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# Anti-migration and Combustion Catalytic Performances of Ferrocenyl Compounds of Anilines and Alkylamines Synthesized by Click Reaction

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**Abstract**. To enhance anti-migratory performance and combustion catalytic activities of neutral ferrocene-based burning rate catalysts (BRCs), nine ferrocenyl 1,2,3-triazolyl compounds of anilines and aliphatic amines (Fc-ATAZs, 1–9) were synthesized by click reaction and characterized by NMR, UV/Vis, FT-IR, and MS. TG and DSC studies confirmed that the Fc-ATAZs are highly thermal stable. Cyclic voltammetry results implied that 1 and 6 are reversible redox systems. The anti-migration and anti-volatility tests showed that the Fc-ATAZs are low-migratory and low-volatile compounds.Combustion catalytic ac-

### Introduction

Ferrocene is a classic organometallics and its discovery was known as a milestone in the history of organometallic chemistry due to its high thermal and chemical stabilities, excellent electrochemical properties and easy modification.<sup>[1]</sup> Ferrocene and its derivatives have been widely applied in industry, agriculture, medicine, aerospace and other fields.<sup>[1]</sup> One of their important applications is to use them as combustion modifiers in car and rocket engines to improve combustion efficiency of fuels. Alkylferrocenes are usually utilized as additives in composite solid propellants to enhance combustion rates and decrease pressure index of the propellants.<sup>[2]</sup> Initially, mononuclear ferrocenyl compounds such as n-butylferrocene (NBF) and tert-butylferrocene (TBF) were employed in the propellants as burning rate catalysts (BRCs). It is found, however, that these compounds exhibit high-volatility during fabrication of the propellants and high-migratory trends during long-time storage of the propellants, due to their lower molecular weights.

Then a series of dinuclear ferrocenyl derivatives including 2,2-bis(ethylferrocenyl)propane (catocene), 2,2-bis(butylferrocenyl)propane (BBFPr) and 2,2-bis(butylferrocenyl)pentane (BBFPe) were developed, among them catocene was commercialized due to its excellent combustion efficiency, lower mi-

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tivity results of the Fc-ATAZs revealed that they are highly active for promoting thermal disintegration of AP, RDX and HMX. Compounds **3**, **2** and **8** can increase released heats of AP, RDX and HMX, respectively, by 132%, 112% and 36%, respectively, being the highest in each case. Most of them are more active than the reported analogs derived from phenols and benzoic acids. They, except **9**, are more active than catocene and can be used as potential BRCs in composite solid propellants.

gration tendency and acceptable synthetic costs.<sup>[3]</sup> Although catocene is currently applied broadly in composite solid propellants as BRC, some unavoidable problems still exist. It was reported that the mixture of catocene and ultra ammonia perchlorate (AP) exhibited highly electrostatic sensitivity during the propellant curing and in some cases gave rise to dangerous issues.<sup>[3a]</sup> Catocene can migrate slowly to the surface of the propellant grain to form a brown shell, which can be ignited easily. The enlargement of the burning area will increase gas pressure in the combustion chamber and lead to unsteady combustion process of the propellants, and lastly could pose a potential explosion danger towards the solid rocket engine.<sup>[4]</sup>

In last few decades researchers have taken great efforts to overcome high-migration and high-volatility problems of the marketed ferrocene-based BRCs by means of diverse approaches including, for examples, developing ferrocenyl group-grafted polymers and dendrimers, introducing concepts of coordination chemistry and ionic liquid, increasing molecular weights of the ferrocene-based BRCs by synthesizing polynuclear ferrocene derivatives, incorporating polar atoms (O and/or N) in the alkylferrocene molecules to improve their molecular polarity and interaction with other components in the propellants.<sup>[5-9]</sup> The famous one is butacene, which was synthesized by grafting ferrocenylalkylsilyl groups to hydroxylterminated polybutadiene (HTPB) main chain to form a prepolymer, which can be cross-linked with TDI to form elastomers in the propellants. In this case, butadiene played roles as both ferrocene-based BRC and modified binder in a composite solid propellant and has been marketed in European and Latin America.<sup>[5]</sup> Researchers also modified HTPB polymeric molecules with ferrocenyl groups by other methods and the composite propellants containing ferrocene-modified HTPB prepolymers exhibited excellent combustion properties.[6a,6b] F. J Xiao and L. Wang et al. synthesized ferrocenyl group-

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incorporated polymers and dendrimers and found that they are low- and even non-migratory ferrocenyl derivatives.<sup>[6c–6f]</sup> *H. Y. Zhao, Y. F. Yuan* and our groups prepared transition-metal coordination compounds derived from ferrocenyl-containing ligands and found that the new complexes show no migration properties and high catalytic activity in the AP thermal decomposition.<sup>[7]</sup> *C. Morales-Verdejo* and co-workers obtained a few homo- and hetero-nuclear metallocenes, which are good antimigration BRC candidates.<sup>[8]</sup>

In the last decade our group developed a large number of ionic ferrocenyl compounds to retard high-migration issues of alkylferrocenes by introduction the concept of ionic liquids.<sup>[9]</sup> Recently, by means of the well known copper-catalyzed azide alkyne cycloaddition (CuAAC) approach,<sup>[10]</sup> we synthesized a series of ferrocene-functionalized 1,2,3-triazolyl compounds with phenols and benzoic acids as starting materials, and we found that they show excellent anti-migration ability and can be described as non-migratory ferrocenyl compounds.[11] On comparison with a OH or a COOH group, a NH<sub>2</sub> group can generally introduce two ferrocenyl 1,2,3-triazolyl units into a new compound by the synthetic method we used for the synthesis of the ferrocenyl compounds of phenols and benzoic acids<sup>[11]</sup> and more nitrogen and iron contents are favorable for enhancing catalytic activity of a ferrocene-based BRC. Herein we designed and synthesized nine novel ferrocenyl derivatives (Fc-ATAZs) with anilines or alkylamines as precursors (Scheme 1). The molecular structures of the Fc-ATAZs were characterized completely by <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV/Vis spectroscopes, FT-IR, high-resolution MS and elemental analysis. Their thermal stability was measured by DSC and TG. Electrochemical properties were investigated by cyclic voltammetry (CV). Migration and volatility tendency were evaluated by the method we used, with ferrocene (Fc) and catocene as references.<sup>[11]</sup> Their effects on the thermal disintegration of main oxidizers including AP, RDX and HMX were obtained by DSC and/or TG techniques.



Scheme 1. Molecular structures of the Fc-ATAZs compounds 1–9 of aniline and alkylamines.

## **Experimental Section**

**Materials and Equipment:** Azidomethylferrocene was synthesized as that described previously.<sup>[10b]</sup> RDX, AP and HMX were offered by Xi'an Modern Chemistry Research Institute. <sup>1</sup>H and <sup>13</sup>C NMR spectra

were conducted on a Bruker Avance 400 MHz spectrometer. Highresolution ESI-MS were acquired on a Bruker maXis spectrometer. UV/Vis absorption spectra were performed on a UV-2450 spectrophotometer. Elemental analyses were achieved using a Vario EL III Elemental Analyzer. TG and DSC studies were executed on Q50 and HS-1 models, respectively, under N<sub>2</sub> (50 mL min<sup>-1</sup>) at 5 °C·min<sup>-1</sup> with sample mass between 2.95–3.05 mg. Cyclic voltammetry (CV) studies were recorded using a CHI660C analyzer, on which a platinum working electrode and an Ag/Ag<sup>+</sup> reference electrode were used. The tested compounds were solved in deoxygened 0.1 mol·L<sup>-1</sup> *n*Bu<sub>4</sub>NPF<sub>6</sub>-DMSO supporting electrolyte before the measurement.

Synthesis of Compounds 1-9: Owing to the similar preparation method of 1-9, N,N-bis(1-ferrocenylmethyl-1H-1,2,3-triazol-4-ylmethyl) aniline (1) was taken as an example:<sup>[11]</sup> In a 100 mL roundbottom flask, 50 mL dried DMF and aniline 1.39 g (15.0 mmol) were added, then 7.91 g (50.0 mmol) K<sub>2</sub>CO<sub>3</sub> was added stepwise and stirred at 70 °C for 2 h. Then 2.94 mL (37.5 mmol) propargyl bromide was added dropwise, the mixture was then stirred and heated for 8 h. The reaction mixture was cooled to room temperature and filtered. The DMF in the filtrate was then removed completely by using rotary evaporator under vacuum. The purified N,N-dipro-2-ynylaniline was collected by column chromatography using n-hexane/ethyl acetate (v:v) 5:2 as eluent. In 70 mL methanol 1.01 g (6.0 mmol) N,N-dipro-2ynylaniline and 2.92 g (12.1 mmol) azidomethylferrocene were added, followed by a solution of 0.69 g (2.82 mmol) CuSO<sub>4</sub> 5H<sub>2</sub>O in 20 mL water. Aqueous solution of 0.58 g (2.82 mmol) sodium ascorbate prepared freshly was added and stirred for 24 h at room temperature. After removal of the solvents under vacuum, the desired product 1 was collected by using chromatographic technique with dichloromethane/ methanol (v:v) 3:1 as elute.

*N*,*N*-bis(1-Ferrocenylmethyl-1*H*-1,2,3-triazol-4-ylmethyl) aniline (1): Yellow powder. Yield: 3.33 g (85.2%). M. p.: 152.6–154.1 °C. **FT-IR** (KBr):  $\tilde{v} = 3316$  w, 3087 m, 2935 w, 1681 w, 1591 s, 1501 vs, 1445 m, 1376 m, 1314 s, 1224 s, 1162 m, 1106 m, 1044 s, 989 m, 940 m, 822 vs, 732 s, 683 m, 483 vs. cm<sup>-1.1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.28$  (s, 2 H), 7.18 (t, 2 H), 6.85 (d, 2 H), 6.72 (t, 1 H), 5.19 (s, 4 H), 4.61 (s, 4 H), 4.19 (t, 8 H), 4.18 (t, 8 H), 4.13 (s, 10 H). <sup>13</sup>C **NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta = 147.96$  (NCC<sub>5</sub>H<sub>5</sub>), 145.31 (NCCH), 129.28 (NCCH), 121.40, 117.75, 113.68 (C<sub>6</sub>H<sub>5</sub>), 81.18, 68.93, 68.88 (C<sub>5</sub>H<sub>4</sub>), 68.74 (C<sub>5</sub>H<sub>5</sub>), 49.99 (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>), 46.89 (CCH<sub>2</sub>N). **MS** (*m*/*z*, ESI<sup>+</sup>), 652.1552 [M + H<sup>+</sup>]. C<sub>34</sub>H<sub>33</sub>Fe<sub>2</sub>N<sub>7</sub>+H: 652.1574. C<sub>34</sub>H<sub>33</sub>Fe<sub>2</sub>N<sub>7</sub> (651.14): calcd. C, 62.69; H, 5.11; N, 15.05%; found: C, 62.54; H, 5.24; N, 15.10%.

*N*,*N*,*N*',*N*'-tetrakis(1-Ferrocenylmethyl-1*H*-1,2,3-triazol-4-ylmethyl) *o*-dianiline (2): Yellow powder. Yield: 6.51 g (88.6%). M. p.: 112.0–113.5 °C. FT-IR (KBr):  $\bar{\nu} = 3402$  w, 3087 m, 2935 w, 2938 w, 1646 w, 1487 m, 1432 m, 1328 s, 1217 s, 1113 s, 1044 vs, 919 m, 822 vs, 739 m, 483 vs. cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.32$  (s, 4 H), 6.75 (s, 4 H), 5.13 (s, 8 H), 4.45 (s, 8 H), 4.19–4.07 (m, 36 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 144.35$  (NCCH), 142.33 (NCC<sub>5</sub>), 122.81 (NCCH), 122.73, 121.66 (C<sub>6</sub>H<sub>4</sub>), 81.68, 68.84, 68.76 (C<sub>5</sub>H<sub>4</sub>), 68.58 (C<sub>5</sub>H<sub>5</sub>), 49.78 (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>), 45.56 (CCH<sub>2</sub>N). MS (*m*/*z*, ESI<sup>+</sup>), 1247.2412 [M + Na<sup>+</sup>], 701.4944 (M-(FcCH<sub>2</sub>C<sub>2</sub>N<sub>3</sub>HCH<sub>2</sub>+FcCH<sub>2</sub>N<sub>3</sub>H<sub>2</sub>)). C<sub>62</sub>H<sub>60</sub>Fe<sub>4</sub>N<sub>14</sub>+Na: 1247.2421, for C<sub>37</sub>H<sub>33</sub>Fe<sub>2</sub>N<sub>8</sub>: 701.1527. C<sub>62</sub>H<sub>60</sub>Fe<sub>4</sub>N<sub>14</sub>(1224.25): calcd. C,60.81; H, 4.94; N, 16.01%; found: C, 60.91; H, 4.82; N, 16.08%.

*N*,*N*,*N*',*N*'-tetrakis(1-Ferrocenylmethyl-1*H*-1,2,3-triazol-4-ylmethyl) *m*-dianiline (3): Yellow powder. Yield: 6.13 g (83.4%). M. p.: 106.4–107.5 °C. FT-IR (KBr):  $\tilde{v} = 3094$  m, 2928 w, 1715 w, 1591 s, 1494 m, 1445 m, 1321 s, 1217 m, 1182 s, 1106 m, 1037 s, 926 m, 808

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vs, 697 w, 497 vs. cm<sup>-1</sup>. <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.44 (s, 4 H), 6.94 (t, 1 H), 6.38 (s, 1 H), 6.20 (d, 2 H), 5.19 (s, 8 H), 4.51 (s, 8 H), 4.22 (s, 8 H), 4.16 (s, 8 H), 4.13 (s, 20 H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 149.09 (NCCH), 145.45 (NCC<sub>5</sub>), 129.85, 121.88 (NCCH), 103.78, 99.28 (C<sub>6</sub>H<sub>4</sub>), 81.42, 68.89, 68.87 (C<sub>5</sub>H<sub>4</sub>), 68.80 (C<sub>5</sub>H<sub>5</sub>), 49.91 (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>), 46.90 (CCH<sub>2</sub>N). **MS** (*m*/z, ESI<sup>+</sup>), 1247.2419 [M + Na<sup>+</sup>], 701.4942 (M-(FcCH<sub>2</sub>C<sub>2</sub>N<sub>3</sub>HCH<sub>2</sub> + FcCH<sub>2</sub>N<sub>3</sub>H<sub>2</sub>)). C<sub>62</sub>H<sub>60</sub>Fe<sub>4</sub>N<sub>14</sub>+Na: 1247.2421, for C<sub>37</sub>H<sub>33</sub>Fe<sub>2</sub>N<sub>8</sub>: 701.1527. C<sub>62</sub>H<sub>60</sub>Fe<sub>4</sub>N<sub>14</sub> (1224.25): calcd. C, 60.81; H, 4.94; N, 16.01%; found: C, 60.76; H, 4.99; N, 16.06%.

*N*,*N*,*N*',*N*'-tetrakis(1-Ferrocenylmethyl-1*H*-1,2,3-triazol-4-ylmethyl) *p*-dianiline (4): Light brown powder. Yield: 6.02 g (81.8%). M. p.: 176.1–177.4 °C. **FT-IR** (KBr):  $\tilde{v}$  = 3094 m, 2921 w, 2845 w, 1646 m, 1522 vs, 1438 m, 1363 m, 1314 s, 1217 s, 1113 m, 1030 s, 933 m, 815 vs, 718 m, 490 vs. cm<sup>-1.1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 7.84 (d, 4 H), 6.72 (s, 4 H), 5.22 (s, 8 H), 4.40 (s, 8 H), 4.27 (s, 8 H), 4.14 (s, 28 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 145.11 (NCCH), 141.67 (NCC<sub>5</sub>), 121.88 (NCCH), 116.97 (C<sub>6</sub>H<sub>4</sub>), 81.39, 68.89 (C<sub>5</sub>H<sub>4</sub>), 68.72 (C<sub>5</sub>H<sub>5</sub>), 53.50, 49.90 (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>), 47.32 (CCH<sub>2</sub>N). **MS** (*m*/*z*, ESI<sup>+</sup>), 1247.2436 [M + Na<sup>+</sup>]. C<sub>62</sub>H<sub>60</sub>Fe<sub>4</sub>N<sub>14</sub>+Na: 1247.2421. C<sub>62</sub>H<sub>60</sub>Fe<sub>4</sub>N<sub>14</sub> (1224.25): calcd. C, 60.81; H, 4.94; N, 16.01%; found: C, 60.56; H, 5.19; N, 15.81%.

*N*,*N*,*N*',*N*'-tetrakis(1-Ferrocenylmethyl-1*H*-1,2,3-triazol-4-ylmethyl) benzidine (5): Yellow powder. Yield: 6.95 g (89.1%). M. p.: 127.9–130.1 °C. FT-IR (KBr):  $\tilde{v} = 3406$  m, 3073 m, 2921 w, 1605 s, 1508 vs, 1438 m, 1376 m, 1307 m, 1217 s, 1099 m, 1044 s, 995 m, 933 m, 808 s, 476 s cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.34$  (s, 2 H), 7.31 (s, 2 H), 7.30 (s, 4 H), 5.20 (s, 8 H), 4.63 (s, 8 H), 4.20 (s, 8 H), 4.17 (s, 8 H), 4.13 (s, 20 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 146.58$  (NCCH), 145.28 (NCC<sub>5</sub>), 130.52 (NCCH), 127.08, 121.45, 114.10 (C<sub>6</sub>H<sub>4</sub>), 81.17, 68.94, 68.88 (C<sub>5</sub>H<sub>4</sub>), 68.73 (C<sub>5</sub>H<sub>5</sub>), 50.00 (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>), 46.99 (CCH<sub>2</sub>N). MS (*m*/*z*, ESI<sup>+</sup>), 1323.2747 [M + Na<sup>+</sup>]. C<sub>68</sub>H<sub>64</sub>Fe<sub>4</sub>N<sub>14</sub>+Na: 1323.2734. C<sub>68</sub>H<sub>64</sub>Fe<sub>4</sub>N<sub>14</sub> (1300.28): calcd. C, 62.79; H, 4.96; N, 15.08%; found: C, 62.73; H, 4.90; N, 15.01%.

*N*-(1-Ferrocenylmethyl-1*H*-1,2,3-triazol-4-ylmethyl) *o*-nitroaniline (6): Orange yellow powder. Yield: 2.12 g (84.8%). M. p.: 139.8– 141.2 °C. FT-IR (KBr):  $\tilde{v} = 3373$  m, 3157 w, 3087 w, 1620 s, 1572 s, 1502 s, 1474 m, 1411 m, 1355 m, 1257 vs, 1222 s, 1160 s, 1162 m, 1104 w, 1048 m, 1044 s, 810 m, 748 m, 580 w, 503 m, 482 m cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>):  $\delta = 8.33$  (s, 1 H), 8.18 (d, 2 H), 7.42 (t, 1 H), 7.38 (s, 1 H), 6.96 (d, 1 H), 6.69 (t, 1 H), 5.28 (s, 2 H), 4.63 (d, 2 H), 4. 26 (s, 2 H), 4. 21 (s, 2 H), 4. 17 (s, 5 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 144.81$  (NCCH), 144.65 (NCC<sub>5</sub>), 136.33 (NCCH), 132.46, 126.84, 121.06, 116.06, 114.11 (C<sub>6</sub>H<sub>4</sub>), 80.63, 69.15 (C<sub>5</sub>H<sub>4</sub>), 68.93 (C<sub>5</sub>H<sub>5</sub>), 50.24 (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>), 39.08 (CCH<sub>2</sub>N). MS (*m*/*z*, ESI<sup>+</sup>), 417.0882 (M <sup>+</sup>). C<sub>20</sub>H<sub>19</sub>FeN<sub>5</sub>O<sub>2</sub>: 417.0888. C<sub>20</sub>H<sub>19</sub>FeN<sub>5</sub>O<sub>2</sub> (417.09): calcd. C, 57.57; H, 4.59; N, 16.78%; found: C, 57.45; H, 4.66; N, 16.69%.

*N*,*N*,*N*',*N*'-tetrakis(1-Ferrocenylmethyl-1*H*-1,2,3-triazol-4-ylmethyl) ethylenediamine (7): Yellow powder. Yield: 6.36 g (90.2%). M. p.: 139.0–141.5 °C. **FT-IR** (KBr):  $\bar{v} = 3094$  m, 2935 w, 2817 m, 1654 w, 1549 w, 1438 m, 1328 s, 1217 s, 1113 m, 1037 vs, 1002 m, 919 w, 815 vs, 704 w, 490 vs. cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.60$  (s, 4 H), 5.24 (s, 8 H), 4.26 (s, 8 H), 4.16 (s, 28 H), 3.65 (s, 8 H), 2.61 (s, 4 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 144.20$  (NCCH), 122.90 (NCCH), 81.41, 68.91 (C<sub>5</sub>H<sub>4</sub>), 68.86 (C<sub>5</sub>H<sub>5</sub>), 50.88 (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>), 49.89 (NCH<sub>2</sub>CH<sub>2</sub>), 48.19 (NCCH<sub>2</sub>N). **MS** (*m*/*z*, ESI<sup>+</sup>), 1177.2602 [M + H<sup>+</sup>], 898.2133 (M-FcCH<sub>2</sub>C<sub>2</sub>N<sub>3</sub>HC). C<sub>58</sub>H<sub>60</sub>Fe<sub>4</sub>N<sub>14</sub> +H: 1177.2601, for C<sub>44</sub>H<sub>48</sub>Fe<sub>3</sub>N<sub>11</sub>: 898.2142. C<sub>58</sub>H<sub>60</sub>Fe<sub>4</sub>N<sub>14</sub> (1176.25): calcd. C, 59.21; H, 5.14; N, 16.67%; found: C, 59.10; H, 5.06; N, 16.80%. *N*,*N*,*N*',*N*',*N*''-**pentakis**(**1-Ferrocenylmethyl-1***H***-1**,**2**,**3**-triazol-4-ylmethyl) diethylenetriamine (8): Light brown powder. Yield: 6.36 g (80.6%). M. p.: 81.5–83.5 °C. **FT-IR** (KBr):  $\tilde{v} = 3406$  w, 3087 m, 2921 m, 2824 m, 1626 m, 1432 m, 1321 s, 1217 m, 1099 m, 1050 vs, 1002 s, 926 w, 815 vs, 711 w, 490 vs. cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.56$  (d, 4 H), 7.43 (d, 1 H), 5.22 (s, 10 H), 4.25 (s, 10 H), 4.14 (d, 35 H), 3.62 (s, 10 H), 2.70–2.41 (m, 8 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 144.16$  (NCCH<sub>2</sub>), 122.91 (NCHC), 81.47 (C<sub>5</sub>H<sub>4</sub>), 68.86 (C<sub>5</sub>H<sub>5</sub>), 51.88, 51.56 (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>), 49.84 (NCCH<sub>2</sub>), 49.03 (NCH<sub>2</sub>CH<sub>2</sub>), 48.10 (NCH<sub>2</sub>CH<sub>2</sub>). **MS** (*m*/*z*, ESI<sup>+</sup>), 1499.3478 [M + H<sup>+</sup>], 1258.3176 (M-FcCH<sub>2</sub>N<sub>3</sub>). C<sub>74</sub>H<sub>78</sub>Fe<sub>5</sub>N<sub>18</sub> + H: 1499.3482, for C<sub>63</sub>H<sub>67</sub>Fe<sub>4</sub>N<sub>15</sub>+H: 1258.3135. C<sub>74</sub>H<sub>78</sub>Fe<sub>5</sub>N<sub>18</sub> (1498.34): calcd. C, 59.30; H, 5.25; N, 16.82%; found: C, 59.12; H, 5.40; N, 16.71%.

*O*,*N*,*N*-tris(1-Ferrocenylmethyl-1*H*-1,2,3-triazol-4-ylmethyl)-2aminoethanol (9): Yellow powder. Yield: 4.32 g (80.2%). M. p.: 44.9–46.5 °C. **FT-IR** (KBr):  $\bar{v}$  = 3087 w, 2921 s, 2845 m, 1633 m, 1445 m, 1328 m, 1210 m, 1106 s, 1044 vs, 989 s, 815 s, 711 w, 482 vs. cm<sup>-1</sup>. <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.53 (s, 2 H), 7.46 (s, 1 H),), 4.26 (s, 6 H), 4.17 (m, 21 H), 3.72 (s, 4 H), 3.62 (t, 2 H), 2.68 (t, 2 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.99, 144.23 (NCCH<sub>2</sub>), 122.68, 121.95 (NCHC), 81.23, 80.88 (C<sub>5</sub>H<sub>4</sub>), 69.05 (OCH<sub>2</sub>CH<sub>2</sub>), 68.97, 68.95, 68.87, 68.76 (C<sub>5</sub>H<sub>5</sub>), 64.47 (OCH<sub>2</sub>), 52.60 (NCH<sub>2</sub>), 50.00 (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>), 49.93 (NCH<sub>2</sub>CH<sub>2</sub>), 48.36 (NCH<sub>2</sub>). **MS** (*m*/*z*, ESI<sup>+</sup>), 921.1802 [M + Na<sup>+</sup>], 701.4944 (M-FcC). C<sub>44</sub>H<sub>46</sub>Fe<sub>3</sub>N<sub>10</sub>O +Na: 921.1802, for C<sub>33</sub>H<sub>37</sub>Fe<sub>2</sub>N<sub>10</sub>O, 701.1851. C<sub>44</sub>H<sub>46</sub>Fe<sub>3</sub>N<sub>10</sub>O (898.19): calcd. C, 58.82; H, 5.16; N, 15.59%; found: C, 58.70; H, 5.22; N, 15.52%.

**Supporting Information** (see footnote on the first page of this article): DSC and TG curves of **1–9**. FT-IR spectra of **1–9**; UV/Vis and of **1–9** in CH<sub>3</sub>CN; Cyclic voltammograms of **6** in 0.1 M  $nBu_4PF_6$ -DMSO at different scan rates; Photo of the simulated composite propellant samples containing **1**, **3**, **5**, **7**, ferrocene and catocene after 1–4 weeks migration at 50 °C; DSC curves of AP and AP + 1–5 wt.-% **1**; DSC curves of RDX and RDX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX with 1–5 wt.-% **1**; DSC curves of HMX and HMX + 1 wt.-% **1**–**9**; Table of the redox potentials of the ferrocene/ferrocium couples from cyclic voltammetry of compounds **1–9** in 0.1 M *n*Bu4PF6-DMSO and compound **6** at scanning rates of 0.1–0.3 V/s as well as <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESI-MS spectra of **1–9**.

# **Results and Discussion**

#### Synthesis and Characterization

The novel ferrocenyl 1,2,3-triazolyl compounds Fc-ATAZs (1–9) were prepared by the traditional CuAAC-based synthetic strategy. However, stronger bases such as NaOH or NaH should be used instead of  $K_2CO_3$  for the synthesis of propargyl-containing intermediates of compounds 7–9. Notably, only one H atom of the NH<sub>2</sub> group in *o*-nitroaniline was substituted by propargyl group during the reaction even if stronger and more equivalent of bases or propargyl bromide were used in the reaction, a similar situation has been encountered in the reaction of picric acid with propargyl bromide, where no reaction was detected.<sup>[11]</sup> The strong acidity of the precursors maybe responsible for their inertness in the reaction. The DSC curves of the Fc-ATAZs (Figure S1, Supporting Information) showed that the new compounds are highly thermal-stable, with the initial thermal decomposition peaks being higher than

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220 °C. Their thermal stability were further verified by their TG curves (Figure S2, Supporting Information). In their FT-IR spectra, the strong intensity absorption peaks in the range of 1216–1222 cm<sup>-1</sup> can be ascribed to the stretching vibrations of C-N bonds. The strong bands around 1600 cm<sup>-1</sup> are assigned to the stretching vibrations of benzene ring skeletons. The absorption peaks located in the regions of 3096-3089, 1114-1096, 824–820 and 500–488  $\text{cm}^{-1}$  confirmed the appearance of ferrocenyl groups in each new compound. The medium and strong bands in the range of 923–936 and  $1039-1050 \text{ cm}^{-1}$ , respectively, suggested the formation of characteristic 1,2,3triazolyl rings in the new compounds (Figure S3, Supporting Information). In the FT-IR spectrum of compound 6 it is found that the characteristic stretching vibration of N-H bond is at 3370 cm<sup>-1</sup>, and that the asymmetric and symmetric stretching vibrations of the NO<sub>2</sub> group are at 1570 and 1355  $\text{cm}^{-1}$ , respectively. In their <sup>1</sup>H NMR spectra, the chemical shifts of the proton atoms of the 1,2,3-triazolyl groups locate between 7.60 and 7.26 ppm. In their <sup>13</sup>C NMR spectra, carbon atoms of the ferrocenyl groups resonated in the range of 68-81 ppm. The high solution mass spectra of the new compounds indicated consistency of their calculated and determined molecular weights, which confirmed that the as-synthesized compounds are the target compounds 1-9.

In the UV/Vis absorption spectra of the new compounds **1**–**9** in DMSO (Figure S4, Supporting Information), the strong absorption bands around 290 nm can be assigned to the  $\pi$ – $\pi$ \* transitions of phenyl and cyclopentadienyl groups, the shoulders and the strong peaks between 314 and 332 nm are appointed to the charge–transfer bands of the ferrocenyl groups. The wide absorption bands spanning 330 nm to 550 nm peaked around 430 nm are ascribed to the  $\pi$ – $\pi$ \* transitions of the ferrocenyl groups. The common weak absorptions of the ferrocenyl groups. The common weak absorptions of the Fe (II) ions, assigned to their d–d transitions, peaked in the range of 440–450 nm, are totally overlapped by the strong  $\pi$ – $\pi$ \* transitions of the ferrocenyl groups.<sup>[12]</sup> The strong electron-withdrawing nitro group in compound **6** weaken strongly the absorption bands of the ferrocenyl group around 320 nm.

#### Electrochemical Behavior

For a BRC, it is believed that during combustion catalysis at least an electron gain and loss process is involved. Moreover, electrochemical property of a ferrocenyl compound is usually studied due to electrochemical activity of the ferrocenyl group. Electrochemical behavior of compounds **1–9** is therefore investigated. CV curves of **1–9** in DMSO in the presence of 0.10 M Bu<sub>4</sub>NBF<sub>4</sub> are illustrated in Figure 1 and  $E_p^{a}$ ,  $E_p^{c}$ ,  $\Delta E_p$ ,  $E_p^{1/2}$ , and  $I_p^{a}/I_p^{c}$  are listed in Table S1 (Supporting Information). Only one pair of redox peak for each ferrocenyl compound appears in their CV curves although they are multinuclear ferrocenyl compounds except compound **6**, indicative of a simultaneous transfer of more electrons occurred in these compounds, due mainly to no conjugation being found in the new compounds. The  $E_p^{1/2}$ ,  $\Delta E_p$  and  $I_p^{a}/I_p^{c}$  in the ranges of 428–560 mV, 87–168 mV, and 1.08–1.22 (except  $I_p^{a}/I_p^{c} = 3.49$ 

for 4), respectively, suggested that compounds 1 and 6 display reversible ferrocene/ferrocenium waves. It is additionally noted that the oxidation potentials of the Fc-ATAZs are much higher than those of TBF, NBF and catocene, suggested that the new compounds exhibit higher anti-oxidative ability on comparison with these neutral ferrocenes in DMSO. The strong electron-withdrawing nitro groups in 6 exert negligible effect on the redox potentials of the ferrocenyl group in 6. The electrochemical behavior of the new ferrocenyl compounds may give us a deep insight into the catalytic activity and electron-transfer mechanisms of ferrocene-based BRCs towards thermal decomposition of AP during combustion. Moreover, effect of scan rates on the CV of 6 was investigated with different scan rates between 0.1-0.3 V·s<sup>-1</sup> and the results are shown in Figure S5 (Supporting Information). It was found that peak currents (anode and cathode) were linearly dependent on the square roots of scan rates, implying a diffusion-controlled process in the electrochemical property of the tested compound, as observed for electrochemical properties of the ferrocenyl compounds reported earlier.[13]



Figure 1. Cyclic voltammograms of 1-9 in 0.1 mol·L<sup>-1</sup>  $nBu_4NPF_6$ -DMSO with a scanning rate of 0.1 V·s<sup>-1</sup>.

#### Anti-migratory and Anti-volatility Studies

Alkylferrocenes, such as NBF, TBF and catocene, as additives move slowly to the surface of a composite solid propellant grain during its prolonged storage and thus cause concentration increase on the surface, which would give rise to unexpected problems and even danger during combustion of the propellant. For retarding high-migration problem of alkylferrocenes, we synthesized nine ferrocene-containing 1,2,3triazolyl compounds with aniline and alkylamine derivatives as precursors. Anti-migration performance of the compounds **1**, **3**, **5**, and **7** were measured with Fc and catocene as references. Sample preparation and *anti*-migration determination are similar to that described,<sup>[11]</sup> From the photos shown in Figures S6–S11 (Supporting Information). it is noted that both catocene and Fc diffused significantly after only one week test, while the tested four Fc-ATAZs showed marginable movement



after four weeks aging. No evident migration of the tested compounds is due mainly to the strong hydrogen bonding between nitrogen atoms of 1,2,3-trizolyl groups of the compounds and NH<sub>4</sub><sup>+</sup> of AP and the terminal OH groups of HTPB prepolymer, and secondarily to the weak interactions between the novel ferrocene derivatives and the propellant components.<sup>[14]</sup> The migration distances vs. aging time are illustrated in Figure 2. It is observed that both Fc and catocene moved to both sides obviously (2.5 cm and 1.7 cm, respectively) after four weeks migration. However, the tested four Fc-ATAZs kept almost no migration over a four-week period (< 0.2 cm), intimating that the new ferrocenes exhibit high anti-migration behavior, as we observed earlier for other ferrocenyl derivatives with similar molecular structures.<sup>[11]</sup>



**Figure 2.** Migration distances of the simulated composite propellant samples containing **1**, **3**, **5**, **7** after 1–4 weeks migration at 50 °C. [Fc (ferrocene) and Cat (catocene) were used as references].

It is well known that neutral alkylferrocene-based BRCs with small molecular weights exhibit evident volatility during curing of composite propellants using the alkylferrocenes as BRCs and thus leads to deposition on the inner shell of the rocket engines and uneven distribution within the propellant grain. Moreover, the sublimation and volatility behavior of the alkylferrocenes during fabrication probably give rise to unexpected issues and even danger.<sup>[3-5]</sup> A ferrocene-based BRC should have high anti-volatility. Therefore, TG technique was employed to evaluate anti-volatility performance of the new Fc-ATAZs and catocene (as reference) at 70 °C for 24 h. The results are shown in Figure 3. It can be seen that catocene exhibits ca 4.50% weight-loss after 24 h, intimating that catocene is a relatively high-volatile ferrocenyl compound. By contrast, the novel Fc-ATAZs showed marginable weight-loss, among them 7 exhibiting the highest weight-loss (0.71%), suggesting that the new ferrocenyl compounds exhibit much high antivolatility ability upon comparison with catocene. Again, the TG analysis verified that introduction of 1,2,3-triazolyl group into ferrocenyl derivatives can effectively improve anti-migration and anti-volatility ability of ferrocene-based BRCs.

#### **Catalytic Performances**

AP is one of the main components in a AP-based composite solid propellant and its weight percentage is about 70 wt%.

# 99.29% Cat 2 3 4 95.50%

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100

99

98

97

96

95

Weight (%)

Figure 3. TG curves of 1-9 and Cat (catocene) at 70 °C for 24 h.

The combustion behavior of AP has therefore close correlation with combustion process of composite solid propellants. Researchers in the BRC field often study catalytic activity of a BRC towards AP thermal degradation and the results are of reference value for their combustion performance in a solid propellant.<sup>[15]</sup>

In last decades researchers discovered that AP and Al powder have a few shortcomings during combustion. These drawbacks include releasing strong smoke and corrosive chlorine gas during their combustion and will cause decrease of signal receiving abilities of IR sensors and increase detecting possibilities by enemy radars. In this situation, other oxidizers, mostly RDX or HMX, are suggested to be used to partly substitute AP and Al powder to overcome their shortcomings. Therefore, thermal degradation behavior of RDX and HMX with the new compounds as additives was additionally evaluated.

Addition content of the new Fc-ATAZs in these three oxidizers was optimized with compound **1** as references. The test results, shown in Figures S12–S14 (Supporting Information), suggested that the optimal concentrations of the Fc-ATAZs in AP, RDX and HMX are 5 wt%, 5 wt% and 1 wt%, respectively. Therefore, in AP and RDX the new compounds each was added in 5 wt%, and in HMX each of them was used in 1 wt%.

DSC curves of the pure AP and its mixtures were displayed in Figure 4. It was observed that the thermal disintegration of AP is composed of three stages: phase-transition peaked at 244 °C, low-temperature decomposition (LTD) peaked at 293 °C and high-temperature decomposition (HTD) peaked at 406.6 °C. Similarly, the DSC curves of the mixtures each exhibits three steps, too. The phase-transition peak temperature of AP shifts right a few degree in the mixtures, indicating that the new ferrocenes exerted no significant effect on AP phase transition. However, in DSC curves of AP + 5 wt % **1–9**, small exothermal peaks ranged from 188 to 202 °C appear, which can be ascribed to the heat release peaks formed by the catalytic effect of the in-situ produced nano iron oxides through redox reactions of ferrocenes with AP.<sup>[16]</sup> These types of insitu formed nano iron oxides have been mentioned by others allgemeine Chemie

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who studied on the combustion of AP with ferrocene-functionalized additives.<sup>[15d,17]</sup> The peak of high decomposition temperature (HDT) stage of AP at 406.6 °C move dramatically to lower temperature when the Fc-ATAZs are used as additives. It was noted that DSC curve of each mixture shows two exothermal peaks, the former being 306-312 °C, and the latter being 342–360 °C.



Figure 4. DSC curves of AP and mixtures AP + 5 wt % 1-9.

The results revealed that the Fc-ATAZs as additives exert great effect on the thermal degradation of AP and accelerate decomposition rate of AP, as we observed previously.<sup>[9,11]</sup> The appearance of two peaks at HTD stage of AP in each DSC curve figures out that the decomposition mechanism of the mixtures is probably different from that of pure AP. The released heats of the mixtures are from -1180 to  $-1730 \text{ J} \cdot \text{g}^{-1}$ , with 5 wt % 3 +AP being the highest, which is by 123.2% higher than that of pure AP ( $-746 \text{ J}\cdot\text{g}^{-1}$ ) and higher by 32.8% than the released heat of 5 wt % catocene +AP ( $-1303 \text{ J}\cdot\text{g}^{-1}$ ). Additionally, it was also noted that the heats released by the mixtures 5 wt % 1–5 +AP are all higher than that of the mixture containing AP and 5 wt % O,O',O''-trikis-(ferrocenylmethyl-1*H*-1,2,3-triazol-4-ylmethyl) pyrogallol ether (-1478 J·g<sup>-1</sup>), which released the highest heat among the mixtures earlier.<sup>[11]</sup> The results demonstrated that the ferrocenyl 1.2.3-triazolyl compounds derived from anilines are more active than those from phenols and benzoic acids towards the AP decomposition. It was also found that the heats released by the mixtures of 5 wt % 7–9 + AP are lower than those of 5 wt % 1–5 +AP, hinting that the ferrocenyl compounds derived from alkylamines are unfavorable in the combustion catalysis towards AP thermal disintegration on comparison with those of the anilines.

From TG curve of AP illustrated in Figure 5, it was observed that AP began its weight-loss from 268 °C and ceased its thermal degradation at 395 °C. When 5 wt% Fc-ATAZs was doped in AP, the mixtures began their weight-loss from lower temperatures and ceased their thermal disintegration in the range of 241–251 °C, which are lower by 44–54 °C than that of AP itself, indicative of the decomposition temperature advance of AP with the new ferrocenes as additives. The TG results verified again that the Fc-ATAZs exert favorable effect on the AP thermal degradation.



Figure 5. TG curves of AP and mixtures AP + 5 wt % 1-9.

DCS curves of RDX and its mixtures with new ferrocenes **1–9** are illustrated in Figure 6. The DSC curve of pure RDX exhibits only one exothermic peak at 237 °C. The curves of the mixtures each, however, has two exothermic peaks, located in the range of 191–207 °C and 226–235 °C, respectively. In each DSC curve, the first peak appeared mainly before the endothermic peak of RDX and another one showed after the endothermic peak of RDX, which have been observed in our reported DSC curves earlier,<sup>[11]</sup> which is due to the partial polymerization of RDX molecules in the samples. The advance of the peak temperature of RDX suggested that the new ferrocenyl compounds as additives can considerably accelerate the thermal degradation of RDX. The released heat increased from  $-831 \text{ J}\cdot\text{g}^{-1}(\text{RDX})$  to  $-1261 \text{ to } -1648 \text{ J}\cdot\text{g}^{-1}(\text{mixtures})$  dramati-



Figure 6. DSC curves of RDX and mixtures RDX + 5 wt % 1–9.

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cally, intimating that the novel ferrocenyl compounds have marked effects on the thermal disintegration of RDX.

As illustrated in Figure S15 (Supporting Information), all mixtures exhibit lower peak temperatures than HMX itself, and the heats released by all mixtures (-1155 to  $-1425 \text{ J} \cdot \text{g}^{-1}$ ) are higher by 10–36% than that of HMX ( $-1046 \text{ J}\cdot\text{g}^{-1}$ ). Taking both peak temperature and released heat into account, all Fc-ATAZs compounds exert positive effect on the thermal disintegration of HMX. If the released heats of the mixtures of HMX + 1 wt % 1–9 are compared with those reported previously, it was found that HMX can release more heat with 1-9 as additives than with the ferrocenyl compounds derived from phenols and benzoic acids as additives.<sup>[11]</sup> In the reported compounds previously, some compounds even made negative effect on the HMX thermal degradation, with released heats being lower than that of HMX itself.<sup>[11]</sup> At lower temperatures, ferrocene compounds are difficult to be oxidized into iron oxides by both RDX and HMX, since they are classic nitramines. Therefore the new compounds exerted no significant effect on the decomposition peak temperatures of RDX and HMX, which explains why shifts of the decomposition peak temperatures of both oxidizers are within a few degrees.

#### Conclusions

In summary, nine ferrocenyl 1,2,3-triazolyl compounds derived from anilines and aliphatic amines were synthesized, aiming to enhancing anti-migratory abilities of the usual neutral ferrocene-based BRCs, and ameliorating the combustion catalytic activities of their analogues derived from phenols and benzoic acids. The evaluation results concluded that the new ferrocenes are highly thermal stable. The new compounds are of almost no migration and low volatility by the introduction of polar nitrogen atoms into their molecules. And the novel ferrocenyl compounds show highly catalytic activity in the thermal degradation of AP, RDX and HMX, and are more active than their analogues derived from phenols and benzoic acids reported previously. Currently, the synthesis of ferrocenyl 1,2,3-triazolyl compounds derived from nitrogen-rich energetic compounds such as imidazoles, pyrazoles and 1,2,4triazoles and evaluation of their combustion catalytic properties are underway in our laboratory.

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Anti-migration and Combustion Catalytic Performances of Ferrocenyl Compounds of Anilines and Alkylamines Synthesized by Click Reaction

