Fused aromatic networks as a new class of gas hydrate inhibitors

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ABSTRACT

Fused aromatic networks (FANs) are attracting considerable interest in the scientific community because of their intriguing electronic properties and superior physiochemical stability due to their fully fused aromatic systems. Here, a three-dimensional (3D) cage-like organic network (3D-CON) and a vertical two-dimensional (2D) layered ladder structure (designated as V2D-BBL structure) were studied as materials for gas hydrate inhibitors because of their outstanding stability in high-pressure/low-temperature and periodically incorporated molecular building blocks. The V2D-BBL structure demonstrated remarkable performance, inhibiting the formation of both methane (CH4) and carbon dioxide (CO2) hydrates, comparable to conventional lactam-based polymers. It was determined that the designed perimene moiety in the V2D-BBL structure enables synergistic interactions with the host (water) and guest (CH4) molecules involved in hydrate nucleation. Given their pre-designability and inherent stability, the FANs hold enormous potential as gas hydrate inhibitors for industrial applications.

1. Introduction

Gas hydrates are crystalline inclusion compounds formed when small gas molecules are incorporated into hydrogen-bonded water frameworks under high pressure and low-temperature conditions [1,2]. Unfortunately, gas hydrates can be spontaneously formed in gas and oil pipelines, resulting in the blockage and rupture of supply lines, leading to enormous economic losses and environmental disasters. For this reason, hydrate formation in pipelines is a significant problem in the oil and gas industries [3,4].

In the past, thermodynamic hydrate inhibitors (THIs) such as methanol and monoethanol glycol have been widely used for hydrate prevention in deepwater operations [5]. However, a high concentration of THIs (20–50 wt%) is required for optimum efficiency, which has economic and environmental consequences. These issues have led to intensive research to develop kinetic hydrate inhibitors (KHI). KHI retard the nucleation and growth of gas hydrates, preventing pipeline blockages upstream and downstream in oilfield operations, and have demonstrated remarkable efficiency, even in smaller amounts (~1 wt%) [5-9]. Among developed KHI [7], lactam-based polymers such as polyvinylpyrrolidone (PVP) and poly(N-vinylcaprolactam) (PVCap) have received particular attention because of their excellent performance [8,10]. However, these polymer-based KHI are hard to handle during injection because they are sticky and are also difficult to recover. Their intrinsic low cloud point (30–40 °C) in low-temperature and high-salinity gas/oil fields is a particular problem because their precipitation from aqueous solutions decreases their inhibition efficiency [9,11-13]. Accordingly, developing new KHI to replace conventional polymers is highly desirable for the industry, especially if coupled with a deep study on the inhibition mechanism.

Multiple types of porous organic polymers (POPs) have recently been synthesized, with lightweight, rigid covalent linkages and porous structures [14-17]. One of the unique subclasses of POPs, fused aromatic networks (FANs), have demonstrated versatile physical and chemical properties [18-20]. Their building blocks can be periodically incorporated into network structures with fully fused aromatic rings, devoid of rotatable single-bond connectivity. As a result, FANs have both extraordinary physicochemical and structural stability and high
porosity [21,22]. In addition, their structural features can be readily tuned, which makes FANs promising materials for practical applications such as water splitting [23], electronics [20], gas storage [24], and the uptake of hazardous chemicals [25].

Here, for the first time, we employed FAN structures as KHI s because of their intrinsic beneficial features that other porous materials don’t have. Their outstanding stability and rigid porosity against hydrolysis even in high-pressure/low-temperature conditions prompted us to investigate the use of FANs as gas hydrate inhibitors. In addition, the abundant hydrogen bonding sites in periodically doped heteroatoms interact well with water, helping to disrupt gas hydrate formation. In this study, we employed two FAN materials, a three-dimensional (3D) pyrazine-based FAN structure (3D-CON) [24] and a poly(benzimidazobenzophenanthroline)-based FAN structure (V2DBBL structure) [26]. Both materials were successfully synthesized via a simple wet-chemical reaction on a gram scale. The resultant FANs exhibited superior stability and high surface area with remarkable gas storage performance. Significantly, the V2DBBL structure has a perinone unit, which is structurally similar to lactam-based polymers. We determined the inhibition mechanism of the materials using molecular dynamics (MD), Fourier-transform infrared spectroscopy (FT-IR), and in-situ Raman spectroscopy.

2. Experimental section

2.1. Materials

All the reagents, solvents and reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise specified. All the solvents were degassed with nitrogen purging before use. The reactions were carried out under a nitrogen atmosphere using oven-dried glassware.

2.2. Instrumentation

Fourier-transform infrared (FT-IR) spectra were measured using a Spectrum 100 (Perkin-Elmer, USA) with a KBr pellet and attenuated total reflection (ATR) mode. Magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were obtained at room temperature on an Agilent VNMRS 600 spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted on an X-ray Photoelectron Spectrometer Thermo Fisher K-alpha (UK). Scanning electron microscope (SEM) measurements with Pt coated samples were obtained by a Field Emission Scanning Electron Microscope Nanonova 230 (FEI Inc., USA). The thermogravimetric analysis (TGA) was carried out using an STA 8000 thermal analyzer at a heating rate of 10 °C min⁻¹ under air and nitrogen atmosphere. High-resolution transmission electron microscopy (HR-TEM) was performed using a JEM-2100F microscope (JEOL, Japan) under an operating voltage of 200 keV. TEM samples were prepared by drop-casting an ethanol dispersion of the material onto the Quantifoil holey carbon TEM grid and dried at 50 °C under vacuum. The nitrogen adsorption–desorption isotherm was obtained using the Brunauer-Emmet-Teller (BET) method on BELSORP-max (BEL Japan, Inc., Japan).

2.3. Synthesis of fused aromatic networks (FANs)

The 3D-CON and V2D-BBL structures were synthesized following literature-reported procedures [24,26]. The 3D-CON was obtained from a reaction between triptycene hexahyamine (THA) hexahydrchloride and hexaketocyclolhexane (HKH) octahydrate in a solvent mixture (ethylene glycol and acetic acid) at 393 K. The V2D-BBL structure was formed by polycondensation between THA and naphthalenetetracarboxylic dihydride (NDA) in polyphosphoric acid (PPA) as a solvent. The resulting 3D-CON and V2D-BBL structures are depicted in Fig. 1. The 3D-CON consists of stable fused aromatic pyrazine rings (Fig. 1a), and the V2D-BBL structure comprises vertically oriented perinone units (Fig. 1b).

2.4. Measurement of hydrate onset temperature using a high-pressure autoclave

The onset temperatures of CH₄ and CO₂ hydrates in the presence of inhibitors were measured using a high-pressure autoclave reactor manufactured with 316 stainless steel (Fig. S1). The reactor with an internal volume of 70 cm³ was filled with 30 g of solution and immersed into an ethylene glycol–water bath circulator (RW-2025G, JEIO Tech, Republic of Korea). The reactor was flushed with CH₄ gas or CO₂ gas with a purity of 99.95 % (MS Gas CO₂, Republic of Korea) at least 3 times and pressurized to 10.0 MPa (CH₄) and 3.5 MPa (CO₂) at 285.8 K. To measure the onset temperature of CH₄ hydrate in the presence of inhibitors, a temperature-ramping method (cooled down from 285.8 K to 270.7 K) with vigorous agitation by an impeller-type stirrer was adopted to observe the inhibition performance of each inhibitor. The onset temperatures of CH₄ and CO₂ hydrates in the presence of samples are summarized in Table S1.

2.5. Measurement of time-dependent Raman spectra using in-situ Raman spectroscopy

To collect time-dependent Raman spectra of CH₄ hydrate in the presence of PVCap and V2D-BBL structure, a fiber-coupled Raman spectrometer (SP-550, Horiba, France) with a multichannel air-cooled CCD detector and a 1,800 grooves/mm grating was used under an isothermal and isobaric condition (ΔT = 4.5 K and 8.0 MPa). A Raman probe was attached to a jacketed reactor with an internal volume of 250 cm³, and each Raman spectrum of CH₄ hydrate was obtained at an exposure time of 150 s.

2.6. Measurement of chemical oxygen demand (COD)

The chemical oxygen demand (COD) of PVCap, PVP, V2D-BBL structure, and 3D-CON was determined colorimetrically using an HS-COD-MR kit (HUMAS, Korea). The analysis of each sample was performed in triplicate.

2.7. Computational method

To observe the more detailed growth behaviors of CH₄ hydrate in the presence of PVCap unit and the V2D-BBL structure in a micro-scale, molecular dynamics (MD) simulations were performed with GROMACS source code [27]. Three different sets were prepared; Set 1: CH₄ and H₂O molecules only, Set 2: one PVCap unit with CH₄ and H₂O molecules, Set 3: one V2D-BBL structure unit with CH₄ and H₂O molecules. The OPLS-AA model was utilized to describe CH₄ molecules, one PVCap unit, and one V2D-BBL structure unit and the TIP4P-ice model was used to describe H₂O molecules [28,29]. In particular, the PVCap unit and V2D-BBL structure unit were prepared via the LigParGen site using the Mulliken charge obtained by ab initio calculation with the B3LYP hybrid functional and the 6-31G basis set [30-32]. In each set, all molecules were packed using the PACKMOL software, which is specialized in making periodic boundary boxes [33]. For Set 1, only 1602 H₂O and 267 CH₄ molecules were initially packed, whereas, for Set 2 and Set 3, the additives (PVCap unit and V2D-BBL structure unit) were added in the same configuration as Set 1 and repacked. As a result, all compiled periodic boxes had a size of 4.01 × 4.01 × 4.01 nm³. After the system boxes were designed, every set was initially energy-minimized before the main calculations. Subsequently, a short 100 ps NVT calculation was conducted at 260 K for the relaxation of given systems. Then, long 300 ns NPT calculations were carried out at 500 bar and 260 K. The Lennard-Jones interactions of molecules in the system boxes were de-
The 3D-CON and V2D-BBL structures were respectively synthesized following literature-reported procedures \[24,26\]. The 3D-CON was obtained from a reaction between triptycene hexamine (THA) hexahydrochloride and hexaketocyclohexane (HKH) octahydrate in a solvent mixture (ethylene glycol and acetic acid) at 120 °C. The V2D-BBL structure was formed by polycondensation between THA and naphthalene-carboxylic dianhydride (NDA) in polyphosphoric acid (PPA) as a solvent. The resulting 3D-CON and V2D-BBL structures are depicted in Fig. 1. The 3D-CON consists of stable fused aromatic pyrazine rings (Fig. 1a), and the V2D-BBL structure composes of vertically oriented perimeter units (Fig. 1b).

To confirm the structural formation of pyrazine rings in 3D-CON and benzimidazole rings and pyrrolidinone moieties in the V2D-BBL structure, Fourier-transform infrared (FT-IR) and solid-state \(^{13}\)C cross-polarization magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy were employed.

The formation of pyrazine rings was confirmed by the appearance of peaks at 1353, 1458 and 1616 cm\(^{-1}\) in the FT-IR spectrum of the 3D-CON (Fig. 1c). The FT-IR spectrum of the V2D-BBL structure exhibited a C – N – C moiety peak (1378 cm\(^{-1}\)) and C = N bonds (1626 cm\(^{-1}\)) in the benzimidazole ring (Fig. 1c). Furthermore, the appearance of a peak at 1701 cm\(^{-1}\) indicated carbonyl (C = O) bonds in the pyrrolidone moiety.

Solid-state \(^{13}\)C CP-MAS NMR spectra of the 3D-CON and V2D-BBL structure showed four and five well-matched peaks, as expected from the structures, respectively (Fig. 1d). The 3D-CON showed sp\(^3\) bridge carbon (a) and aromatic sp\(^2\) carbons in triptycene (b, c) and pyrazine ring (d, e) peaks. Along with sp\(^3\) bridge carbon (a’), aromatic sp\(^2\) carbon in triptycene (b’, c’) and benzimidazole moiety (d’, e’), the V2D-BBL structure exhibited an additional carbonyl (C = O) peak (f’) and pyrene carbon peak (g’), which are even well-matched with \(^{13}\)C NMR of small model compounds [39]. These results confirmed the formation of the designed 3D-CON and V2D-BBL structures.
X-ray photoelectron spectroscopy (XPS) was conducted to probe the bonding nature of the samples. The XPS survey spectra revealed only carbon (C 1s), nitrogen (N 1s) and oxygen (O 1s) peaks (Fig. S3 and S4). The N 1s spectrum of 3D-CON could be deconvoluted into the main C – N = C in pyrazine ring (398.7 eV) and minor C – NH₂ (399.9 eV) peaks at the edges (Fig. 1e). The deconvoluted N 1s spectrum of the V2D-BBL structure revealed C – N = C and tertiary N at 398.6 and 400.7 eV, respectively (Fig. 1e). These results support the formation of the target structures. The other deconvoluted C 1s and O 1s spectra of both samples agree with the expected structures (Fig. S3 and S4).

The 3D-CON and V2D-BBL structure morphologies were observed using scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM). Both samples revealed a few tens of micrometer grain size and uniform micropores (Fig. S5 and S6).

The porosities of the 3D-CON and V2D-BBL structure were studied by nitrogen adsorption–desorption isotherms measured at 77 K and 1 bar (Fig. S7). Both materials exhibited a steep nitrogen uptake in the low-pressure range (0–0.01), indicating a highly microporous nature [40]. The specific surface areas of the 3D-CON and V2D-BBL structures were similar, 1506 and 1530 m² g⁻¹, respectively. Compared to 3D-CON, the V2D-BBL structure revealed relatively high hysteresis between adsorption and desorption isotherms. This is because the pore surfaces of the V2D-BBL structure have a higher gas binding force than 3D-CON, which is attributable to the highly polarizable perinone groups.

Thermogravimetric analysis (TGA) revealed that the 3D-CON and V2D-BBL structures were thermally stable under both air and nitrogen atmospheres (Fig. S8). The decomposition temperature of both samples was above 823 K. Their high physicochemical stability should be associated with their fused aromatic structures.

### 3.2. Performance of FANs as KHSs

Over the past century, a new breed of KHSs has been extensively developed, including amino acids, nature-derived polymers, ionic liquids, and metal–organic frameworks (MOFs) [41–45]. Given the inherent features of FANs, including periodically distributed heteroatoms, high specific surface area, and structural stability, we expected FANs would have enormous potential as gas hydrate inhibitors.

The onset temperature (T_onset) is the temperature at which gas hydrates start to form during the cooling process at a constant rate and can be detected by an abrupt pressure drop caused by gas hydrate formation (Fig. 2a). The lower T_onset of CH₄ hydrate in the presence of KHSs means better inhibition performance. To examine the inhibition performance of the KHSs used in this study, we compared the T_onset of CH₄ hydrate in the presence of reference polymer-based inhibitors (PVP and PVCap) and FANs (3D-CON and V2D-BBL structure) (Fig. 2b).

As shown in Fig. 2b, the T_onset for pure water was 284.5 K, whereas those for PVP and PVCap were 281.1 K and 277.5 K, respectively, which agreed with results in the literature [44,46]. Notably, the FANs (3D-CON and V2D-BBL structure) demonstrated remarkable inhibition effects (V2D-BBL structure: 277.5 K and 3D-CON: 279.0 K). It should be noted that the T_onset of CH₄ hydrate in the presence of the V2D-BBL structure was comparable to the performance of the PVCap. This was attributed to the unique perinone linkages of the V2D-BBL structure, which is structurally similar to the lactam-based polymers (PVP and PVCap). The experimental results indicated that the V2D-BBL structure could significantly inhibit hydrate nucleation.

To gain insights into the inhibition mechanisms of the V2D-BBL structure and PVCap, molecular dynamic (MD) simulations were conducted. The changes in the potential energies of the three given sets (pure water, V2D-BBL structure unit, and PVCap unit) are illustrated in Fig. 3a. According to previous studies, the growth and dissociation of a given hydrate structure in MD simulations are highly related to the potential energy of the total system [47–49]. In other words, an increase in potential energy indicates the dissociation of the ordered hydrate structure over time. Meanwhile, the gas hydrate structure formation leads to a decline in the potential energy profile over time. Fig. 3a shows that only pure water resulted in the steady growth of the CH₄ hydrate structure. More detailed molecular behaviors during gas hydrate nucleation and growth in each system can be observed in Fig. 3b. A significant amount of blue-colored lines appeared after 100 ns for pure water, which indicates that the identified hydrate structure has abruptly grown from the beginning.

However, the V2D-BBL structure unit and PVCap unit solutions exhibited significantly different behaviors compared to pure water. As shown in Fig. 3a, the potential energies of both the V2D-BBL structure and PVCap increased slightly over time, implying that the hydrate structure was not developed until 300 ns. These trends are clearly visualized in snapshots taken from MD simulations of CH₄ hydrate growth in the presence of the V2D-BBL structure and PVCap (Fig. 3c and 3d). A partial hydrate blob formed temporarily between 0 and 100 ns, but diminished slowly until the end of the simulation. In the presence of the V2D-BBL structure and PVCap, CH₄ molecules gathered readily and thus were prevented from contacting the host water cages. The MD
Fig. 3. Molecular dynamic (MD) simulations. (a) Potential energy profiles of pure water (black), PVCap solution (orange), and V2D-BBL structure solution (purple) from 300 ns NPT calculation. System box snapshots of (b) pure water, (c) PVCap unit and (d) V2D-BBL structure unit during the simulation. Hydrogen atoms of the guest CH₄ are omitted to make snapshots clearly visible. Identification of the hydrate structure was made using the CHILL + algorithm [38].
snapshots shown in Fig. 3c and 3d demonstrate that the V2D-BBL structure and PVCap effectively inhibited the CH₄ hydrate formation by congregating guest CH₄ molecules and affecting the temporary blob hydrate structure.

To investigate interactions between host molecules (water) for hydrate formation and the inhibitor materials, FT-IR spectra of the samples were measured before/after water adsorption in ATR mode. The peak at 1632 cm⁻¹ assigned to the carbonyl bond (C = O) in lactam-ring of PVCap dramatically shifted to 1612 cm⁻¹ after water uptake because charge delocalization transforms C = O bonds to C – O⁻, indicating a decrease in electron cloud density such as the proposed structure in Fig. 4a (bottom) [50,51]. The charge delocalization occurs because the abundant electronegative oxygen pulls the lone pair electrons of the nitrogen. In addition, a peak shift from 1477 to 1482 cm⁻¹ was observed because the C – N – C bond becomes like C = N⁺ – C after H₂O uptake. This charge delocalization enables materials to interact well with water molecules (host), and the PVCap showed good performance as a KHL. Similar peak shifts were found in the FT-IR spectrum of the V2D-BBL structure (Fig. 4b). Peak shifts from 1704 to 1697 cm⁻¹ occurred for the carbonyl (C = O) groups and the C – N – C moiety in the benzimidazole ring, from 1378 to 1382 cm⁻¹. These peak shifts are strong evidence of charge delocalization in the proposed structures, as shown in Fig. 4b (bottom).

Meanwhile, there was no peak shift after water adsorption in the FT-IR spectrum of 3D-CON (Fig. 4c), implying weak interaction with water, and it exhibited a lower performance than other KHS. It is clear that the superior KHL performance of the V2D-BBL structure comes from charge delocalization, which results in strong interaction with the host molecules (water).

The crystal growth and cage-filling behaviors of CH₄ hydrate in the presence of PVCap and V2D-BBL structure were examined using in-situ Raman spectroscopy (Fig. S9) to investigate the inhibition mechanism of the new KHS. For pure water, two distinguishable Raman peaks were observed at 2905 cm⁻¹ and 2915 cm⁻¹, which correspond to CH₄ molecules enclathrated in the large (5₁₂₆) and small (5₁₂) cages of iH hydrate, respectively (Fig. 5a). These two distinct peaks started to appear simultaneously after hydrate nucleation and increased gradually until 150 min, at which CH₄ hydrate formation was almost completed. In Fig. 5a, the peak area ratio of the large (5₁₂₆) to small (5₁₂) cages after 600 min was 3.3, which is similar to the cage ratio in the unit cell of iH hydrate.

Meanwhile, totally different growth behaviors were observed for the CH₄ hydrate in the presence of the PVCap and V2D-BBL structure, even for the same pressure and temperature conditions. The Raman spectra of the CH₄ hydrate in the presence of PVCap indicated that CH₄ molecules started to be readily enclathrated in the small (5₁₂) cages at the early stage of hydrate formation, and the Raman peak for the small (5₁₂) cages at 2915 cm⁻¹ continued to grow gradually (Fig. 5b). However, the Raman peak for CH₄ molecules captured in the large (5₁₂₆) cages was not pronounced during the hydrate growth, and this was associated with the specific inhibition of PVCap on the large (5₁₂₆) cages (Fig. 5b). In the presence of the V2D-BBL structure, a similar cage-specific inhibition behavior was also observed (significant inhibition of the large cages) (Fig. 5c). The slower growth of the small (5₁₂) cages and specific inhibition of the large (5₁₂₆) cages in the presence of the V2D-BBL structure was attributed to its guest-gathering effect and stronger interaction toward host (water) molecules, as revealed in Figs. 3 and 4.

The potential of FANs as KHSs for CO₂ hydrate was further investigated. Both the 3D-CON and V2D-BBL structures showed better inhibition of CO₂ hydrate compared to the polymer-based inhibitors of PVP and PVCap (Fig. S10). Furthermore, the FANs were found to have lower chemical oxygen demand (COD) values (Fig. S11). The lower T السنة for CO₂ hydrate and the smaller COD values of the V2D-BBL structure and 3D-CON indicate that FANs can also be effectively used as KHSs for CO₂ hydrate, which might be formed during the CO₂ injection process, for enhanced oil recovery (EOR) and CO₂ sequestration.
4. Conclusions

Fused aromatic networks (FANs) are one of the unique subclasses of porous organic polymers (POPs), with logically designed structures using various organic building blocks. Their fully fused aromatic systems endow them with extraordinary stability and porosity, which are crucial for practical applications. Herein, those advantages motivated us to employ the 3D-CON and V2D-BBL structure as kinetic hydrate inhibitors (KHIs), which delay hydrate formation in pipelines. Promising KHIs are highly needed because the formation of gas hydrates in pipelines is a significant problem in the oil and gas industries. Here, the V2D-BBL structure showed high potential as an inhibitor and as an alternative to conventional lactam-based polymers such as PVP and PVCap. The $T_{vapd}$ of CH$_4$ hydrate formation for the V2D-BBL structure was found to be 277.5 K, comparable to PVCap. This is because of the abundant perinone moieties, as confirmed by combined theoretical and structural analyses. The periodic incorporation of perinone units and high specific surface area enables it to interact well with the host (water) and guest (CH$_4$) molecules, delaying the formation of CH$_4$ hydrate at low-temperature/high pressure. Since FANs have not been studied as KHIs to date, these findings will be a guide to design a unique class of KHI materials for future industrial applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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