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Building Block Dependent Morphology Modulation of Cage Nanoparticles and Recognition of Nitroaromatics

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Abstract: Morphology of nanomaterials has a high impact on their chemical/physical properties, while controlled synthesis of such materials with desirable morphology is a grand challenge. This article presents the role of a building block on the morphology of organic cage particles. In this context, three organic cages (A_3X_2, B_3X_2) and C_3X_2) have been devised from triphenylamine based dialdehydes and a flexible triamine (X) utilizing dynamic imine chemistry. All the synthesized cages have been characterized by various spectroscopic techniques, which suggested the formation of [3+2] assembled architectures. Though the cages are isostructural, structural variation in the aldehyde building blocks imparted by the incorporation of phenyl moieties into the triphenylamine core produces morphologically diverse cage particles as indicated by scanning electron microscopy. The synthesized cages have been found to be fluorescent; the reduced analog $(A_3X_2^r)$ of cage A_3X_2 has been tested to explore the use of this material as chemosensor for the detection of nitroaromatic explosives. Experimental findings suggest high selectivity and sensitivity of the cage compound (A₃X₂^r) towards picric acid (PA) among the various nitroaromatics tested. A theoretical investigation on fluorescence quenching has been carried out which suggests that the ground-state charge transfer complex formation along with resonance energy transfer (RET) process could be the main reason behind such selectivity of the cage towards PA.

Introduction

Discrete three-dimensional (3D) nano-architectures due to their structural aesthetics and wide applications in catalysis, sensing, gas storage/separation have long been a subject of great interest among the scientific community around the globe.^[1] To this end, the main focus has been paid to metal-ligand assemblies where design principle is solely relying on directional nature of coordination bond to articulate metal centers with appropriate organic spacers.^[2] Conversely, construction of analogous architectures utilizing traditional covalent synthesis involves a tedious multistep process which generally leads to a low yield of the desired product.^[3] However, the advent of the *dynamic covalent chemistry*^[4] in recent years has provided us easy

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synthetic access to such architectures from simple building blocks. In this context imine based architectures have been most extensively investigated considering the truly reversible nature of the imine bonds, which allows 'proof reading' and 'error checking' processes to achieve thermodynamically most stable assembly. ^[5] Our group has recently demonstrated that such dynamic nature of imine bonds allows self-sorting/self-selection process in organic cage formation.^[6]

On the other hand, controlling morphology is one of the key strategies to modulate chemical/physical properties of nanomaterials. A number of studies on semiconductors have suggested that morphology of such materials determines optoelectronic properties, photo energy conversion efficiency, photocatalytic activity, band gap etc.[7] It has been found that simple tuning of the morphology of the co-ordination polymeric nanomaterials brings a dramatic change in their gas adsorption property.^[8] Accordingly, several chemical/physical methodologies like sol-gel process, micelles, chemical precipitation, vapor deposition, hydrothermal synthesis etc. have been developed in recent times to tune the structural features of nanomaterials.^[9] Despite of substantial progress in this direction, the controlled synthesis of nanomaterials with desirable morphology is still a challenging task; while for organic cages such studies are in infancy. Recently Mastalerz and coworkers have shown the importance of reaction condition and the role of solvents on formation of nano-spheres of organic cages.^[10] Cooper and coworkers suggested that steric congestion on cage vertices has a direct influence on their solid-state packing, that further alters void volumes.^[11] Therefore, it could be anticipated that simple tuning of the building blocks (aldehyde or amine) may generate different fascinating nanostructures of the cage compounds. At this juncture, herein, we first report the building block dependent tuning of the morphology of organic cage particles. In this context three structurally similar [3+2] condensed imine architectures have been synthesized via Schiff-base condensation of triphenylamine based dialdehydes (A, B and C) and a flexible triamine X; and their morphology has been investigated by scanning electron microcopy. Apart from morphological tuning of cage particles the reduced analogue of the cage A₃X₂ has been utilized for the detection of nitroaromatics.

Results and Discussion

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Scheme 1. Synthetic routes of aldehyde building blocks (a) B, (b) C and (c) [3+2] condensed imine cages.

Cage particles synthesis and characterization: All the cages were prepared adopting the typical synthetic methodology, which involves Schiff-base condensation between the flexible triamine [X= tris(2-aminoethyl)amine] and a dialdehyde (A or B or C). It is worth-mentioning here that Cooper and coworkers earlier obtained cage A_3X_2 by employing a different synthetic methodology.^[12] Aldehyde B was obtained through Suzuki coupling reaction between 4,4'-diformyl-4"-bromotriphenylamine (1) and phenylboronic acid (2). To obtain aldehyde C, Suzuki coupling between 4,4'-dibromotriphenylamine (3) and 4-formylphenylboronic (4) acid was carried out (Scheme 1). Assynthesized cage materials were characterized by multinuclear NMR (¹H, ¹³C), FTIR and ESI/MALDI-MS analyses. Mass-spectrometric analysis unambiguously suggested the formation of [3+2] condensed cages.

We were interested in understanding the role of building block especially the aldehyde on the morphology of such covalent cages. In this context, after synthesis and characterization of the cages, they were re-dissolved in chloroform and slowly precipitated out by adding *n*-pentane onto it to obtain the desired cage particles. As synthesized cage particles were drop-casted onto a carbon tape and dried overnight before scanning electron microscopic (SEM) analysis. Following this strategy, at first, we analyzed the morphology of cage A_3X_2 particles, which showed the formation of '*flower*' like particles (Figure 1a).

Interesting to note that no other morphologies was detected, which indicates high uniformity of the product. In-depth investigation of the structure suggests that the entire architecture consists of several nano-petals, which are connected to each other through the center. To our surprise, in the case of cage B_3X_2 a completely different picture was observed (Figure 1b). SEM analysis suggests the formation of agglomerated spherical particles, having a smooth surface. On the other hand, cage C_3X_2 generates block shaped crystalline particles (Figures 1c and S15) with sharp edges.

A closer inspection into this matter suggests that the structural variation (shape and size) in the aldehyde building block is responsible for the change in morphologies. For instance, the structural difference between aldehydes **A** and **B** arises due to *para*- substitution of phenyl moiety onto the bare phenyl ring of the aldehyde **A**. In the case of aldehyde **C**, two arms containing formyl moieties of aldehyde **A** have further been extended by incorporating two phenyl moieties between the core triphenylamine unit and aldehyde groups. We believe that such variation in π -electron cloud brings difference in non-covalent interactions (especially π - π , C-H... π interactions) during the

formation of cage particles (or precipitation), which is manifested in their morphologies.



Figure 1. SEM images of cage particles (a) A_3X_2 , (b) B_3X_2 , (c) C_3X_2 and aldehydes (d) A, (e) B and (f) C.

X-ray crystal structure of aldehyde A suggests the formation of an infinite 3D network via weak C-H...O interactions between the phenyl rings of adjacent molecules, whereas no evidence of π - π and/or C-H...π interactions have been observed.^[13] In contrast, the incorporation of two more phenyl rings into the core triphenylamine moiety provides strong 'parallel-displaced' πstacking between the two adjacent phenyl rings, where the interplanar distance between two parallel rings is ~3.4 Å and the distance between the ring centroids is ~3.9 Å, leading to the formation of layer structure, as observed in the X-ray crystal structure of aldehyde C (Figure S16). Similarly, X-ray crystal structure of the cage A_3X_2 revealed crystal packing without any involvement of π -cloud in the non-covalent interactions,^[12] whereas the crystal structure of the cage C_3X_2 showed the presence of C-H... m interactions between phenyl rings of two adjacent molecules (Figure 2). Therefore, it is guite evident that the mode of interaction/s between cage molecules can be tuned by modulating π -cloud of building blocks. We anticipated that signature of such changes in the mode of noncovalent interaction could be observed in the morphology of the aldehyde building blocks. Therefore, to get a further insight into the matter, the morphologies of aldehyde building blocks were investigated. Following the same synthetic strategy as adopted for the cage particles synthesis, all the aldehydes' particles were synthesized. As anticipated, a considerable difference in their morphology was observed in SEM analysis (Figures 1d-1f). Moreover, it could be seen that there is a visible similarity in morphological features of the cage particles with their corresponding aldehyde building blocks (Figure 1). These experimental results undoubtedly

indicate the role of structural features of the building block on the cage morphology.



Figure 2. (a) Ball and stick diagram of the X-ray crystal structure of cage C_3X_2 and (b) intermolecular C-H... π interaction between two adjacent cage molecules.

Detection of nitroaromatics: Cheap and easy accessibility of nitroaromatic compounds (NACs) make them as one of the common constituents of landmines.^[14] Chemical explosives are known to undergo very rapid exothermic reaction with the liberation of gaseous species. NACs are considered as secondary explosives with burning velocity in the order of km s⁻¹. Apart from their use as explosives, NACs are also valuable chemicals in dye industry, pharmaceuticals, agrochemicals and for the manufacture of rocket fuels.^[15] Excessive use of such chemicals can contaminate ground water and soil, leading to health related problems like anemia, skin allergies, abnormal liver function etc.^[16] Hence, for homeland security and to prevent environmental pollution; fast, reliable and accurate detection of NACs is one of the growing global concerns. To this end, several detection techniques based on surface-enhanced Raman spectroscopy. GC-MS, ion-mobility spectroscopy (IMS) and others have been developed for the detection of NACs. Most of such techniques require sophisticated instrumental facilities, which limit their use for in-field testing.^[17] In contrast, fluorescence-based detection technique has been found to be very attractive due to the low-cost portable instruments, fast response times, high sensitivity and specificity.^[18] Last few decades have witnessed the development of several conjugated polymers/oligomers and small-moleculebased fluorescent materials.^[19] In this endeavor, cage compounds as sensory materials for NAC explosives is a very recent development.^[20]

All the three imine cages (A_3X_2, B_3X_2, C_3X_2) were found to be fluorescent in nature, which encouraged us to investigate their potential use as sensory materials. To this end, reduced analog of cage A_3X_2 (imine cages are generally sensitive towards acids or bases) was considered for the detection of NACs. Reduced cage $A_3X_2^r$ was derived from the cage A_3X_2 by sodium borohydride reduction of dynamic imine bonds in a binary solvent mixture EtOH-CHCl₃ (1:1; v/v). The UV/Vis spectrum of $A_3X_2^r$ exhibits an absorption band from 260 to 400, with an absorption maximum at 305 nm. Excitation at 305 nm produces a very high

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Stokes shift of 125 nm to generate an emission band with an emission maximum at 430 nm. This cage compound has been found to be highly fluorescent in nature both in solution (quantum yield; $\Phi_{DCM} = 0.37$) and solid (quantum yield; $\Phi_{S} = 0.18$) states. To investigate its potential use as chemosensor for the detection of NACs, we carried out fluorescence titration of the cage A₃X₂^r with several nitroaromatics such as picric acid (PA), 2,4-dinitrophenol (2,4-DNP), 4-nitrophenol (4-NP), 2,4-dinitrotoluene (2,4-DNT), 3,4-dinitrotoluene (3,4-DNT), 4-nitrotoluene (4-NT), 4nitrobenzoic acid (4-NBA), 3,5-dinitrobenzoic acid (3,5-DNBA), 1,3-dinitrobenzene (1,3-DNB) and nitrobenzene (NB). Interestingly, out of these nitroaromatics, only PA induces substantial quenching.



Figure 3. The change in fluorescence intensity of cage $A_3X_2^r$ in DCM upon gradual addition of PA. Inset shows the visual change in fluorescence of the cage $A_3X_2^r$ solution under UV light upon addition of 2 eq PA.

As portrayed in Figure 3, gradual addition of only 2 eq PA to a 1×10^{-5} M solution of cage $A_3 X_2^r$ in DCM attenuated 98 % of initial fluorescence intensity. In contrast, other nitroaromatics especially non-nitrophenolic compounds induced a negligible effect on the fluorescence intensity of the cage (Figure 4). This result clearly suggests very high selectivity and sensitivity of cage $A_3 X_2^r$ towards PA compare to the other nitroaromatics.



Figure 4. Fluorescence quenching efficiencies of different nitroaromatic analytes towards $A_3 X_2^r$.

The relative intensity against the concentration of PA was plotted to estimate the quenching constant. Notably in the presence of PA Stern-Volmer plot bends upward (Figure 5) rather than being linear, a typical signature of quenching through static or static in combination of a dynamic pathway.^[21] In this context, it is important to note that dynamic quenching operates through the diffusion controlled collision between the excited fluorophore and the quencher, when the following linear equations could be applied.^[22]



Figure 5. I_0/I of the cage $A_3X_2^r$ versus concentration of PA in DCM.

Here I₀ and I stand for the fluorescence intensities, whereas τ_0 and τ represent the lifetime of the fluorophore before and after the addition of the quencher Q, respectively. kq is the rate constant for the diffusion controlled bimolecular quenching reaction, whereas $\tau_0 k_q$ is equal to the dynamic quenching constant K_D.

On the other hand, static quenching could be explained either by a sphere of effective quenching model [Eq. (3)] or by a ground state non-fluorescent complex model [Eq. (4)]

$I_0/I = e^{Vq[Q]}$	(3)
$I_0/I = K_s[Q] + 1$	(4)

Here, static quenching constants in the effective sphere and complex models are denoted as V_q and K_s, respectively. When the concentration of the quencher is low, $e^{Vq[Q]}\approx V_q[Q] + 1$, and thus eqn 4 can be considered as an approximation of equation 3. Furthermore, for simultaneous static and dynamic quenching equations 5 and 6 could be derived.

 $I_0/I = (K_D [Q] + 1) e^{Vq[Q]}$ $I_0/I = (K_D [Q] + 1) (K_s [Q] + 1)$ (5) (6)

It is worth mentioning here that the dynamic quenching is associated with the decrease in fluorescence lifetime of the fluorophore in the presence of quencher, whereas fluorescence lifetime remains unchanged in static mechanism due to the formation of the non-fluorescent complex or a *dark state* between the fluorophore and the quencher, where unbound fluorophore displays their lifetime. In order to investigate the involvement of

dynamic mechanism in quenching process lifetime measurement (Figure S17) of the cage compound in presence of PA was carried out, which indicated that the quenching process operates in a static pathway. Therefore, equation (3) or (4) is more applicable for this system. In order to estimate the quenching constant associated with PA we applied a more convenient exponential quenching equation $I_0/I = Ae^{K[Q]} + B^{[21]}$ Thus from this nonlinear curve fitting the quenching constant corresponding to PA was found to be 2.6×10^5 M⁻¹, which is markedly higher than other nitroaromatic compounds. Such a high value of quenching constant associated with PA is the manifestation of strong interaction between the cage and PA.

PA is known to have the highest acidity among the nitrophenols due to the presence of maximum number of electron withdrawing nitro groups. Thus it can easily transfer its acidic -OH proton to any basic functional group to form a strong acid-base adduct. Therefore, it is quite expected that the cage compound $A_3X_2^r$ with 2° amine groups can form a strong ion pair with PA (protonated cage and picrate), which is supported by the change in ¹H NMR spectral pattern of the cage in presence of PA (Figure S18). Perturbation in UV-Vis spectral pattern of $A_3X_2^r$ with a new band at ~ 420 nm in the presence of PA is in good agreement with this fact (Figure S19). Moreover, there was a distinct colour change observed from colourless to pale yellow upon addition of PA to the solution of $A_3X_2^r$ (Figure S20). We did not notice any such changes in the cage solution in the presence of other nitroaromatics. These experimental results undoubtedly indicate the stronger interaction between PA and the cage in comparison to the other nitroaromatics.

Unlike previous reports, gas phase DFT calculations reveal no possibility of electron transfer between the protonated cage and free picrate based on the energy level diagram of molecular orbitals (MOs) (Figure S21). Therefore, to understand the observed new bands in UV- Vis spectrum above 350 nm, we carried out TD-DFT (B3LYP/6-31G) calculation on protonated cage-picrate complex in PCM model using DCM as a solvent (Figure 6).

Calculated UV-Vis spectrum correlates quite well with the experimental spectrum, having absorption maxima at 298 nm in comparison to experimental 305 nm (Figure 6b). TD-DFT calculation further suggests that bands at 360 nm and 420 nm are the result of electronic transitions from HOMO-9 to LUMO+2, HOMO-10 to LUMO+1 and HOMO-10 to LUMO. It is worth mentioning here that only HOMO-9 orbital is localized on protonated cage, while HOMO-10, LUMO, LUMO+1, LUMO+2 orbitals correspond to picrate (Figure 7). Thus bands above 350 nm are a combination of charge transfer band of the protonated cage-picrate complex as well as due to absorption of picrate. However, the high sensitivity of the cage towards PA suggests that ground-state charge transfer complex formation may not be the only reason behind the fluorescence quenching.

Fluorescence quenching through non-radiative energy transfer from excited fluorophore to the quencher, known as excitation energy transfer (EET) and resonance energy transfer (RET) are well-known quenching processes.^[23] The key requirement for such a process to occur is the spectral overlap between the emission spectrum of the fluorophore and the absorption spectrum of the quencher, whereas higher spectral overlap leads to a better quenching.



Figure 6. (a) DFT (B3LYP, 6-31G) optimized structure of the protonated $A_3X_2^{r-}$ picrate complex in DCM and **(b)** experimental absorption spectrum (curve line) with TD-DFT calculated absorption spectrum (vertical lines) of the complex.



Figure 7. Frontier molecular orbitals of $A_3X_2{\rm r}\mbox{-}{\rm PA}$ complex involve in the absorption bands above 350 nm.

To investigate these issues UV-Vis spectra of nitroaromatics and the emission spectrum of the cage were monitored, which did not indicate any significant overlap (Figure S22) and thus ruled out the possibility of energy transfer process. However, as mentioned earlier that PA exists as picrate in solution in presence of the cage compound, the emission spectrum of the cage and the absorption spectrum of picrate (PA+triethylamine) were investigated (Figure S23). Experimental outcome indicated a large spectral overlap, indicating the high possibility of energy transfer from protonated cage to picrate, which is further facilitated by the close proximity due to ion pair formation.

Recently, based on theoretical calculations Jelfs and coworkers have postulated that the high selectivity of the amine based cage compounds towards PA is due to encapsulation of picrate to form stable host-guest complex, where fluorescence guenching is due to photo-induce electron transfer (PET) process.^[24] They also believe that the amine cage is not enough strong base to deprotonate PA without the extra stabilization through electrostatic interaction between the protonated cage and the encapsulated picrate. However, our experimental result (¹H NMR) does not indicate such encapsulation of picrate, as no chemical shift in NMR spectrum of picrate was observed (Figure S18). Earlier Ghosh and coworkers reported similar cage-picrate complex, in which picrate is laying outside the cage cavity and strongly attached to the protonated cage through electrostatic interaction. [25] Therefore, in the present scenario PA is believed to quench the fluorescence of the cage through a ground state charge transfer and EET/RET process.

For practical application especially in forensic and analytical sciences, contact mode analysis is a very useful detection technique. In this context solution of PA was spotted onto a Whatmann filter paper strip coated with cage $A_3X_2^r$, which left a dark spot under a portable UV lamp. Moreover, black patches could be observed under UV-light after rubbing a small amount of solid PA sample onto the filter paper strip. These experimental results indicate reasonable sensitivity of the cage towards PA both in solid and in solution.

Conclusions

In summary, three structurally analogous [3+2] assembled iminebased organic cages (A₃X₂, B₃X₂ and C₃X₂) were synthesized using dynamic imine chemistry and characterized by various spectroscopic techniques. The synthesized cages were designed from triphenylamine based aldehydes, where small variation in shape and size of the aldehyde building blocks was achieved through incorporation of phenyl moieties onto the triphenylamine core. Such structural variation of the building blocks has been found to have significant role on the morphology of the cage particles, indicated by the scanning electron microscopic analysis. Our present observation on the change in morphology of organic cage nanoparticles by simple tuning the building blocks is quite interesting. Crystal structure analysis of the aldehyde C and cage C_3X_2 indicated that increase in π -electron density by increasing the number of phenyl rings in the building block modulates the mode of noncovalent interaction through $\pi...\pi$ or C-H... π interactions between the adjacent molecules. Such non-covalent interactions could be the key reason behind the change in morphology during the particles formation.

The synthesized cages were found to be highly fluorescent in nature due to the presence of triphenylamine moiety. Therefore, to explore the potential use of these materials to detect nitroaromatics, reduced analogue of cage A_3X_2 was tested. Experimental results pointed out the high sensitivity and selectivity of this cage material towards PA among the various nitroaromatics tested. Based on the experimental results and theoretical calculations it has been ascertained that the higher quenching ability of the PA is attributed to the stronger interaction with the cage and resonance energy transfer process.

Experimental Section

Materials and Methods: All the chemicals and solvents were procured from commercial sources and were used without further purification. The NMR spectra were recorded on Bruker 400 MHz instrument. 4,4'dibrotriphenylamine and 4,4'-diformyl-4"-bromotriphenylamine were prepared according to the reported procedures. $^{\mbox{\tiny [26]}}$ The chemical shifts (δ) in the ¹H NMR spectra are accounted in ppm relative to tetramethylsilane (Me₄Si) as an internal standard (0.0 ppm) in CDCl₃. High-resolution mass spectra were recorded on a Q-TOF instrument by electrospray ionization (ESI) technique using standard spectroscopic grade solvents. MALDImass spectrum was recorded on a Bruker UltrafleXtreme instrument. Electronic absorption and emission spectra were recorded using a Perkin-Elmer LAMBDA 750 UV-Visible spectrophotometer and a HORIBA JOBIN YVON made Fluoromax-4 spectrometer respectively. The PXRD spectrum was recorded in PANalytical EMPYREAN instrument. IR spectra were recorded on a Bruker ALPHA FTIR spectrometer. Scanning electron microscopy (SEM) was performed on a Carl-Zeiss Ultra 55 at an operating voltage of 5-20 kV.

Aldehyde B: In a 100 mL flame dried double-neck round-bottom flask 565 mg (1.50 mmol) of 4,4'-diformyl-4"-bromotriphenylamine and 366 mg (3.00 mmol) of phenylboronic acid were taken in 50 mL THF and into that 20 mL aqueous solution of 560 mg (4.00 mmol) K₂CO₃ was added. The resulting mixture was stirred under nitrogen atmosphere at room temperature for 10 minutes followed by addition of 90 mg (0.08 mmol) of Pd(PPh₃)₄ and heated to reflux 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 Na₂SO₄. The desired aldehyde was obtained as pale yellow solid after silica gel column chromatography in DCM. Isolated yield: 48% (271 mg, 0.71 mmol). ¹H NMR (CDCI₃, 400MHz): δ 9.91 (s, 2H),7.80 (d, 4H), 7.61(m, 4H), 7.46 (t, 2H), 7.35 (m, 1H), 7.24 (m, 6H); ¹³C NMR (100 MHz, CDCl3): δ 190.9, 152.4, 145.1, 140.4, 139.5, 131.9, 131.8, 129.4, 129.2, 128.1, 127.6, 127.4, 123.4. FTIR (cm⁻¹): v 3031, 2810, 2730, 1685 (CH=O), 1576, 1494, 1430, 1312, 1272, 1211, 1157, 1113, 1007, 819, 760, 727, 696, 667, 561, 520.

Aldehyde C: In a 100 mL flame dried double-neck round-bottom flask 0.81 g (2.00 mmol) of 4,4'-dibromotriphenylamine and 0.69 g (5.00 mmol) of 4-formylphenylboronic acid were taken in 50 mL THF and into that 20 mL aqueous solution of 1.40 g (10.00 mmol) K₂CO₃ 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(PPh₃)₄ and heated to reflux for 36 h. After completion of the reaction, THF was removed and the aqueous part was extracted with dichloromethane (50 mL x 3). Organic part was then dried over Na₂SO₄. The desired aldehyde was obtained as yellow solid after silica gel column chromatography using

DCM-Hexane (4:1, v/v) as eluent. Single crystals of this compound were obtained by slow evaporation of an ethyl acetate solution. Isolated yield: 65 % (590 mg, 1.30 mmol). ¹H NMR (CDCl₃, 400MHz): δ 10.04 (s, 2H), 7.94 (d, 4H), 7.74 (d, 4H), 7.57 (d, 4H), 7.34 (dd, 2H), 7.19-7.23 (m, 6H), 7.13 (t, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 192.3, 148.4, 147.4, 146.9, 135.3, 134.2, 130.8, 130.1, 128.7, 128.5, 127.5,125.9, 124.5. FTIR (cm⁻¹): v 2920, 2852, 1682 (CH=O), 1587, 1519, 1402, 1386, 1319, 1273, 1212, 1170, 1108, 1007, 806, 750, 693, 556.

A₃X₂: Cage A₃X₂ has been synthesized according to a modified synthetic procedure. ^[12] In a 250 mL round bottom flask 50 mL CH₃CN solution of triamine X (102 mg, 0.70 mmol) was added dropwise to a stirring solution of aldehyde A (301 mg, 1.00 mmol) dissolved in 100 mL CH₃CN. The resulting reaction mixture was stirred at room temperature for overnight. During this time period, a pale yellow precipitate was formed, which was filtered and washed with CH₃CN several times. Isolated yield: 70 % (254 mg, 0.23 mmol). ¹H NMR (CDCl₃, 400MHz): δ 7.64 (s, 6H, CH=N), 7.30 (t, 6H), 6.8-7.19 (br m, 33H, ArH), 3.26-3.71(br s, 12H), 2.78 (br s, 12H).¹³C NMR (100 MHz, CDCl₃): δ 161.0, 149.3, 146.9, 131.3, 130.1, 129.5, 127.0, 125.5, 122.7, 60.4, 57.1.

B₃X₂: In a 100 mL round bottom flask 20 mL CHCl₃ solution of triamine X (26 mg, 0.18 mmol) was added slowly to a stirring solution of aldehyde **B** (100 mg, 0.26 mmol) dissolved in 50 mL CHCl₃. The resulting reaction mixture was heated to reflux for 24 h. After the completion of the reaction, the solvent was removed and the solid material was washed with EtOH several times to obtain desired cage compound as yellow solid. Isolated yield: 64 % (73 mg, 0.06 mmol). ¹H NMR (CDCl₃, 400MHz): δ 7.67 (s, 6H, CH=N), 6.9-7.6 (m, 51H, ArH), 3.32-3.60 (br, s, 12H), 2.80 (br, s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 161.0, 149.2, 146.2, 140.6, 138.1, 131.5, 129.6, 129.3, 128.6, 127.7,127.2, 127.0, 123.0, 60.4, 57.2. ESI-HRMS (CHCl₃-CH₃CN): m/z for C₉₀H₈₁N₁₁, [M+H]⁺ 1316. 6894 (calcd 1316.6788), [M+2H]²⁺658.8428 (calcd, 658.8416). FTIR (cm⁻¹): v, 3035, 1684, 1583, 1494, 1310, 1273, 1219, 1161, 1104, 829, 758, 688, 521.

C₃**X**₂: This cage was synthesized from aldehyde **C** (135 mg, 0.30 mmol) and amine **X** (29 mg, 0.20 mmol) following the same synthetic methodology as employed for the cage **B**₃**X**₂. Rod shaped single crystals were obtained within a few days by layering a solution of **X** in ethanol onto a chloroform solution of **C** in a closed glass vial. Isolated yield: 78 % (120 mg, 0.08 mmol). ¹H NMR (CDCl₃, 400MHz): δ 7.62 (s, 6H, CH=N), 7.56 (d, 12H), 7.43 (d, 12H), 7.32 (m,18H), 7.20 (d, 6H), 7.09 (t, 3H), 6.88 (d, 12H), 3.56 (br s, 12H), 2.82 (br s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 161.9, 148.1, 147.6, 143.2, 135.3, 135.2, 130.0, 129.3, 128.5, 127.3, 125.5, 124.8, 60.4, 56.6. MALDI-TOF MS: m/z for C₁₀₈H₉₃N₁₁, [M+H]⁺1544.58 (calcd 1544.76). FTIR (cm⁻¹): v, 3032, 2950, 1684, 1657, 1590, 1478, 1326, 1274, 1170, 813, 740, 690, 519.

A₃**X**₂**r**: In a 100 mL round bottom flask 20 mL EtOH solution of triamine **X** (51 mg, 0.35 mmol) was added slowly to a stirring solution of aldehyde **A** (105 mg, 0.50 mmol) dissolved in 50 mL DCM. The resulting reaction mixture was stirred at room temperature for 24 h. Then into this solution, 227 mg (6.00 mmol) of NaBH₄ was added portion wise and stirred at room temperature for overnight. After completion of the reaction, the solvent was completely removed and onto that water was added. The insoluble material was then filtered out to obtain the desired material as white powder. Isolated yield: 72 % (132 mg, 0.12 mmol). ¹H NMR (CDCl₃, 400MHz): δ 7.10 (t, 6H), 6.92(d, 15H), 6.77 (d, 18H), 3.53 (s, 12H), 2.71 (s, 12H), 2.62 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 148.5, 146.9, 135.1, 129.5, 129.3, 124.7, 124.2, 122.9, 55.5, 54.1, 48.5. ESI-HRMS (CHCl₃-CH₃CN): m/z for C₇₂H₈₁N₁₁, [M+H]⁺ 1100.6564 (calcd 1100.6755), [M+2H]²⁺ 550.8329 (calcd 550. 8416). FTIR (cm⁻¹): v, 2971, 2928, 2848, 1513, 1257, 1091, 1014, 792, 693, 611.

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Method for nitroaromatic detection: For solution state fluorescence experiments 2 mL of $A_3X_2^r$ solution (10⁻⁵ M) was taken in an all transparent quartz cuvette and PA stock (10-3 M) in DCM was added gradually to the medium. The solutions were mixed thoroughly and after each addition change in emission intensity was recorded at room temperature. All the compounds were excited at 305 nm and their corresponding emission was observed. Both the excitation and emission slit widths were kept 2 nm for all the measurements. The Stern-Volmer constants were calculated from steady-state titration experiments by employing the fluorescence emission intensity ratio (I_0/I) as a function of increasing PA concentration. For selectivity test, 120 µL of different NACs solutions of identical strength (10-³ M) were added to the 2 mL cage solution (10⁻⁵ M) independently and the corresponding change in emission intensity was monitored. The fluorescence efficiency was plotted against the PA concentration. The fluorescence lifetime of the sensors was measured by fitting the curve with triple exponential decay profile. For contact mode detection 10 µL 10⁻³ M PA solution was added onto filter paper strip coated with the $A_3X_2^r$ and its effect on test strip was monitored under visible and UV-light. Also 10 mg grinded PA was added on the test strip and rubbed with a thin spatula and the image was recorded under UV-light.

Method of cage particle formation by slow precipitation: The process of slow precipitation was performed at room temperature. To a 1 ml chloroform solution (2 mg/mL) of the samples in a 4 mL glass vial, 2 mL of *n*-pentane was added and was kept overnight to induce ppt. The ppt was collected by centrifugation and was washed with cold *n*-pentane several times and dried under vacuum to afford final product.

Sample preparation for SEM: For SEM sample preparation, TED PELLA double coated carbon conductive tape was cut into 8 mm × 8 mm sizes and was attached to SEM sample holder. 2 mg of each sample was evenly deposited on the other side of the carbon tape using thin spatula and was kept under vacuum desiccator for 6 h before data collection.

Computational methodology: Geometries of all cages were optimized and harmonic frequencies were calculated using B3LYP level of theory in conjunction with 6-31G basis set. All theoretical calculations were performed using Gaussian 09 Rev D 0.1 package. ^[27] Harmonic frequencies of all normal modes were found to be positive, which indicates all the optimized geometries have attained global minima. The theoretical absorption spectrum of the protonated cage-picrate complex was calculated in dichloromethane using polarization continuum model.

X-ray crystal data collection and structure solution: X-ray data of aldehyde C and cage C_3X_2 were collected on a Bruker D8 QUEST CMOS diffractometer using the SMART/SAINT software, [28] equipped with a low temperature device. Diffraction quality crystal was mounted on a loop coated with traces of paraton oil. The intensity data was collected at 100(2) K by using graphite monochromatic Mo-Kα radiation (0.7107 Å). The structures were solved by the direct method and refined by full-matrix least squares on F², employing the SHELXL-2014^{29]} incorporated in WinGX.^[30] Empirical absorption corrections were applied with SADABS.^[31]All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed by using the riding models and refined isotropically. Due to weak diffraction of C₃X₂ single crystal at 100 K one of the disordered phenyl rings of C_3X_2 was refined with SIMU restraints and AFIX 66 constraints. Disordered solvent molecules were treated by using the SQUEEZE program in PLATON. [32] Crystallographic data and refinement parameters are provided in Table S1. CCDC numbers: 1502517 and 1502518.

Acknowledgements

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Control over Morphology: Morphology of isostructural [3+2] selfassembled organic imine based architectures has been found to greatly depend on the structural features of aldehyde building block. Furthermore, high fluorescent nature of such architectures has been utilised to detect nitroaromatic explosives. In this direction reduced analogue of one of the cages has been tested, which found to be very selective and sensitive towards picric acid (PA).



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