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# Self-Exfoliated Guanidinium-Based Ionic Covalent Organic Nanosheets (iCONs)

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**ABSTRACT:** Covalent organic nanosheets (CONs) have emerged as functional two dimensional materials for versatile applications. Although  $\pi$ - $\pi$  stacking between layers, hydrolytic instability, possible restacking prevents their exfoliation on to few thin layered CONs from crystalline porous polymers. We anticipated rational designing of a structure by intrinsic ionic linker could be the solution to produce self-exfoliated CONs without external stimuli. In an attempt to address this issue, we have synthesized three self-exfoliated guanidinium halide based ionic covalent organic nanosheets (iCONs) with antimicrobial property. Self-exfoliation phenomenon has been supported by molecular dynamics (MD) simulation as well. Intrinsic ionic guanidinium unit plays the pivotal role for both self-exfoliation and antibacterial property against both gram-positive and gram-negative bacteria. Using such iCONs we have devised mixed matrix membrane which could be useful for antimicrobial coatings with plausible medical benefits.

## **INTRODUCTION**

Covalent organic nanosheets (CONs) are two dimensional (2D) materials constructed by symmetrically arranged organic linkers, along two dimension, via strong covalent bonds.<sup>1</sup> In recent years, researchers have made considerable efforts to synthesize monolayer or few layered CONs, which could emerge as a porous functional material with a plethora of applications owing to their easy and pre-designable functionalization opportunity.<sup>1, 2</sup> On this line, few layered CONs have been synthesized from 2D crystalline porous polymers (CPPs) often known as covalent organic frameworks (COFs)<sup>3</sup> and covalent triazine frameworks (CTFs),<sup>4</sup> using conventional exfoliation techniques such as ultrasonication<sup>1c</sup> and mechanical delamination.<sup>1a,b,d</sup> However, the major reasons that prevent the formation of monolayer or few layered CONs by these methods include (i) strong  $\pi$ - $\pi$  stacking between the layers,<sup>1-4</sup> (ii) hydrolytic instability for most of the CPPs,<sup>5</sup> (iii) possible restacking;<sup>6</sup> and most importantly, (iv) challenging synthetic procedures to obtain the exfoliated nanosheets.<sup>1e,7</sup> However, these shortcomings could be surpassed easily by rational design of chemically stable CONs with inbuilt ionic character to induce self-exfoliation. Moreover, if the ionic building block itself possesses biological significance, the synthesized CONs could be directly used for biomedical applications without further post synthetic modifications. Nevertheless, the self-exfoliation of 2D CPPs and exploring its biological significance in a single domain is unprecedented and thus remains a daunting task. In the same pursuit, we have introduced the concept of rational design to self-exfoliate guanidinium halide based porous ionic Covalent Organic

Nanosheets (iCONs) for antimicrobial applications. Positively charged guanidinium units result in interlayer repulsion to self-exfoliate into few layered iCONs. These iCONs showed porosity, chemical stability permanent and potent antimicrobial property against both gram-positive (Staphylococcus aureus) and gram-negative (Escherichia coli) Although substituted guanidinium-based bacteria. conventional polymeric materials are known to demonstrate antimicrobial property;8 but the solubility of guanidiniumbased materials limits their usage in heterogeneous water resistant antimicrobial coatings. Hence, the insolubility of iCONs with antimicrobial property could be the key solution in devising antibacterial coatings useful in biomedical sectors. To validate this conception, we have strategically fabricated iCONs@Polysulfone (PSF) mixed matrix membrane for antimicrobial coatings.

### **EXPERIMENTAL SECTION**

Three of the iCONs (TpTG<sub>Cl</sub>, TpTG<sub>Br</sub>, and TpTG<sub>I</sub>) were synthesized *via* Schiff base condensation reaction between 0.2 mmol 1,3,5-triformylphloroglucinol (Tp) (42 mg) and 0.2 mmol amines (TG<sub>X</sub>) (TG<sub>Cl</sub>: 28 mg or TG<sub>Br</sub>: 37 mg or TG<sub>I</sub>: 47.4 mg) in a sealed Pyrex tube using dioxane: water in the ratio 2: 0.6 mL. The reaction mixtures were charged into Pyrex tube and sonicated for 20 min. The mixtures were degassed under liquid N<sub>2</sub> (77K) by freeze-pump-thaw cycles for three times and the Pyrex tube was then vacuum sealed. The reaction mixtures were allowed to attend



**Figure 1.** (a) Synthetic scheme of  $TpTG_{Cl}$  monomer (SaTG<sub>Cl</sub>) (left) and of iCONs ( $TpTG_x$ ) (right); where X=Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>; (b) ORTEP diagram of SaTG<sub>Cl</sub> at 50% probability ellipsoid level; (c) Stacking model of SaTG<sub>Cl</sub> showing sandwiched anions between the layers (side view); (d) Comparison of PXRD patterns of the three iCONs; (e) <sup>13</sup>C CP MAS solid-state NMR of iCONs; (f) Modeling of TpTG<sub>Cl</sub> in eclipsed mode (top view); (g) Stacking model showing individual layers (side view).

room temperature and then kept at 120 °C for 3 days.  $TpTG_{Cl}$ ,  $TpTG_{Br}$ , and  $TpTG_{I}$  were obtained as a brown colored precipitate. The product was washed thoroughly with DMAc, water, and acetone respectively and dried at 90°C for overnight to obtain in ~70 % isolated yield.

To obtain detail insights into self-exfoliation of iCONs in presence of water molecules, we performed all atom molecular dynamics (MD) simulations (detailed in Section S8 ESI). The synthesized iCONs were used for antibacterial studies using three different concentrations (100  $\mu$ gmL<sup>-1</sup>, 200  $\mu$ gmL<sup>-1</sup> and 500  $\mu$ gmL<sup>-1</sup>). They were dispersed in autoclaved deionized water and allowed to incubate with bacterial strains *Staphylococcus aureus* and *Escherichia coli* for about 4 h. The resulting mixture was plated in Petri plates containing solidified potato dextrose agar media. The Petri plates were incubated at 37 °C for 24 h and the resulting CFU counts were measured visually. Morphological study of control and treated bacterial samples were carried out by SEM and TEM. Detailed experimental procedures are provided in Section S10 ESI. We further fabricated iCONs mixed matrix membrane using PSF on porous non-woven support fabrics (3329). TpTG<sub>Cl</sub> (5% by wt. of PSF) was added to the PSF solution in DMF, stirred well for another 6 h and degassed for 3 min to remove the trapped gases. TpTG<sub>Cl</sub>@PSF membranes were prepared using Sheen Auto-matic Film Applicator-1132 at 25 °C and exposed in air for 15 seconds prior to dipping in non solvent (water) bath. The knife movement was set to 10 cm.sec<sup>-1</sup> transverse speed with a gap of 250  $\mu$ m. The total thickness of the supported membrane was ~100  $\mu$ m. These membranes were washed with distilled water and stored in aqueous formalin (0.5%) solution. Antibacterial activity of iCONs membrane was evaluated by the growth of bacteria on to it (detailed in Section S11 ESI).

#### **RESULTS AND DISCUSSIONS**

In order to incorporate guanidinium units within a stable iCONs framework, we have synthesized triaminoguanidinium halide (TG<sub>Cl</sub>, TG<sub>Br</sub>, and TG<sub>I</sub>) which assumes a  $C_3$  symmetric planner



**Figure 2.** (a) Nitrogen adsorption isotherm and (b) water vapour uptake of  $TpTG_{Cl}$ ,  $TpTG_{Br}$  and  $TpTG_{l}$  respectively. Figure 2a inset shows pore size distribution of  $TpTG_{Cl}$ .

structure (Section S2, S3, ESI).<sup>9</sup> These C<sub>3</sub> symmetric amines resulted into three 2D iCONs (TpTG<sub>Cl</sub>, TpTG<sub>Br</sub>, and TpTG<sub>I</sub>) when reacted with  $C_3$  symmetric Tp (Figure 1a). PXRD patterns of these three iCONs revealed low crystallinity with the first broad peak at  $2\theta = -9.7^{\circ}$  which corresponds to 100 plane (Figure 1d). The major broad peak at  $2\theta = \sim 27.3^{\circ}$ signified poor  $\pi$ - $\pi$  stacking between the vertically stacked layers (Figure 1d). In order to get precise structural insights, monomeric unit of TpTG<sub>Cl</sub> was synthesized and crystallized (Figure 1a).<sup>10</sup> The single crystal structure of the monomer showed the presence of Cl- anion sandwiched between two monomer units (~3.3 Å), which remain hydrogen bonded [N -H•••Cl<sup>-</sup>; D= 3.29 Å, d=2.57 Å,  $\theta=141.8^{\circ}$ ] with the guanidinium nitrogen and hydroxyl group of salicylaldehyde (Figure 1b).<sup>11</sup> Presence of this loosely bound chloride ions and intrinsic positive charge of guanidinium units (Figure 1c) disturb the  $\pi$ - $\pi$  stacking interactions among the layers in the extended iCONs structure, which we believe is the reason for their low crystallinity. Based on the monomer structure, all three iCONs (TpTG<sub>Cl</sub>, TpTG<sub>Br</sub>, and TpTG<sub>I</sub>) were modeled in possible 2D eclipsed and staggered structure (Figure 1f, Section S4 ESI). The PXRD pattern of fully eclipsed AA structure

matched well with that of experimentally observed PXRD (Figure S6-S11). Although the monomeric units were planner, but ionic layers with sandwiched halide ions in between them created an extremely weak stacking (Figure 1g). This motivated us to believe that the as synthesized polymers would intrinsically self-exfoliate to covalent organic nanosheets.

FTIR spectra of iCONs revealed characteristic C=C stretching frequency at 1597 cm<sup>-1</sup> and C-N stretching frequency at 1291 cm<sup>-1</sup>,<sup>1d, 12</sup> while characteristic carbonyl and primary amine stretching frequency of the precursors was absent (Figure S12). Similarly, <sup>13</sup>C CP-MAS solid-state NMR spectroscopy of TpTG<sub>x</sub> showed a very sharp peak at 100.1 ppm which signified the exocyclic C=C carbon<sup>12</sup> adjacent to the C=O carbon (Figure 1e). Signals representing de-shielded C=C carbon attached to the N was obtained at 150 ppm. Carbon signal of guanidinium C=N appeared at ~162 ppm and a small keto (-C=O) carbon signal was noted in between 180-182 ppm.<sup>1d, 12</sup> The sharp exocyclic double bond signal is the strong evidence of irreversible enol to keto tautomerism in iCONs.12 In addition, TGA profiles of the iCONs demonstrated their thermal stability up to ~225 °C (Figure S14). Permanent porosity of these iCONs was verified using N<sub>2</sub> adsorption isotherms of the activated samples at 77K, where all three iCONs followed Type-II reversible adsorption isotherm. The Brunauer-Emmett-Teller (BET) surface area of TpTG<sub>Cl</sub>, TpTG<sub>Br</sub>, and TpTG<sub>I</sub> were found to be 267, 305 and 298 m<sup>2</sup>g<sup>-1</sup> respectively (Figure 2a). This lower surface area of iCONs could be a result of poor layer stacking, small pore diameter, and pore blocking by the counter anions. Pore size distributions were calculated on the basis of nonlocal density function theory (NLDFT). Due to the lack of proper channelled pore structure and pore blocking by subsequent counter anions, no sharp pore size distributions were obtained (Figure 2a inset, S15). These were consistent with the previous report where delamination of 2D-CPP layers into CONs resulted in destruction of finite porosity.<sup>1d</sup>

Self-exfoliation of all three iCONs resulted in micrometer to sub-micrometer sized sheet directly as observed in SEM (Figure S19); meanwhile, EDX analysis signified C, N, O and corresponding halogens (Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) as major chemical components in TpTG<sub>Cl</sub>, TpTG<sub>Br</sub>, and TpTG<sub>I</sub> (Figure S22). TEM images of TpTG<sub>Cl</sub>, TpTG<sub>Br</sub>, and TpTG<sub>I</sub> also showed thin transparent sheets and they were marginally rippled (Figure 3a, 3b, 3c, S20). Average d spacing value (~3.7 Å) obtained from TEM analysis was consistent with corresponding PXRD analysis (Figure S23). TEM analysis was well supported by corresponding AFM measurements carried out in the tapping mode. iCONs sheets, with high aspect ratio, showed that their range of height profile was around 2-5 nm (Figure 3d, 3e, 3f; S21). This indicates that the iCONs could be exfoliated into 3-6 layers.<sup>1e, 1h, 7a</sup> In order to validate self-exfoliation of iCONs, we further used MD simulation studies (Section S8, ESI). Interestingly, in aqueous medium TpTG<sub>Cl</sub> layers were found to be exfoliated without any external stimuli, as the average interlayer  $\pi$ - $\pi$  stacking distance was increased up to ~5.5-6 Å compared to initial 3.338 Å stacking (Figure 3g, 3h). Hydration shell surrounding the iCONs and sandwiched halide ions (Cl<sup>-</sup> for TpTG<sub>Cl</sub>) further contributed to self-exfoliation mechanism as evident from the simulation studies (Figure S30). Although we have attempted to synthesize CPPs by using neutral ligand (1, 2, 3-triaminoguanidine), but



**Figure 3.** (a), (b), (c) TEM images of TpTG<sub>Cl</sub>, TpTG<sub>Br</sub> and TpTG<sub>I</sub> respectively, (inset shows zoomed in images, scale bar 20 nm); (d), (e), (f) AFM images and height profile of TpTG<sub>Cl</sub>, TpTG<sub>Br</sub> and TpTG<sub>I</sub> respectively (AFM scale bars represent 200 nm); MD simulation snap-shots of TpTG<sub>Cl</sub> in aqueous medium demonstrating self-exfoliation: (g) snapshot at initial state (0 ns), (h) snapshot at 500 ns.

exfoliated sheet like CONs was not obtained for the same as evident from TEM imaging (Figure S25). Alternatively, we mechanically grinded as-synthesized  $TpTG_{Cl}$  and analyzed the PXRD pattern to support the self-exfoliation. No significant alteration in PXRD patterns of as-synthesized and mechanically grinded one was noted, which could be a fare evidence of self-exfoliation phenomenon of iCONs (Figure S18)<sup>1c, 1d</sup>.

These iCONs displayed stable aqueous dispersion for at least 20 days owing to their ionic backbone (Figure S16)<sup>13</sup>. A characteristic Tyndall effect was noted signifying stable colloidal suspension during this time (Figure S16).<sup>1d</sup> Hydrophilic environment within the iCONs back bone was reflected in corresponding water adsorption isotherms as 320, 325 and 350 ccg<sup>-1</sup> water vapour uptake was noted at 0.9 P/P<sub>o</sub> (STP), at 298 K for TpTG<sub>Cl</sub>, TpTG<sub>Br</sub>, and TpTG<sub>I</sub> respectively (Figure 2b). Chemical stability of these iCONs was ensured in different commonly used solvents such as methanol, acetone, THF and water for 7 days (Figure S32, S33). Moreover, these iCONs showed the stability in 3N HCl for 7 days, which has been verified by PXRD and FTIR analysis owing to their more stable tautomeric form (Figure S31).<sup>12</sup>

For antibacterial studies,  $TpTG_{Cl}$  was selected as the model iCONs. In all  $TpTG_{Cl}$  treated sets, colony forming units (CFU) were drastically reduced in a concentration dependant manner for both gram-positive (*Staphylococcus aureus*) and gramnegative (*Escherichia coli*) bacteria (Figure S34). <sup>14, 15</sup> Therefore,  $TpTG_{Cl}$  could be used as antibacterial agent against a broad spectrum of microbial system. Antibacterial activities of  $TpTG_{Br}$  and  $TpTG_{I}$  were also promising (Figure S35; Table T7, ESI). Hence, it could be concluded that the guanidinium core of the iCONs is responsible for such antimicrobial activity. Meanwhile, morphological studies of control and treated bacterial samples were evaluated by SEM and TEM. Control

S. aureus was found to be spherical in shape with smooth, continuous and unbroken cell membranes; while TpTG<sub>Cl</sub> treated bacterial sample showed rupture in morphology as evident in SEM and TEM imaging (Figure 4a, 4b). The same observation was noted for E. coli where the control sample showed uniform rod shaped morphology and the treated ones illustrated shrunken, twisted rod like morphology (Figure 4c, 4d).<sup>14</sup> Planner guanidinium units are known to demonstrate strong binding with the oxoanions of phosphate through two point hydrogen bonding interactions.<sup>16</sup> We speculate, positively charged iCONs could interact with bacterial cells followed by the disruption of negatively charged phospholipid bilayer (Figure 4e).<sup>17</sup> This would result leaching out of the cellular content and subsequently death of the bacteria. Although electrostatic interactions between positively charged guanidinium units and phospholipid bilayers play the pivotal role for antibacterial response of the iCONs; hydrogen bonding interactions between the keto groups of iCONs and phospholipids might have contributed to the antibacterial mechanism as well.<sup>18</sup> Morphological alteration and antibacterial response of iCONs was further verified by live/dead cell imaging study (Figure S36) and cell cycle analysis (Figure S37) of control and treated bacterial cells.

Inspired by antibacterial property and good dispersibility of iCONs we have attempted to device a mixed matrix antimicrobial membrane with PSF and  $TpTG_{Cl}$  on a porous support (Section S11, ESI). The resultant membrane ( $TpTG_{Cl}@PSF$ ) was found to be robust, free standing, stable and highly flexible (Figure 4f, Figure S38). SEM image illustrates the cross section of the fabricated composite membrane (Figure 4g); the presence of iCONs materials was clearly observed as noted by elemental mapping (Figure S39).  $TpTG_{Cl}$  was not leached out from the composite membrane



**Figure 4.** (a) SEM images and (b) TEM images of control and  $TpTG_{Cl}$  treated *S. aureus*, (c) SEM images and (d) TEM images of control and  $TpTG_{Cl}$  treated *E. coli*, (e) Schematic representation for its mode of action between bacteria and iCONs, (f) Digital image of  $TpTG_{Cl}@PSF$  mixed matrix membrane, (g) SEM image of the  $TpTG_{Cl}@PSF$  mixed matrix membrane, Antibacterial property of  $TpTG_{Cl}@PSF$  mixed matrix membrane by growth of (h) *S. aureus* and (i) *E. coli* on to it.

materials even after a prolonged period of water treatment conveying good stability as noted by FTIR (Figure S40). It is noteworthy to mention that soluble nature of guanidiniumbased compounds in aqueous/organic medium limit their processability for heterogeneous membrane fabrication. Although AgCl-PAF-50 composites have been used for antimicrobial coatings, aqueous instability of such boronic acid based materials could not be ruled out.<sup>15</sup> In contrast; insolubility, aqueous stability and inherent antimicrobial property of iCONs without further doping paved the way for heterogeneous membrane formulation overcoming the drawbacks. Even iCONs are unlikely to engender oxidative stress since electrostatic interaction of guanidinium unit is responsible for antibacterial response. Notably, the membrane was hydrophilic in nature with a water contact angle of ~53° at the water-air interface (Figure S38a inset) and allows the permeation of water through it (27 lm<sup>-2</sup>h<sup>-1</sup>). Prior to the antimicrobial evaluation of the membrane, activity of PSF was also checked which showed no significant antimicrobial activity (Figure S42). Antibacterial activity of this TpTG<sub>Cl</sub>@PSF membrane was evaluated by growth of the bacteria on to it; in contrast, we took a normal filter paper as a control.<sup>19</sup> Interestingly in filter paper, both the S. aureus and E. coli retained morphological integrity (Figure S43) which justified no significant antibacterial property. While in TpTG<sub>CI</sub>@PSF membrane both showed shrunk and rupture of the morphology (Figure 4h, 4i) demonstrating antibacterial property.

#### In summary, we have rationally designed guanidinium-based self-exfoliated antimicrobial porous iCONs. Judiciously designed iCONs were comprised of few thin layers, thanks to the intrinsic charge within the framework back bone and sandwiched anions in between the layers. Since synthesis of thin layered intrinsically ionic 2D materials are challenging, selfexfoliation by incorporation of ionic guanidinium linker could be an alternative to obtain thin layered 2D material without further post modifications. As synthesized iCONs demonstrated chemical stability and good antibacterial activity against both gram positive (S. aureus) and gram-negative bacteria (E. *coli*). We speculate electrostatic interactions between positively charged iCONs and negatively charged phospholipid bilayer of bacterial membrane resulted in such antibacterial response. Taking into account these observations we fabricated antibacterial TpTG<sub>CI</sub>@PSF membrane which could have potential medical benefits. Considering the water permeance and antibacterial property of this membrane, water purification process is currently underway in our laboratory.

## ASSOCIATED CONTENT

**Supporting Information** Synthesis and crystallographic details of ligand, molecular dynamics simulation study, biological experiments, membrane fabrication, characterization details are provided in Supporting Information file.

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# CONCLUSION

#### **Author Contributions**

<sup>‡</sup>S.M, S.K, B.P.B have contributed equally.

#### Notes

The authors declare no competing financial interests.

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59 60

