Structural and computational investigation of an imine-based propeller-shaped macrocyclic cage

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Abstract

In this study, we present the synthesis, spectroscopic and structural characterization of self-assembling gem-dimethyl imine based molecular cage (IMC). Self-assembling macrocycles and cages have well-defined cavities and have extensive functionalities ranging from energy storage, liquid crystals, and catalysts to water splitting photo absorber. IMC has large voids i.e., 25% of the total crystal volume thus could accommodate wide substrates. The synthesized imine-based molecular cages are stabilized by coaxial π bonded networks and long-range periodic van der Waal and non-bonded contacts as observed from the crystal structure. IMC also has typical properties of soft condensed matter materials, hence theoretical prediction of stress and strain tensor along with thermophysical properties were computed on crystal system and were found to be stable. Molecular dynamics revealed IMC is stabilized by, strong interactions between the interstitial phenyl rings. Density functional theory (DFT) based physicochemical properties were evaluated and has band gap of around 2.38 eV (520 nm) similar to various photocatalytic band gap materials.

Keywords Gem-dimethyl · Macrocyclic cage · Thermophysical analysis · Morphology · Photophysics

1 Introduction

Macrocyclic compounds generally feature multiple rings or caged structures [1]. Organic macrocyclic cages and related coordinated complexes have shown wide range of applications from molecular catalysis to gas storage devices [2]. The robustness and flexibility to accommodate large substrates improve their utility in storage applications [3]. The spatial and temporal geometry of macrocyclic cages are important to accommodate various substrates. Coordination with different metal ions leads to the formation of metallosupramolecules exhibiting excellent

host–guest interactions [4]. Imine-based molecular cages have favorable physicochemical properties as conductive polymers [5, 6]. Porphyrin-based photoabsorber has unique band gap width by virtue of heterocyclic conjugated system [7]. The presence of oxygen in photoabsorber architecture is known to induce triplet excitation and hence reduces the degree of electron delocalization [8, 9]. Imine-based macrocycles require molecular robustness, as they are prone to hydrolysis in acidic environment leading to undesirable oligomeric polymorphism either cyclic or acyclic. Template-derived self-assembling macrocyclic cages offer potential commercial applications

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as photoabsorber. The caged organic framework having higher spatial occupancy with π -conjugated systems has many adjunct functions in the area of catalysis and gas adsorptions. Metal–organic frameworks having appropriate band gap and molecular geometry can also be used for water splitting applications [2, 10, 11].

Physicochemical, thermo-physical, molecular elasticity and stress–strain tensor are important parameters to design a robust metal organic framework to realize macroscale applications. Physicochemical parameters of photoabsorber directs activation energy, energy gap and chemical hardness of the system. Elasticity analysis will reveal the relative pressure limit that the system can withstand without volumetric deformations. Stress and strain analysis also predicts the molecular robustness, stability and compressions.

The coordination of the macrocycle with metals generally induces polymorphisms in crystals. One of the main steps in water splitting is the oxidation of water, which is both thermodynamically and kinetically demanding. Effective catalysis lowers the kinetic barrier thereby enhances the rate of oxygen production. In this regard, transition metal ions and oxides [such as TiO_2 , Mn^{2+} , Ru^{2+} , etc.,] are generally characterized as useful catalytic elements [12]. Metal–organic frameworks (MOF) with bigger macrocyclic cages having higher aromaticity and tend to have self-excitation properties. Also, it is necessary to create macrocyclic structures having desirable physiochemical properties. Most of the studied compounds have macrocyclic tetrapyrroles groups [13]. Numerous energy harnessing molecules are macrocyclic in nature, like chlorophyll made of porphyrins [14]. Recently, graphene has been proposed to have superconductivity [15] and is believed to be useful for water splitting applications if a macrocyclic

architecture is suitably incorporated [16]. Hence, structural analysis of macrocyclic cages becomes important to design above mentioned useful frameworks. Along with conformational features, intermolecular arrangement and molecular interactions play a crucial role in the packing of molecules in crystalline materials having desired physicochemical properties [17].

Self-assembling macrocyclic cages are particularly quite useful as they require reduced number of user-derived inputs for conformational assembly [18]. The synthesized *gem*-dimethyl based cage that has been analysed in this work tends to have self-assembling characteristics. In that direction, this report explains the structural description of *gem*-dimethyl imine based macrocyclic cage, followed by FTIR and NMR characterization. Simulation of IMC crystal with unit cell, dimension of $2 \times 2 \times 2$ were taken to evaluate thermophysical and mechanical properties. Density functional theory based physicochemical properties were also evaluated to identify the electronic distribution of *gem*-dimethyl based imine-based macrocyclic cage for photocatalytic like application.

2 Results and discussion

The crystal structure of imine-based macrocyclic cage (IMC) (Fig. 1a) shows the presence of three molecules in the asymmetric unit with three-fold symmetry. Crystal data and structure determination details are listed (Table 1 and S1). The IMC acquires macromolecular tricyclic arrangement to form a propeller-shaped architecture with three paddles A, B and C linking the central triphenylamine moieties to form a cage structure (Fig. 1b). The displacement ellipsoid plot for all the three cages

Fig. 1 Representation of imine based macrocyclic cage. **a** Chemical representation of IMC, **b** Stick representation of IMC having propeller-shaped architecture having three paddles A, B and C, **c** Thermal ellipsoid plot (50% probability) of a symmetric unit of non-hydrogen atoms

with 50% probability is shown in Fig. 1c. For clarity, IMC molecules with the numbering scheme are shown in Figure S1. Paddles with five aromatic rings and two *gem*-dimethyl methyl groups make them hydrophobic. This architecture which consists of two triphenylamine moieties [average distance between nitrogen atoms ($N_x \dots N_y = 5.17 \text{ \AA}$) [Table S2, Figure S 2] connected by three *gem*-dimethyl groups through imine linker provide a void within the cage. Three phenyl rings connected to the central Nitrogen are tilted relative to one another to avoid steric hindrance. Fifteen IMC molecules are packed in a triclinic unit cell having a 3_1 screw component along the Z direction with molecule placed at 1/2 and 1/3 translations.

A total of 15 IMC molecules can be packed in a unit cell which measures around 7 nm wide. The crystal packing is stabilized by T-Shaped π - π interactions along with parallel displaced van der Waals intermolecular interactions. The unit cell of IMC packed with the molecule is shown in Figure S7. Some of the main interatomic contacts which stabilize the packing of IMC are listed in Table S3 along with symmetry codes. Packing and structure of IMC are stabilized by weak π - π interactions. The centroid distance of phenyl moiety in IMC is given in Table S4, (Figure S3). Contact map of IMC and its molecular packing interaction patterns are shown in Figure S4. The methyl groups also show interactions with phenyl ring through methyl- π interactions. All the *gem*-dimethyl groups are held closely (with an average distance of $2.3 \text{ \AA}$) which reveal the compactness of the IMC system (in the crystal) as shown by the distance map (Figure S5). The contact surface and void space were analyzed with the probe radius $1.2 \text{ \AA}$ as shown in Figure S6. Void volume in the crystal is calculated to be 25% of the total crystal volume. From the experimental i.e. from the crystal structure, the volume of the crystal is $23896.25 \text{ \AA}^3$ and the void volume is $6197.03 \text{ \AA}^3$.

2.1 FT-IR and NMR analysis

IMC molecular crystals were dissolved in CHCl_3 and CDCl_3 for FT-IR and NMR analysis respectively. FT-IR which was recorded at room temperature shows the presence of $\text{CH}=\text{N}$ stretching (around 1636 cm^{-1}) and aromatic $\text{C}=\text{C}$ (around 1595 cm^{-1}). Proton NMR recorded for IMC shows peaks at δ (ppm) are 8.27 (s, 6H), 7.66 (d, $J=7.9 \text{ Hz}$, 12H), 7.45–7.35 (m, 9H), 7.02 (dd, $J=8.5, 13.4 \text{ Hz}$, 24H), 6.95–6.90 (m, 12H), 6.55 (s, 3H), 1.64 (s, 36H). Corresponding Carbon NMR reveals peaks at δ (ppm) 158.5, 150.1, 149.4, 148.5, 148.4, 131.8, 131.1, 130.2, 127.4, 124.0, 122.0, 120.0, 42.8, 30.

2.2 Macrocyclic system generation

IMC system periodically arranged in a lattice with a unit cell of dimension $2 \times 2 \times 2$ with a molecule having centroid fit is shown in Fig. 2. The whole system was subject to energy minimization by fixing the Lewis structure and connectivity using conjugate minimization. Orthorhombic periodic boundary condition in a vacuum with IMC system placed at the centre of mass was used as the starting structural assembly for all the molecular dynamics simulations.

2.3 Thermophysical parameter analysis

Theoretical glass transition temperature T_g and coefficient of thermal expansion were determined based on volumetric residual density expansion of the unit cell at different temperature from 200–600 K by molecular dynamics simulation. An increment of 25 K was used to reach from 200 to 600 K and for each 25 K increment, a 20 ns simulation was carried out to understand the change in residual density. This type of in-depth simulation analysis for each step aid in understanding the stability of crystal packing thereby overall stability of cages in that particular packing

Fig. 2 IMC molecules in unit cell along with unit cell packing of order $2 \times 2 \times 2$ of molecules having centroid fit

arrangement. The value of T_g and coefficient of thermal expansion are 444 K and $175.95 \times 10^{-6} \text{ K}^{-1}$ at 298.15 K, respectively. The result suggests a sudden increment in a specific volume of the system with heavy positional fluctuations at the temperature above 400 K. Bilinear fit for IMC (MC-51) system as a function of temperature and specific volume is shown in Fig. 3a.

2.4 IMC's response to mechanical stress

Systematic analysis of stress and strain was carried to measure the mechanical properties of the IMC in a periodic lattice arrangement. Huge discontinuous void spaces make IMC non-resilient to strain. Lower mechanical stability can be attributed as the consequence of greater residual voids in between the macrocyclic cage in the present arrangement. Chloroform removed structure was considered for calculations that would have reflected on the decreased stability. But the disordered nature of the chloroform (CHCl_3) itself explains the non-interacting behaviour of IMC with the solvent and hence the "stability by the solvent" factor is practically absent. Stress and strain scatter plot of the system is shown in Fig. 3b. The elastic anisotropy of the macrocycle system on X-axis is given in Fig. 3c.

2.5 Physicochemical parameter analysis.

The crystal structure was taken directly to analyse the ground state population energy. The orbital energy pattern shows the possibility of different absorption and excitation patterns corresponding to different electron delocalization (resonance) states. Except the phenyl ring attached with *gem*-dimethyl groups, all the other phenyl rings can assume resonance with the remaining structural part. Phenyl rings at the tertiary amine nitrogen (central

Nitrogen) which are twisted with one another from co-planarity and the possibility of rotation of the phenyl group adjacent to imine group might hinder the electron delocalization efficiency. The physicochemical parameters of IMC molecule were calculated with B3LYP 6–31(d,p) basis set to assess the orbital energy. The HOMO–LUMO orbital map of IMC with 4 delocalized states is shown in Fig. 4. The physicochemical parameters of IMC are given in Table 2. Lower order photocatalytic band gap materials are essential in tailoring optical performance during engineering functional materials. IMC has the band order of 2.38 eV [21] and has promising photoreceptive characteristics as photoabsorber.

2.6 Intermolecular packing analysis.

There are three molecules packed in the asymmetric unit. The molecules were clustered into three groups based on clustered energy. The packing lattice energy of the molecule of first three clusters are $122.1 \text{ kJ mol}^{-1}$, $119.1 \text{ kJ mol}^{-1}$ and 30.7 kJ mol^{-1} respectively. The packing fraction with lattice energies is shown in Figure S8.

3 Experimental section

3.1 Molecular crystallizations

A solution of benzene trialdehyde (0.010 g, 0.061 mmol) in acetonitrile (ACN) was slowly added to a solution containing *gem*-dimethyl amine (0.032 g, 0.09 mol) in ACN. 50 μl of acetic acid was added to the ACN solution and was kept undisturbed for 7 days to obtain pale yellow colored, needle-shaped crystals. A detailed synthesis of the IMC, macrocycle 10 is as reported [22]

Fig. 3 Thermophysical and mechanical analysis of macrocyclic cage MC-51. **a** Thermophysical plot relating temperature with respect to specific volume, **b** Stress strain analysis, and **c** elastic property of macrocyclic cage MC-51

Fig. 4 Delocalized orbital plot of 4 HOMO–LUMO occupied state of isolated MC-51 molecule

3.1.1 X-Ray data collection and Refinement

X-ray diffraction and intensity measurements of the *gem*-dimethyl compound were obtained on Bruker SMART APEX CCD diffractometer with graphite-monochromatized ($\text{MoK}_\alpha = 0.71073 \text{ \AA}$) radiation. The X-ray data collection was monitored by the SMART program [23]. Lorentz factor, polarization and absorption of the crystal data were corrected using SAINT and SADABS programs. The initial structure was solved using SIR92 and further refinement was done using SHELXL [20] with full matrix least-squares refinement on structure factors. Geometrical packing analysis and their diagrams were generated using Mercury suite [24].

Initial structure refinements revealed the presence of chloroform in the lattice but were heavily disordered. The phenyl ring which links two *gem*-dimethyl methylene groups is also found disordered from planarity. To overcome these, squeeze procedure was carried by masking the regional density map keeping only the ordered macrocyclic structure and AFIX66 procedure was employed. Since the IMC system is in a disordered state, the hydrogen atoms were not assigned. In comparison with structures from CCDC, some deviations were observed among certain geometrical parameters. It has to be mentioned here that the IMC crystals were fragile and did not pose higher order stability.

3.2 NMR and FT-IR analysis.

NMR spectroscopic investigation was carried out to obtain chemical shift δ ppm in reference to TMS. IR spectroscopy

was recorded using CHCl_3 or Nujol on Bruker-FTIR spectrophotometer.

3.3 Macrocyclic system generation.

The Macrocyclic cages were periodically arranged to the lattice value of $2 \times 2 \times 2$ order with the connectivity of basis. The molecular system was minimized to correct all the Lewis structure and atomic bond orders. Polak-Ribiere Conjugate Gradient (PRCG) conjugate minimization was carried out with 10,000 maximum iteration steps with the convergence of $0.001 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. The system was prepared in the orthorhombic periodic boundary condition using system builder Materials science suite [25].

3.4 Thermophysical analysis.

Molecular dynamics simulation-based thermophysical properties calculation was done using Desmond [26]. The protocol of simulation involves system relaxation. The relaxation protocol involves minimization of the system for 100 ps Brownian dynamics at 10 K with 24 ps simulation of NVT ensemble at 300 K and 700 K, respectively with 1 ns equilibration at 300 K followed by 20 ns at a different temperature range from 200 to 600 K to evaluate the differential converged density of the system. The bilinear fit was performed to analyze the glass transition temperature T_g . The coefficient of thermal expansion was generated based on change in density with respect to temperature.

Table 1 Crystal data and structure determination details

Crystal data	
Chemical formula	$C_{68.40}H_{10}Cl_0N_{4.80}O_0$
M_r	888.73
Crystal system, space group	Trigonal, $P3_1$
Temperature (K)	293
a, c (Å)	32.1333 (11), 26.7232 (9)
V (Å ³)	23,896.2 (18)
Z	15
Radiation type	Mo K α
μ (mm ⁻¹)	0.06
Crystal size (mm)	0.30 × 0.25 × 0.15
Data collection	
Diffractometer	CCD area detector
Absorption correction	Multi-scan
Bruker SADABS	
T_{min}, T_{max}	0.983, 0.990
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	168,498, 58,948, 42,901
R_{int}	0.073
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.613
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.099, 0.280, 1.01
No. of reflections	58,948
No. of parameters	11
No. of restraints	1
H-atom treatment	H-atom parameters not defined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.52, -0.46
Absolute structure	Refined as an inversion twin
Absolute structure parameter	3.3 (15)
Computer programs: Bruker SMART [19], Bruker SAINT [19], SHELXL [20]	

3.5 Elastic constants evaluation of the mechanical response of the system

The stress is evaluated by accounting change in pressure tensor from initial and final deformation using Desmond [26]. 20 ns molecular simulation was run to analyze the

stress of the system as a function of strain. The system was run in NVT ensemble at 300 K. The strain is determined based on parameter $\eta = 0.5$ which is volume conserved uniaxial strain to relate the transverse strain λ .

$$\lambda = 1 - (1 + \epsilon)^{-\eta}$$

The strain is analyzed on X-axis based on fractional increment in uniaxial length given by equation.

$$L_K = L_0(1 + k\epsilon)$$

Elastic properties such as Tension anisotropy, Shear anisotropy, Lamé Lambda, Lamé Mu, Young's Modulus, Shear Modulus, Lamé Bulk Modulus, and Poisson Ratio were evaluated based on strain calculations.

3.6 Physicochemical parameter determinations

Crystal structure optimized with the adiabatic Born–Oppenheimer approximation using DFT B3LYP 6–31(d,p)[27] basis set till stationary potential state with lowest saddle point was found out with Berny algorithm by means of self-consistent field (SCF) geometry optimization with energy embodied direct inversion in the iterative subspace (GEDDIS) method [28]. The energy was analyzed based on ground state (S_0) derived orbital states. The orbital computations and optimization are done with Avogadro [29] and Gaussian 03, respectively[30].

3.7 Intermolecular Interaction energy

The intermolecular lattice energies were calculated using OPIX program [31, 32]. The summation of inter lattice energy is computed by UNI force fields where the pairwise atom–atom interactions are calculated. The overall intermolecular potential was calculated as the summation of UNI force field parameters consisting of coulombic, polarization, and dispersion and repulsion energy terms, respectively. Intermolecular potential associated with centrosymmetric assembly can also be identified.

Table 2 Physicochemical parameters of IMC molecule

Compound Name	Ionisation potential(I) (eV)	Electron affinity (A) (eV)	gap energy, ΔE	Chemical Hardness(η)	Softness(S)	Chemical Potential (μ)	Electronegativity (χ)	Electrophilicity index (ω)
MC-51	5.80	3.42	2.38	1.19	0.84	-4.61	4.61	8.92

4 Conclusions

Self-assembling macrocyclic cages has wide ranging applications from energy storage to photoabsorber. Here self-assembling gem-dimethyl frameworks was constructed and spectral and crystallographic investigation were carried out. The major stabilizing force of crystal packing are π - π intermolecular networks between phenyl groups also observed from molecular dynamics simulations. Elastic, thermophysical, mechanistic properties also were computed to analyse the stability of the imine based macrocyclic molecular geometry. The gem-dimethyl group tends to be moderately stable and crystal system can withstand intermediate mechanical stress. It has similar band gap value to that of photocatalytic materials, and indicates suitability in constructing MOF's with catalytic applications. These cages has to be further be incorporated with MOF's to engineer functional materials having catalytic and gas storage applications.

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Compliance with ethical standards

Conflict of interest Authors declare no conflict of interest.

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