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## Synergy between Covalent Organic Frameworks and Surfactants to Promote

## Water-Based Lubrication and Corrosion-Resistance

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ABSTRACT: Corrosion and friction undulation caused by water-lubricated mechanical devices severely restricts the development of water-based lubricant in practical industries. In this paper, a kind of triazine-based covalent organic framework (TriC) nanomaterial is fabricated as the water-based lubricant additive, and two kinds of surfactant, Coconut diethanol amide (CDEA) and Tween 85 (T-85), were chosen carefully as water-based modifiers, respectively. Then, friction behaviors were evaluated using both composite dispersions as the lubricants, compared to the either component alone, on an SRV-V tribometer under the high contact pressure. The dramatic reduction in friction coefficient (72.2% and 74.4%) and wear rate (98.0% and 95.8%) is come true by adding 0.1 wt% TriC into CDEA and T-85 aqueous solutions with 1% concentration in comparison with the pure water. More importantly, the perfect anti-corrosion on the worn surface of the steel disk is observed during the rubbing process. Subsequently, the preferably competitive adsorption of TriC on the surface of friction pair and two uniquely assembled film configurations depended on surfactant structure are proposed to elaborate the opposite difference in friction and wear resistance as well as perfect anti-corrosion.

**KEYWORDS:** Covalent Organic Frameworks, Anti-corrosion, Synergy Effect, Water-based Lubricant, Surfactant.

## **1.INTRODUCTION**

The large-scale application of hydrocarbon lubricants in modern mechanical components, such as bearings, gears, transmission shafts, etc. has given rise to severe environmental deterioration and durative ecological damage due to the directly discharging or spilling in operation.<sup>1-2</sup> In addition, the resource depletion and energy dissipation of oil lubricants are currently ubiquitous concerning issues. Therefore, alternative green and safe lubricants have attracted unprecedented research interest. Water, in the light of low cost, eco-friendliness, non-inflammability, and super thermal conductivity feature, is considered to be the one of most promising alternatives.<sup>3-6</sup> However, frustration caused by harsh corrosion, low viscosity, high surface tension, and poor friction behavior makes its practicability restricted greatly.

Over the past decade, considerable efforts have been devoted to developing various strategies to solve the above-mentioned issues. Surfactants, natural macromolecules, and polymers have been preferentially considered to modify the viscosity and surface tension to improve the friction.<sup>7-12</sup> For example, Stokes et al.<sup>10</sup> explored the lubrication behavior of polysaccharides solution on the ball-on-disk pairs, revealing that the friction coefficient relied on the viscosity of the polysaccharides solution across the hydrodynamic regime at the constant shear rates of approximately 10<sup>4</sup> s<sup>-1</sup>, yet depended on the adsorbed film properties and lubricant's viscosity across the mixed regime at high shear rates. Li et al.<sup>11</sup> investigated the friction behaviors of fluorinated and hydrocarbon two surfactants on SiO<sub>2</sub>-Mica friction pairs, demonstrating that the surfactant exerts excellent lubrication properties in water solutions via the assembled micelle layers attached on the surfaces. Additionally, the larger hydrophobic attraction of the fluorinated surfactant carbon chain and the stiffness of the micelle layer result in a more intriguing load-bearing capacity. On the

other hand, advanced nanoadditives, such as carbon-based materials, inorganic particles, oxides, sulfides, etc.<sup>13-19</sup> have been exploited to overcome the restriction in low load capacity and thin lubricating film of water. These studies showed that the size of nano additives will allow them to reach the contact region, where nano additives can function as bearing balls (zero and one dimension, 0D and 1D, respectively)<sup>13,14,17</sup> or a buffer coating (two-dimension, 2D)<sup>15,16,19</sup> to reduce the friction stress by coupling with the mending and repair effect for anti-wear. In particular, the inherent nature of the weak van der Waals (vdW) force between two adjacent layers of 2D materials enables the lower shear stress to slide against each other, and the intralayer atoms bound by covalent bonds enables the durability and reliability of the mechanical strength, leading to the super excellent friction behavior. Despite the development of surfactants or analogs and nano additives to exalt the friction properties of water lubricants, the high cost, time-consuming preparation, unfriendly operating process and modified necessity of nano additives, as well as the deficient anti-corrosion properties, and poor degradation of the surfactants engender the great limitation in the practical application of water-based lubricants. Besides, the types of additives suitable for water are deficient, and also the influence of additives on the friction properties of water is still not fully clear.

Covalent organic frameworks (COFs), since it was reported first by Prof. Yaghi and coworkers in 2005,<sup>20</sup> have drawn great attention for application in catalysis, separation, energy fields, drug delivery and so on.<sup>21-25</sup> COFs often are constructed by molecular units consisting of lightweight elements (such as C, N, O, B and H), where the elements are linked by firm covalent bonds. In addition, the topological structure of COFs relies on the geometric configuration of the monomer unit to be grown in either a 2D or 3D manner. Given the planar configuration of almost all the molecular

units, the 2D layered COFs are easiest to be attained under the drive of spontaneous  $\pi$ - $\pi$  stacking forces, which triggers the inspiration to achieve novel water-based additives. To the best of our knowledge, COFs used as water-based additives have been scarcely reported. The fact is that a) the fast degradation and decomposition of COFs linked by boronate ester bonds and imide bonds into water represents the most popular bonding mode, b) the high hydrophobicity of COFs linked by C-C bonds weakens the dispersibility and stability of additives, and c) the weak affinity of steady COFs on the friction pair surface is unfavorable to the formation of protective film. Therefore, overcoming the intrinsic limitation of COFs and investigating the friction properties of COFs for use as water-based additives is of great interest and is challenging.

Consideration on the water-based additives over the past researches, however, has mainly focused on either surfactants or nano materials, and thus their contribution to mitigating friction is donated individually. We believed that combining surfactant with nano additives in the water-based lubricant would produce the cooperative and cofunctional act on the friction properties, due to less attention paid to the combining surfactants and nano additives. Herein. we choose C<sub>3</sub>-symmetric 2,4,6-trichloro-1,3,5-triazine and melamine monomers to construct a 2D conjugated triazine-based covalent organic frameworks (TriC) by the solvothermal reaction shown in Scheme 1a and 1b. The covalent C-N linkages among the monomers ensures the stability of the skeleton in water and the mechanical strength of the as-prepared TriC. The triazine ring feature can not also strengthen the interaction, in virtue of hydrogen bond formation, between the TriC and water molecules for dispersion, but also can enhance the affinity of TriC on the friction pair due to the rich lone electronic pairs in N element, as shown in Scheme 1c. Meanwhile, in order to better reflect the

aims at achieving cooperation and cofunction, several surfactants were well selected to co-function with the TriC based on the view of molecular structures in Fig. S1. Because the molecular structure determines the type and strength of the interaction between the surfactant and guests including the steel disk, additives, and water, the premeditation is quite necessary to promote the friction reduction, anti-wear, and anti-corrosion of water, especially in anti-corrosion, since corrosion is the fatal problem limiting the application of water-based lubricants in metal mechanical components. As expected, the lubricant systems combining the TriC with surfactants exhibit much better tribological performances than either of the single ingredients. Especially in CDEA and T-85 lubricants with TriC additive, the synergy effect not only strengthens the resistance of friction and wear, but also perfects the anti-corrosion ability, upon water as a base lubricant. Versatile explorations were performed and found that a) the synergy effect enhances the wettability, improving the overspreading of lubricant on the surface of the steel disk and toughness of lubricating film, and b) the preferentially competitive adsorption of the TriC on the surface of the steel disk is the key to promoting the friction properties and anti-corrosion, which are better than those of CDEA and T-85. Eventually, based on these results, the lubrication mechanism of the synergistic interaction to enhance the friction, wear and anti-corrosion of water was proposed.



**Scheme 1**. (a) Schematic representation of reaction formula of TriC; (b) Stick-ball structure of Melamine and Cyanuric chloride monomer, respectively; (c) Four pores of space-filling diagram of TriC, H atom is omitted.

### 2. EXPERIMENTAL SECTION

**2.1 Preparation of Triazine-based Covalent Organic Frameworks (TriC**). Unless stated, all chemicals were used without further purification. In a typical experiment, the suitable amount of melamine (1.2 mmol, 1.512 g) was measured and added into *N,N*-dimethylformamide (DMF, 70 mL) solvent with triethylamine (Et<sub>3</sub>N, 3.0 mL), the mixture was stirring manually under sonication for 10 min, followed with cyanuric chloride (1.0 mmol, 1.845 g) adding, the resulting mixture was sonicated with intermittent stirring for 30 min to gain a gel. The gel was sealed in a Teflon-lined stainless steel autoclave and heated to 100 °C for 24 h. After cooling, the light yellow solution was poured into 500 mL deionized (DI) water with sonication for 30 min, the white precipitate was isolated by centrifugation at 5000 rpm and rinsed with DI water several times to remove the residuals and solubles, then freeze-dried to collect the

white powder. The as-prepared triazine-based covalent organic frameworks was denoted to TriC.

**2.2 Preparation of Dispersion Lubricants**. The solutions of various surfactants were prepared by measuring 10 wt% surfactant into each glass vessel (30 mL) with 10 mL deionized water in. After shaking and sonication, each solution was transparent and liquid. Then, TriC (0.01 g) was measured carefully and transferred into each solution and pure water, each mixture was treated by sonication for 3 hours to give dispersion lubricants. The solution and pure water without TriC were used as references.

**2.3 Adsorption Test**. The surface of steel disks (AISI 40300 stainless steel,  $\varphi = 24$  mm × 7.9 mm) used to test, firstly, were polished using 800 and 1200 grit SiC abrasive paper, then, followed with acetone wash (50 mL × 3 times) under the mild sonication for 2 min each time to get rid of the adsorbed water and abrasives. When final treatment was finished, the steel disk was taken out one by one, and blown dry with nitrogen flow quickly, then immersed into the corresponding test solutions for 5 min. Finally, the steel disks were taken out again and rinsed with absolute alcohol to remove the unadsorbed and unstable stuff as well as water, subsequently, and blown dry with nitrogen flow for XPS test.

**2.4 Wettability Test**. The surface of steel disks used to test were treated according to the procedure of adsorption test, only the immersion time was set up for 10 min. After blown with nitrogen flow, a droplet of the DI water having volumes of 4.0  $\mu$ L was put onto the surface of steel disk treated. The contact angle was determined automatically on the basis of a contour curve-fitting method using the software. Three sites on the same surface were chosen to repeat the contact angle measurements for either sample. **2.5 Corrosion Test**. The surface of steel disks used to test were treated according to the procedure of adsorption test, only the immersion time was set up for 48 h at 25 °C.

#### **ACS Applied Nano Materials**

After done, the steel disks were taken out again and rinsed with absolute alcohol to remove the unadsorbed and unstable stuff as well as water, and blown dry with nitrogen flow for observation.

**2.6 Characterization**. Powder X-ray diffraction (XRD) pattern was obtained on a DMAX U1TIMA IV using Cu-K $\alpha$  radiation ( $\lambda$ = 1.54056 Å) over the 2 $\theta$  ranging from 5° to 80°; The chemical states were explored by X-ray photoelectron spectroscopy (XPS, Nexsa, Thermo Fisher Inc); The morphology, element mapping and high resolution micro structure were observed by field emission scanning electron microscope (FESEM, FEI Quanta FEG 250, 20 kV), and transmission electron microscopy (TEM, FEI Tecnai G2 F20, 200 kV); The chemical band was determined by Fourier transform infrared spectra (FTIR, Perkin-Elmer, 400-4000 cm<sup>-1</sup>); The optical photographs of corrosion surface were taken by optical microscope (OLYMPUS -BX53M); The contact angle tests were recorded by an optical contact angle goniometer (Atteneion, Biolin Scientific, Sweden); The size distribution was measured by particle sizer and zeta potential analyzer (NanoBrook Omni, 0.3-10 µm).

**2.7 Friction Test**. The friction tests were performed on the reciprocating friction and wear tester (optimal-SRV-V, Germany) using the ball-on-disk apparatus, at the normal load of 100 N, frequency of 25 Hz, amplitude of 1 mm, and duration time for 30 min. For each trial, a running-in process was employed at 50 N for 30 s, and at least three times for each trial were conducted to ensure repeatability. The upper ball of AISI 52100 steel ( $\varphi = 10$  mm), and the lower disk of AISI 30400 stainless steel ( $\varphi = 24$  mm × 7.9 mm) with the hardness about 700-800 HV were chosen to be tribo mates, due to such two stuff wildly applied into the practically mechanical parts, such as bearing, gear, turbine, transmission, etc. The wear volumes of the worn surface on

the lower friction pairs were measured with a 3D profiler (BRUKER-NPFLEX). The morphology of worn spots was observed by SEM, and the chemical composition of the surface of worn spots was determined by XPS. The mechanical properties of wear scars were measured on a nanoindenter (Hysitron TI-950, America) with a Berkovich indenter. Yet, a peak load 3 mN and a depth of 30 nm were applied with a loading and unloading rates were both 0.1 nm s<sup>-1</sup> for three times at different locations.

#### **3. RESULTS AND DISCUSSION**

3.1. Structure and Chemical Property. The crystalline structure of the TriC was determined by powder X-ray diffraction (XRD) and plotted in Fig. 1a. The diffraction peaks at  $2\theta = 10.4^{\circ}$ , 20.7° and 27.4° can be ascribed to the (010), (220) and (001) planes, indicating that the TriC exhibits a typical 2D layered structure with an interlayer distance of 0.32 nm. The featured chemical bands were analyzed by the FTIR spectra shown in Fig. 1b. The two adjacent peaks at 3376 and 3225 cm<sup>-1</sup> belongs to the stretching vibrations of N-H, and the peaks at 1537 and 1227 cm<sup>-1</sup> can be ascribed to the stretching vibrations of C=N and C-N, respectively.<sup>26</sup> The peak at 808 cm<sup>-1</sup> is attributed to the breathing mode of the triazine ring (inset).<sup>27</sup> X-ray photoelectron spectroscopy (XPS) was conducted to investigate the chemical structure and composition. The survey spectrum in Fig. S2 clearly shows C and N elements at the binding energies of 286.8 eV and 399.2 eV, respectively, as well as a faint O peak at 500.1 eV. The C1s high-resolution spectrum in Fig. 1c can be fitted into four chemical species at 284.8 eV, 286.0 eV, 287.9 eV and 289.8 eV, corresponding to C-C, C-N, C=N and C=O, respectively.<sup>26,28</sup> Furthermore, the N1s spectrum in Fig. 1d can be deconvoluted into two peaks at 399.7 eV and 398.6 eV, attributing to the N-C and N=C chemical species, respectively.<sup>29</sup>



**Fig. 1** The structure and chemical properties characteristics (a) XRD pattern; (b) FTIR transmittance, the inset is core unit; (c) and (d) XPS spectrum of C1s and N1s of TriC, respectively.

The morphology of the TriC was surveyed by SEM and TEM images in Fig. 2. The SEM image shown in Fig. 2a reveals the layered structure with the fluctuant and flexible nature, and the bumpy surface. The elemental mapping image in Fig. 2b shows the homogeneous distribution of nitrogen throughout the skeleton. The TEM image exhibits the flexible and irregular shapes of nanosheets with the curled edge in Fig. 2c, and Fig 2d presents the distinct multip-sheets structure, where a number of bright spots indicate a porous feature coinciding with the illustration mold in Scheme 1.<sup>30</sup> Besides, the size distribution of the TriC as function of the intensity was measured by a particle sizer and zeta potential analyzer and shown in Fig. S3. The average size is estimated to be 3078 nm, corresponding to the concentration of 0.1

wt%, and the asymmetric size range from 100 nm to 10  $\mu$ m can be ascribed to the irregular feature of the sheets.



**Fig. 2** (a) SEM image; (b) Mapping distribution of N element; (c) TEM image; and (d) high resolution TEM of TriC, respectively.

**3.2 Dispersity and Stability.** The dispersity and stability of nano additives is of utmost importance to ensure their proper function in practical friction trial. Thus, the sedimentation experiments of TriC sheets in pure water were recorded and shown in Fig. S4. It is clear that the TriC is highly dispersible in pure water after sonication, but the period of stability is very short (Fig. S4b). Therefore, several surfactants were introduced into the system, and the results revealed that CDEA and T-85 were the best candidates for the improvement of the stability of the TriC (Fig. S4c). Only a slight sedimentation phenomenon emerges, even after settlement for one week (Fig. S4d). It can be speculated that the proper structure of the surfactant is quite efficient to solving the problem of the dispersity and stability of the TriC in water.

**3.3 Friction and Wear.** The commensurable evaluations on the friction behaviors of water lubricants with and without the TriC nanoadditive in surfactant aqueous

Page 13 of 35

#### **ACS Applied Nano Materials**

solution were performed on the ball-on-disk apparatus. Firstly, the friction behaviors of pure water and various surfactant aqueous with a 1% constant mass are investigated. The resulting coefficient of friction (COF) curves are plotted in Fig. 3a, where T-85 gives the lowest COF and smooth evolution, and a comparable COF emerges for CDEA and BS-12. The others present a bit better or worst COF than that of pure water. Thereafter, the wear volumes of all tested samples were calculated and compiled in the histogram in Fig. 3c, where CDEA, T-85 and BS-12 exhibit the optimal candidates among the other lubricants for anti-wear application. And Fig. 3f shows that the highest decrease is up to 93.0% for CDEA, T-85 secondary, up to 92.2%, and followed closely by BS-12, up to 90.5%. It is quite surprising that, for three surfactants, such excellent properties of friction-reduction and anti-wear properties appears. Subsequently, SEM images of the worn surface of all tested samples were shown in Fig. 4, it is clear that compared to pure water (Fig. 4a), surfactants, to a certain degree, exert an effective function in inhibiting corrosion (Fig. 4b-h). Given the anti-friction and anti-wear results from the analysis, much attention was paid to the best candidates, CDEA, T-85, and BS-12. Despite the excellent friction behaviors unearthed, the existing corrosion spots is still needed to be concerned. In particular, for the intramolecular ionic structure of BS-12, more and larger spots were observed on the worn surface due to the salt effect from such an unique structure and tribo-chemical reaction. The obvious corrosion spots along with the fatigue wear for CDEA were observed, while the plastic deformation along with the fatigue wear was dominated for T-85, indicating the structure-dependent corrosion and insufficient intensity of the lubrication film composed of surfactant molecules during the sliding friction. In practical mechanical applications, such corrosion spots can cause the gradual destruction risk or even instantaneous disaster.



**Fig. 3** COF curves of water and surfactant solutions without TriC (a) and with TriC (b), respectively; (c) and (d) the histogram of wear volume without TriC and with TriC, respectively; (e) and (f) the average COF and the wear rate comparison without and with TriC, and insets are graphs magnified on reduction of wear rate.

Under the guidance of the above-mentioned frictional results, the TriC was introduced into the system, then the cooperation and cofunction effect between TriC and surfactants on the friction behaviors of the water lubricant was undertaken with an additive content of 0.1 wt%. Fig. 3b shows the COF curves, where the improvement in the COF from mild to visible was presented compared to individual origin (Fig. 3a). Furthermore, the histogram of the wear volume achieved with the TriC was plotted in Fig. 3d to further unveil the apparent amelioration in the wear-resistance. Herein, Page 15 of 35

attention was still paid to the above three optimal candidates. Comparison of COF with and without TriC additive firstly was performed in Fig. 3e, in which the differentiated value in friction reduction implies the different synergy abilities and intensities due to the structural differences. Under the condition of only dispersing TriC into water, the improvement can be attributed to weakening the shear force owing to the 2D layered structure of TriC as lubrication layer.<sup>31</sup> Opposite to the steady and smooth COF of either surfactant aqueous or blends, the COF curve of water after introducing the TriC is more overtly fluctuant and waved. It is speculated that the choppy structure with the bumpy surface forms the inferior lubrication film with low intensity and integrality, and as a result, that film is easy to be peeled off or cracked during high load sliding. However, the high affinity between the TriC and iron atoms/ions fast replenishes such a loss, leading to the unstable curve is displayed. Subsequently, synergy effect was further verified by the variation of wear rate under with and without the TriC additive in Fig. 3f. Related to the decreased value of 45.9% achieved for water with the TriC, the decreased values of 70.9% for CDEA, 45.8% for T-85 and 20.6% for BS-12 are realized on the basis of each original component, respectively, indicating that the synergy between the TriC and surfactant is correlated with the molecular structure of surfactant.



Fig. 4 SEM images of worn surface lubricated with pure water and various surfactant solutions without (a-h) and with TriC additive (a'-h'). The white bar scale is 50  $\mu$ m for all.

Notably, SEM images of worn surface lubricated with TriC additive present the consolidated anti-wear and anti-corrosion effect in Fig. 4a'-h'. Especially for CDEA and T-85 (Fig. 4b' and 4c'), not only the corrosion spots, but also the fatigue wear are all invisible compared to the original image. BS-12 inhibits better corrosion than the original sample, but its inhibition ability is still not perfect. For pure water, although the distinct furrow with a slight deformation was observed, the less corrosion appears than in the original (Fig. 4a'), which indicates that the TriC has an outstanding anti-corrosion ability. Thereby, the analysis results of the worn surface combining

pure water and the surfactant aqueous with the TriC additive presents an appealing synergy effect, reflecting at anti-corrosion and anti-fatigue wear.

On the basis of the above results, the variation of TriC additive content in CDEA and T-85 surfactant aqueous on the friction behaviors was performed to get insight into the structure-depended synergy effect, respectively. Fig. 5a shows the varied average COF as a function of the TriC concentration in CDEA and T-85 aqueous solutions, respectively. Both solutions have the same best concentration of 0.1 wt%, but CDEA presents a slightly inferior COF throughout the range relative to the one of T-85. On the contrary, in the capacity of anti-wear, CDEA is more superior than T-85 (Fig. 5b). Such opposite frictional performance between CDEA and T-85 fully demonstrates the structure-dependent synergy effect. Reports have revealed that a linear and star-shaped surfactant performed different micelle aggregate morphologies that relied on the headgroups, chain length and genre, concentration, etc.<sup>32-34</sup> Thus, we believed that the intrinsic structural difference between CDEA and T-85 leads to the dramatic synergy effect.



respectively; (b) the wear volume vs TriC concentration in CDEA and T-85 solutions, respectively.

## 3.4 Investigation of Synergistic Action Between the TriC and Surfactant.

3.4.1 Adsorption. Adsorption tests were carried out to explore the contribution of the

TriC additive to the formation of adsorbed film by XPS analyses. Fig. 6 displays the XPS analyses of the surfaces of the as-treated steel disk. N1s spectrum in Fig. 6a certifies that the TriC additive can compete with CDEA and T-85 molecule to adsorb on the steel surface. The more positive shift in the binding energy (400.9 eV) than that of the original TriC additive (398.9 eV) suggests that an intense interaction between the triazine units and metal iron atoms and/or ions appears. That is, the lone pair electrons from the triazine units coordinate to the 3d orbit of the metal iron. The resulting interaction can not only stabilize the adsorbed-film, but also inhibit the corrosion, due to the repression effect of oxygen coordinated to the 3d orbit of the metal iron. From the O1s spectra in Fig. 6b, the same binding energy (532.6 eV for C-O and C=O) is observed for T-85 with (brown line) and without (pink line) the TriC additive, while the proportion of Fe-O species is decreased remarkably under with the TriC, indicating that there is no striking interaction between T-85 and TriC, that is, the synergy effect is weak, and strong competition occurs on the adsorbed-film, due to the decreased content of Fe-O species.<sup>35</sup> Contrarily, the relative strong interaction between CDEA and TriC exists, owing to the positive binding energy shift from 531.7 eV to 532.4 eV, which may be ascribed to the hydrogen bonding interaction. From the Fe2p spectra in Fig. 6c, it can be seen that the negative shift in the binding energy of the oxidized state is more pronounce relative to that of either originals, while the TriC additive exists. The rank of the shift is T-85 (0.41 eV) <CDEA (0.48 eV)  $\leq$  H<sub>2</sub>O (0.57 eV), which further confirms the competitive adsorption and synergy effect between the TriC and surfactant. And, the deviation in the shift value also implies the structure-depended synergy.

3.4.2 Wettability. The lubricating efficiency is dictated by the wettability of the lubricant on the metal interface, where an appropriate wettability is a prerequisite to

form the durable lubrication film. Therefore, the effect of the TriC on the wettability of CDEA, T-85 and pure water lubricant systems was evaluated by the measurement of the contact angle (CA). The variations in the CA are pictured and showed in Fig. 6d. Undoubtedly, compared to pure water (73.3°), CDEA (26.5°) and T-85 (58.6°) cause the CA to decrease remarkably, due to the nature of surfactant reducing surface tension.<sup>36,37</sup> The superiority of CDEA could be ascribed to its polar groups (-OH and -CO-N groups), which can provide highly strong hydrogen bonding interaction associated with water molecule.<sup>38</sup> However, the tribrachia polyether chains of T-85 offers the dominant polar groups (C-O-C) that is weakly polar, which also weakens the hydrogen bonding interaction.<sup>39</sup> While TriC intervened in the systems, as expected, the CA is distinctly decreased relative to that of the original ones. The decreasing CA rank is water  $(15.4^{\circ}) > T-85$   $(10.5^{\circ}) > CDEA$   $(5.2^{\circ})$ . The reason is that the TriC can coordinate to the surface of the metal disk to create an adsorbed layer, where the intermolecular hydrogen bonding interaction between the triazine unit constructed TriC and H<sub>2</sub>O molecules exists, leading to the enhanced wettability. More importantly, the comparison of the decreased CA value declares that TriC has the more powerful competitive adsorption, which enables the achievement of excellent anti-corrosion. And, the smaller value gap indicates that the synergy effect is more forceful between the TriC and CDEA than T-85. This result is also consistent with the analysis in adsorption.



**Fig. 6** XPS spectra (a) N1s; (b) O1s; (c)  $Fe2p_{3/2}$ ; and (d) wetting angle of surface of steel disks treated by water, CDEA and T-85 with and without TriC.

3.4.3 Corrosion. In order to further ascertain the anti-corrosion capacity of the TriC, the corrosion test was performed by soaking the polished and cleaned steel disk into the surfactant aqueous solutions with and without the TriC additive for 48 h, as well as pure water as the reference. The optical photos obtained after the corrosion tests were presented in Fig. 7. It is quite clear that the large areas of serious rust stains with serious were produced on the surface of the steel disk upon treatment with water (Fig. 7b), due to the chemical corrosion reaction that occurred between the oxygen element from water or air and the metal iron. For the surfactant aqueous solution, a slight trace of rust stains along the scratch and a few corrosion pits are observed for CDEA in Fig. 7c, while an obvious flocculent distribution of rust stains throughout the surface is visible for T-85 in Fig. 7, implying that the anti-corrosion ability of the surfactant is

Page 21 of 35

structure-dependent. The fact is that the unique structure of CDEA can form the compact micelles with polar groups acting as the shell and intertwined alkyl chains acting as the core under such high concentrations (1 wt%). Thus, these micelles can adsorb on the surface of the steel disk by polar groups (especially -OH) bonding with metal atoms or ions, and with the assistance of the hydrogen bonding interaction between the adjacent intermicelles, to create a dense and compact adsorbed-film, where the permeation of the corrosion factor is restrained to a large extent. While for T-85, the structural feature of the triple long chains composed of polyether and alkyl species makes its micelles less compact and larger. In addition, considering the relatively weak interaction between the C-O-C groups and metal atoms, the compactness and density of the adsorbed-film is discounted, leading to the inferior inhibition on corrosion. In the presence of the TriC additive, the smooth and clean surface that was observed for CDEA (Fig. 7d), and T-85 (Fig. 7f) was the same as that observed for the blank (Fig. 7a), and the explanation is that the TriC prefers to competitively adsorb on the surface of the steel disk as a prime protective layer, where a great synergy function with the surfactants was rendered synchronically. This observation is a good agreement with the result of the adsorption test. It is the truth that conjugated triazine ring, through the TriC sheet, can feed the dense lone pair and delocalized electrons donating to the 3d orbit of the metal iron, resulting in a powerful interaction on the entire contact surface between the TriC sheet and metal disk. Consequently, this interaction coupling with the synergy effect intensely boosts the corrosion resistance.



**Fig. 7** Optical photos of corrosion surfaces of steel disks treated by (a) blank; (b) water; (c) CDEA; (d) CDEA + TriC; (e) T-85; and (f) T-85 + TriC. Red ring represents corrosion pit. The corrosion areas magnified 10 times for all photos.

3.4.4 XPS analysis of the worn surface. To further understand the improvement of the TriC additive on friction properties, XPS analysis of worn surface lubricated with CDEA and T-85 solution with and without TriC was measured and shown in Fig. 8. The peak of N1s at 399.9 eV can be ascribed to C-N and C=N (Fig. 8a), implying the existence of the adsorbed-film from the TriC additive. However, the peak of C-N for CDEA is located at 400.2 eV. Note that there is an obvious peak at 402.8 eV, which corresponds to the N-O model,<sup>40</sup> and such a peak only was observed for the worn surface lubricated with the TriC additive. It can be speculated that N from the TriC reacts with the O from O<sub>2</sub> or H<sub>2</sub>O under the tribochemical reaction. This reaction can effectively suppress the reaction between the oxygen element and the metal iron, leading to the excellent anti-corrosion ability. This point can prove that the ratio of the Fe-O peaks observed from the O1s spectra significantly decreased for the solution with the TriC additive, compared to that with pure CDEA and T-85 solution (Fig. 8b). The peak of Fe2p can be deconvoluted into four subpeaks at 707.4 eV, 709.5 eV,

 711.8 eV, and 713.7 eV, which corresponds to Fe(0), Fe(II) and two kinds of Fe(III) (Fig. 8c).<sup>41,42</sup> The amount of each Fe species in the different systems was calculated according to the integral area and is listed in Table S1. Based on the area proportion of each subpeak in Table S1, it can be read clearly that the ratio of Fe(II) in the worn scar lubricated with the TriC additive is higher than that without the TriC, in the same surfactant solution. This result indicates the existence of interaction between the TriC and Fe atoms and/or ions, by which the lubricating film can be built up as a protective layer that not only reduces the friction and wear, but also inhibits the corrosion very well.



**Fig. 8** XPS spectra of worn scars lubricated with CDEA and T-85 solution without and with TriC. (a) N1s; (b) O1s; and (c) Fe2p.

3.4.5 Nanoindentation of the worn surface. Deeper insight on the contribution of TriC to the lubricant film was explored by nanoindentation testing the mechanical properties of the wear scar. The typical load-displacement curves obtained from the different wear scars lubricated with CDEA and T-85 solution with and without the TriC was plotted in Fig. 9. From Fig. 9a, it can be observed that the elastic modulus (Er) of the wear scar lubricated with pure water is similar with that of steel substrate,<sup>43</sup> while the hardness decreases by up to 43%, which is due to the fact that the critical corrosion of the wear scar occurs upon pure water as the lubricant. In Fig. 9b, comparisons reveals that T-85 has a higher elastic modulus, and almost an equal one is presented for CDEA and TriC, while the hardness of TriC of 11.87 GPa is lower than that of T-85 and CDEA, and more higher than that of pure water. Such results suggest that the TriC acts as the lubricant film to inhibit the corrosion, as shown in Fig. 4a'. Interestingly, when the TriC encounters with CDEA and T-85, the elastic modulus of both is striking decline up to the similar values in Fig. 9c, further corroborating the competitive adsorption of TriC upon forming the lubricating film. In addition, the much smaller hardness value of CDEA plus the TriC also implies a much stronger synergy effect, due to the hydrogen bonding interaction. Eventually, from the comparison values in Fig. 9d, due to the decreased rank of the elastic modulus and the hardness with the introduction of the TriC into system, it can be concluded that the TriC indeed prefers the competitive adsorption on the surface of the steel disk serving as a lubricating film assisting with CDEA and T-85 micelles, and the film is quite stable during the whole sliding time. The difference, especially in the hardness, also embodies the structure-dependent synergy.



**Fig. 9** Representative force-displacement curves of nano indentation tests with the wear scars lubricated with (a) raw steel substrate and pure water; (b) T-85, CDEA surfactants and TriC additive; (c) T-85 and CDEA blends with TriC additive; (d) comparisons of elastic modulus (blue bars) and hardness (light pink).

### 3.5 Lubricating Mechanism.

Based on the above analyses and friction and wear behaviors, the mechanism model of the TriC promoting the friction behavior of CDEA and T-85 surfactant aqueous lubricants, compared to pure water, is illustrated in Fig.10. Fig. 10a shows the ball-on-disk model and the asperity contact between the tribopairs. In the case of lubrication with pure water, authentic contact between the two friction pairs appears (Fig. 10d), due to the lubrication film consist of the water molecule with the only thickness of ~70 nm,<sup>44,45</sup> which makes it great easy to be breached under a high normal load. Consequently, such bald sliding contact not only leads to wide and deep grooves, but also causes a severe tribochemical reaction that can facilitate the

corrosion activities on the wear surface (Fig. 4a). With regard to the CDEA solution lubricant, the external polar headgroups (-OH) from the micelle, firstly, could grow onto the surface of the steel disk by the adsorption interaction. Then, with the assistance of hydrogen bonding interaction between adjacent intramicelles, the dense and compact assembled film is created on the surface of metal disk (Fig. 10b and 10e). However, for the T-85 solution lubricant, the tribrachia structure discounts the compactness of the micelles, but increases the flexibility. Without doubt, these features are also inherited by the assembled film of the T-85 micelles (Fig. 10b and 10e). Apparently, both the unique assembled structures based on the micellar configuration can greatly reduce friction and wear when used as the lubricating film. However, as the difference in the compactness and flexibility of assembled films, the opposite friction-reduction and anti-wear behavior is observed (Fig. 3e and 3f). Note that under the high load, the assembled film is also easily damaged due to the tribostress and triboheat, resulting in the elastic deformation/damnification. Afterwards, the damnification triggers the occurrence of corrosion that further is deteriorated by the tribochemical reaction (Fig. 4b and 4c). Once upon the TriC introduced into systems, the coordination interaction of the lone pair/delocalized electrons from the triazine unite to 3d orbit of iron is more preferable than the adsorption interaction of CDEA and T-85. This preference facilitates the formation of the adsorbed film of the TriC on the steel disk, firstly. However, due to the wavy structure of the raw TriC, the solidity and tightness of the adsorbed-film can be destroyed or peeled off by the tribostress during the rubbing process, leading to the insufficient lubrication (Fig. 4a'). When TriC encountered with CDEA and T-85, the synergy effect can be triggered under the vdW force and/or hydrogen bonding interaction, which is confirmed by the morphology, ingredient evolution and

elemental distribution of the composite consisting of the TriC and surfactant compared to the raw TriC in Fig. S5. Eventually, the TriC can first adsorb onto the surface of the steel disk to generate the tough and tight foundation layer, where the assembled micelle layer of CDEA and T-85 can be set up, respectively (Fig. 10c). This composite film pattern can better protect the wear surface and buffer the friction stress as well as resist the corrosion (Fig. 10d). Therefore, the synergistic effect between the TriC and surfactant endows water with the excellent friction and anti-corrosion properties.



**Fig. 10** Schematic diagram of lubricating mechanism. (a) sliding and contact models; illustration of formation of micelle film (b) and composite film (c) on the sliding surface, respectively; (d) contact configurations of asperity peaks under the water, micelle film and composite film, respectively; (e) hydrogen bonding shapes between

micelles of CDEA and T-85 surfactants, respectively.

## **4.CONCLUSION**

In this paper, Triazine-based covalent organic frameworks (TriC) was prepared as a kind of additive cooperating with two kinds of surfactants (CDEA and T-85) to promote the friction properties and anti-corrosion of water. Cooperation between the TriC and surfactant realizes the great dispersion and longer stability of the TriC into water. After the friction behavior tests, reduction in friction coefficient and wear rate (72.2% and 98.0%) for the blended lubricant of CDEA and TriC, and (74.4% and 95.8%) for the one of T-85 and TriC were achieved, respectively, compared to the pure water. Meanwhile, in anti-corrosion respect, the composite system also presents an unequaled potential. The experiments performed in adsorption, wettability, and corrosion confirm that the synergy effect between TriC and surfactant exists, which plays a vital role in the improvement of friction properties and the perfection of anti-corrosion. Under the synergy effect, the lubricating film features the dependence of assembled configuration on the structure of surfactant micelle, illuminating the difference of friction behavior and anti-corrosion of two kinds of surfactants. This work firstly confirms the potential and synergy action of covalent organic frameworks nanomaterials as additive cooperating with unique surfactants in anti-friction, anti-wear, and anti-corrosion of water-based lubricant, which may accelerate the progress of water-based lubricant in practical industry.

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Notes

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## **Graphic Abstract:**

