporting Information).

The absorption spectra of **L** and cage [**A**(PF_6^-)] in acetonitrile are shown in Figures S34 and S35 (Supporting Information). **L** displayed broad absorption bands centered at 267 and 320 nm with a molar absorption coefficient (ε) of 2.16 × 10^4 M^{-1} cm^{-1} and 1.03 × 10^4 M^{-1} cm^{-1}, respectively. Upon the formation of

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metallacage [**A**(PF_6^-)], the lowest energy band marginally red-shifted (ca. 5 nm). [**A**(PF_6^-)] exhibits two absorption bands centered at 290 and 325 nm with (ε) = 3.82 × 10^4 and 2.72 × 10^4 M^{-1} cm^{-1}, respectively.

Ligand **L** is weakly emissive at ca. 395 nm in ACN (Figure 4) because of non-radiative decay. However, immobilizing the weakly emissive TPE ligand within a SCC platform causes partial rigidification and stemming of the motions of the phenyl rings in [**A**(PF_6^-)] inducing some fluorescence enhancements. The emission maximum of [**A**(PF_6^-)] underwent a moderate red shift from 395 to 470 nm in ACN at room temperature which is manifested due to the melding effect of rigidification from metallacage formation and new metal-to-ligand charge-transfer (MLCT) processes upon coordination.[29b] However, the limited fluorescence enhancement suggests that the TPE units are not sufficiently rigidified to remove non-radiative decay pathways and also the presence of palladium centers may cause an emission quenching, due to their heavy atom effects. Notably, [**A**(PF_6^-)] showed 5.12-fold fluorescence enhancement over **L**. To examine whether [**A**(PF_6^-)] is still AIE alive, the emission spectra in ACN/H_2O solutions was recorded. The emission intensity remained low in mixed solutions with water content less than 80%. However, upon further increment to 90%, the fluorescence intensity abruptly increased (Figure 5). At 95% water fraction, the emission intensity was approximately 5.45-fold higher than that of its molecularly dispersed species in ACN (Figure S37, Supporting Information). Meanwhile, its emission maximum underwent a ca. 25 nm red shift which is ascribed to the charge-transfer (CT) process within the assemblies in a polar solution.[45]

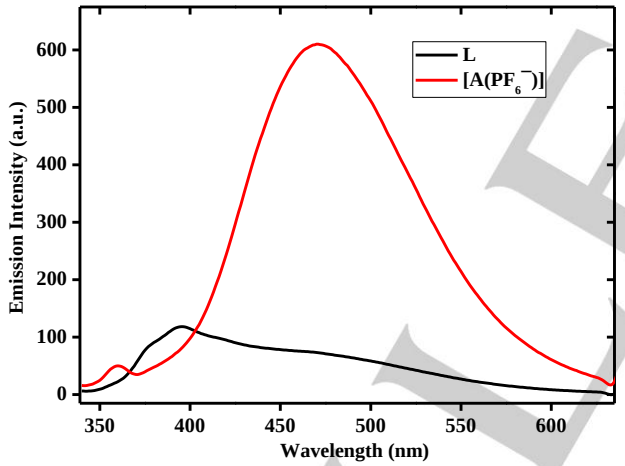

Figure 4. Fluorescence emission spectra of **L** (λ_{ex} = 320 nm, c = 10.00 μM) and [**A**(PF_6^-)] in ACN (λ_{ex} = 325 nm, c = 10.00 μM).

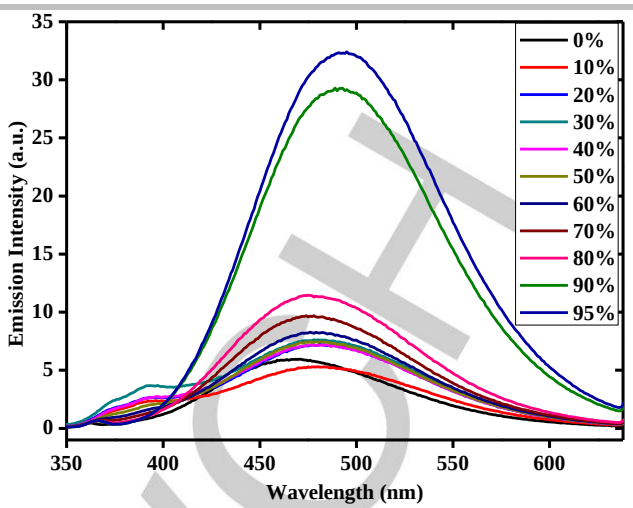

Figure 5. Fluorescence emission spectra of [**A**(PF_6^-)] versus water fraction in ACN/H_2O mixtures (λ_{ex} = 325 nm, c = 10.00 μM).

The AIE characteristics of [**A**(PF_6^-)] in mixed solutions were further probed by changes in quantum yields (Φ_F) using quinine sulfate as a reference. In ACN, relatively low Φ_F values were determined for **L** (0.02%) which increased to 0.2% for [**A**(PF_6^-)] in ACN and further enhanced to 1.56% at 95% water fraction.

The solid-state normalized absorption and emission spectra of **L** and [**A**(PF_6^-)] are shown in Figures S38 and S39, respectively. **L** displayed broad absorption bands centered at 280 and 335 nm. The fluorescence peak observed for solid **L** is likely to be red-shifted (ca. 5 nm) which is attributed to the formation of excimeric species.[43c] Likewise, [**A**(PF_6^-)] exhibited a broad absorption band centered at 400 nm which is moderately red-shifted ca. 75 nm compared to the lowest energy band. However, [**A**(PF_6^-)] fluoresces in the solid state with a band centered at 507 nm (ca. 37 nm red-shifted with respect to dilute solution). The solid-state quantum yield of [**A**(PF_6^-)] was measured to be 2.72% which was higher than that determined for the 95% water fractions (1.56%), consistent with an AIE mechanism. In spite of the low quantum yield value, keeping in mind the strong fluorescence quenching effect of Pd^{2+} ion, it is worth mentioning.

The solvent effects on the emission profiles were also examined. Because of the CT processes within the assemblies, increasing the polarity of the solvent resulted in a quite regular red shift in the emission maximum.[45] The absorption and emission profiles for [**A**(PF_6^-)] in diverse solvents can be found in Supporting Information (Figures S40 and S41). Again, the homogenous nature of the 'solutions' proposed that the aggregates are of nano-dimensions. Consequently, TEM investigation was conducted to provide further insight into the size, shape and morphology of the obtained aggregates. In mixtures with low water content (30%), [**A**(PF_6^-)] self-assembles into irregular nanoparticles. When the water content becomes moderate (50%), it forms regular nanospheres. Such regular nanospheres were further gathered to form bead-like structures at 70% and converted into cross-linking bead microstructures at higher water contents (90%, Figures S42a–d). DLS experiments were performed further to investigate the aggregation process. As shown in Figure S43, when the water content increased from 30 to 70%, the average hydrodynamic diameters (Dh) exhibited a gradual increase from 118 to 1126 nm, which indicated a

gradual aggregation process. At higher water contents, visible particles became dispersed in the ACN/H_2O mixture, which renders the system unsuitable for DLS measurements.

CONCLUSIONS

This article reports the synthesis of a water-soluble Pd^{II}_6 trigonal prism *via* coordination-driven self-assembly without using any template. The barrel was fully characterized by X-ray and other spectroscopic techniques. The confined nanospace of the barrel was successfully used as a molecular vessel for the synthesis of a series of xanthenes via dehydration reaction in aqueous medium under mild reaction condition without using any external catalysts/additives. Such kind of xanthene synthesis generally proceeds via tetraketone intermediates followed by in-situ dehydration at high temperature in anhydrous medium. Our present approach provides a pavement for selective isolation of both cyclized xanthenes and their corresponding non-cyclized intermediates just by mere changing of reaction temperature. While dehydration reactions are generally performed in anhydrous condition, the present approach of using hydrophobic pocket as molecular vessel to perform dehydration reaction in aqueous medium under mild reaction condition is quite interesting. Moreover, the nano-confinement effect in promoting the otherwise unfavorable dehydration reactions in water was reflected from the poor or no yield of the dehydrated cyclized xanthenes or non-cyclized tetraketones in absence of the cage under similar reaction conditions. Due to the presence of AIE active TPE moiety, the hexafluorophosphate salt of the molecular barrel **A** showed aggregation induced emission enhancement in acetonitrile upon addition of water. Surprisingly, the nitrate analogue of the same barrel is soluble in water and didn't show any AIE activity.

EXPERIMENTAL SECTION

Materials and Methods

All the reagents were purchased from different commercial sources and used without further purification. NMR (1D and 2D) spectra were recorded on Bruker 400 MHz spectrometer and the chemical shifts (δ) in the ^{1}H NMR spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as an internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the solvents $CDCl_3$ (7.26 ppm) and D_2O (4.79 ppm). Electrospray ionization mass spectrometry (ESI-MS) experiments were carried out on a Bruker Daltonics (Esquire 300 Plus ESI model) spectrometer using standard spectroscopic-grade solvents. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. Analab μ–ThermoCal10 instrument was used for melting point determinatuin. UV-Visible and fluorescence spectra were recorded in Perkin Elmer Lambda-750 and Horiba Jobin Yvon fluoromax4 spectrophotometers, respectively. Quinine sulfate in 0.1 M H_2SO_4 was used to determine the experimental quantum yields at an excitation wavelength of 365 nm with $\Phi = 0.56$ for all assemblies. The quantum yield measurements were performed in multiplicates with values that were within 10 % error being averaged. The absolute fluorescence quantum yields were measured by Quanta-f Horiba instrument. Transmission electron microscopy was performed on a JEOL JEM-2100F instrument operating at 200 kV Dynamic light scattering (DLS) measurements were performed on the zetaseizer instrument ZEN3600 (Malvern, UK) with a 1738 back scattering angle and He-Ne laser (l=633 nm).

Synthesis of A.

cis-(tmen)$Pd(NO_3)_2$ (M) (34.8 mg, 0.10 mmol) was dissolved in 3 mL H_2O and the yellow clear solution was added to the solid ligand **L** (30.0 mg, 0.050 mmol) and was heated at 50 °C with stirring for 6 h. The solution turned colorless with the consumption of the donor. After the completion of the reaction, the mixture was filtered, concentrated under reduced pressure, and the pure form of complex **A** was obtained as off-white powder by trituration with acetone (Isolated yield: 55.1 mg, 85%). ^{1}H NMR (400 MHz, D_2O): δ = 8.64 (12H, s, H_1), 7.52 (24H, d, J=17.2 Hz, H_2 and H_3), 7.27 (48H, s, H_4 and H_5), 3.09 (24H, s, CH_2), 2.74 (72H, s, CH_3). IR $\tilde{\upsilon}$: 3414, 3242, 3115, 2908, 2358, 1632, 1523, 1470, 1327, 1272, 1127, 1067, 1041, 1005, 958, 807, 760, 656, 514 cm^{-1}. ESI-MS (m/z): 1476.66 $[\mathbf{A}(PF_6)_9]^{3+}$, 1071.26 $[\mathbf{A}(PF_6)_8]^{4+}$ and 828.21 $[\mathbf{A}(PF_6)_7]^{5+}$.

General procedure for the synthesis of non-cyclized intermediate Tetraone system (3a-3n):

Aldehyde **1** (0.02 mmol) and cyclic 1,3-diketones **2** (0.04 mmol) were added to 1 mL aqueous solution of 5 mol% of catalyst **A** and the reaction mixture was stirred at r.t. for respective time periods (Table 2). The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction (monitored by disappearance of the starting material in the TLC), the reaction mixture was extracted with chloroform. The solvents were evaporated in a rotary evaporator and the products were characterized by standard analytical techniques such as (^{1}H & ^{13}C) NMR, FTIR, melting point determination, ESI-MS, X-ray crystallographic analysis and all gave satisfactory results (Supporting Information).

General procedure for the synthesis of cyclized Xanthene system (4a-4o):

Aldehyde **1** (0.02 mmol) and cyclic 1,3-diketones **2** (0.04 mmol) were added to 1 mL aqueous solution of 5 mol% of catalyst **A** and the reaction mixture was heated at 60 °C for respective time periods (Table 3). The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction (monitored by disappearance of the starting material in the TLC), the reaction mixture was extracted with chloroform. The solvents were evaporated in a rotary evaporator and the products were characterized by standard analytical techniques such as (^{1}H & ^{13}C) NMR, FTIR, melting point determination, ESI-MS, X-ray crystallographic analysis and all gave satisfactory results (Supporting Information).

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Keywords: Self-assembly • Supramolecular • Coordination architectures • Cage compounds • Palladium(II)

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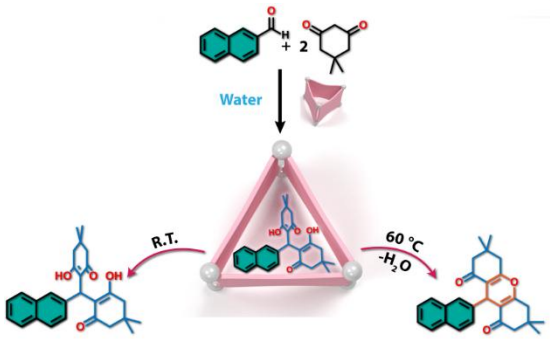

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A Self-Assembled Trigonal Prismatic Molecular Vessel for Catalytic Dehydration Reactions in Water

Layout 2:

FULL PAPER

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