



Synthesis, characterization, migration studies and combustion catalytic performances of energetic ionic binuclear ferrocene compounds



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ABSTRACT

The concept of energetic ionic compounds was introduced to retard migration problems encountered in ferrocene-based burning rate catalysts. Fourteen novel compounds, *N,N'*-bis[(ferrocenylmethylidimethyl)-1,*n*-alkylenediammonium (alkylene chain length $n = 3-6, 8-10$) dinitrate and dipicrate, were synthesized and characterized by NMR, FT-IR, UV-vis spectroscopy, etc. Their thermal stability was determined by TG-DSC technique and found that most of them are thermally stable up to 160 °C. The cyclic voltammetry analysis revealed that the ionic compounds each shows a redox wave for ferrocenyl moiety and the non-conjugated alkylene spacers exert almost no influence on their redox properties. Migration tests showed that their migration tendency is much slower than that of extensively used 2,2-bis(ethylferrocenyl)propane (Catocene) and increases with the extension of alkylene chain length in the cations. Their catalytic performances for thermal decomposition of ammonium perchlorate (AP), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,2,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) were evaluated by DSC method. The ionic compounds presented highly combustion catalytic activity in thermal degradation of AP and RDX. The best catalytic activity in thermodecomposition of AP was obtained with *N,N*-bis(ferrocenylmethylidimethyl)1,3-propylene diammonium dinitrate, **1**. The catalytic activity of **1** is better than that of Catocene and **1** could be used as an alternative to Catocene in hydroxyl-terminated polybutadiene/ammonium perchlorate (HTPB/AP) composite propellants.

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Introduction

Ferrocene-based burning rate (BR) catalysts (combustion modifiers) are an indispensable component in hydroxyl-terminated polybutadiene/ammonium perchlorate (HTPB/AP) composite propellants and their functions are able to enhance burning-rates and meanwhile bring down pressure indexes of the propellants [1,2]. Of which, the well-known ferrocene-based combustion modifiers are *n*-butylferrocene (NBF), *tert*-butylferrocene (TBF) and binuclear 2,2-bis(ethylferrocenyl)propane (Catocene) [3–5]. The first two compounds have disadvantages including easy migration into the insulation layer during curing and storage and evaporation and

sublimation loss during processing, due to the shorter carbon chains on the ferrocenyl ring and lower molecular weights. The binuclear ferrocene derivative Catocene was then developed to retard migration tendency [6]. However, this drawback has not been completely eliminated and the slower migration of Catocene to the surface of propellants grain after long-time storage was still observed [3–5]. Additionally, these ferrocene derivatives, when mixed with ultra-fine ammonium perchlorate (AP), are sensitive to electrostatic discharge, which is very dangerous and even leads to an explosion in the fabrication process of propellants [2]. In order to overcome these flaws, extensive efforts have been devoted to design and synthesize new ferrocene-based burning-rate catalysts, striving for improving their storage stability. Societe Nationale des Poudres et Explosifs (SNPE) of France developed Butacene, which is the HTPB-polymer chemically bound by ferrocene unit, and it is a low-migration catalyst which can be synthesized by “one-pot”

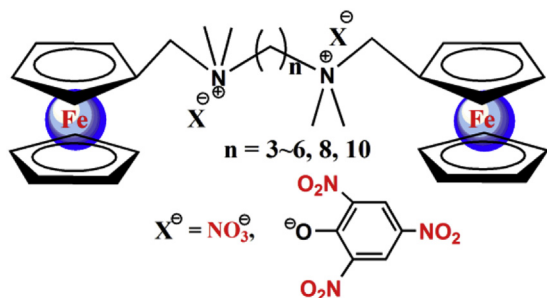
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chloroalkylferrocene process [6]. Additionally, various ferrocene derivatives containing functional groups easy for polymerization such as vinyl, isocyanate are also reported [6b,7,8].

Recently, scientific researchers devoted many efforts to design novel low-migration ferrocene-based BR catalysts. Gao and co-workers have investigated two poly(ferrocenylsilanes) and found that the decomposition temperature peak of AP shifted downwards with addition of one of them [9]. Y. Yuan prepared a few nitrogen-rich binuclear ferrocene derivatives and the combustion catalytic results showed that these ferrocene derivatives show combustion catalytic effects on thermal decomposition of AP [10]. For slowing down the migration rates of ferrocene derivatives, F. Li grafted ferrocenyl moiety on mesoporous silica SBA-15. The migration test showed that the as-prepared ferrocene-bound SBA-15 (Fc-SBA-15) is a low-migration catalyst and exhibited catalytic performance for thermal decomposition of AP. The burning-rate tests displayed that the Fc-SBA-15 enhanced by 43% the BR of AP/HTPB composite solid propellant and brought down the pressure index by 30% [11], but this strategy introduced inorganic non-energetic SBA-15 into the propellant formula. Y. Luo synthesized a few ferrocene end-cap hyperbranched poly(amine-ester) (HPAE-CP-Fe) and hyperbranched poly(amine-ester) (HPAE) and found that HPAE-CP-Fe is more thermally stable than pure HPAE and has good catalytic effect on thermal decomposition of AP [12a]. Additionally, the migration rate of HPAE-CP-Fe is much lower than those of ferrocene and *tert*-butyl ferrocene [12b]. M. Kandaswamy and his coworkers synthesized four different ferrocene-grafted hydroxyl-terminated polybutadiene (Fc-HTPB) samples and the burning-rate of AP-based propellant compositions having these Fc-HTPBs as a binder were much higher (8.66 mm/s) than those achieved with the HTPB/AP propellant (5.4 mm/s) [12e].

Energetic ionic compounds have been paid much attention in last decades due to their characteristic properties such as lower vapor pressures and higher densities. Additionally, the energetic ionic compounds exhibit higher heats of formation, higher thermal stability, a better oxygen balance and more friendly to the environment, compared to their atomically similar non-ionic analogues [13]. For design and synthesis of energetic ionic compounds, a modular design and synthesis concept has been employed using the ionic liquids platform and thus their molecular structures can be easily modified and, theoretically, a limitless combination of cations and anions should be achieved and their properties could be readily altered [13c]. Inspired by the unique properties and synthetic strategy of energetic ionic compounds, we initiated a program recently to design and synthesize energetic ionic ferrocene derivatives using the synthetic strategy of energetic ionic compounds, aiming to retarding the migration rates of neutral ferrocene-based BR catalysts and meanwhile increasing the energy level of the propellants. Herein we designed and synthesized 14 binuclear ferrocene-derived ionic compounds (Scheme 1) and their



Scheme 1. Molecular structures of *N,N'*-bis[(ferrocenylmethyl)dimethyl]alkylenediammonium dinitrates and dipicrates (alkylene chain length $n = 3-6, 8-10$).

migration tendency and catalytic properties for the thermal decomposition of main components of solid propellants were evaluated.

Experimental

Materials and equipment

AP(80–120 μm), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,2,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) are supplied by Xi'an Modern Chemistry Institute. *N,N'*-Dimethylmethylferrocene was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd and both $\text{I}(\text{CH}_2)_n\text{I}$ ($n = 3-6$) and $\text{Br}(\text{CH}_2)_n\text{Br}$ ($n = 8-10$) from Alfa Aesar (Tianjin) Chemicals Co. Ltd. Additional reagents and chemicals used were of AR grade and used as received. All *N,N'*-bis(ferrocenylmethyl)alkylenediammonium diiodides and dibromides were synthesized according to the synthetic procedures for *N,N'*-bis[(ferrocenylmethyl)dimethyl] dodecylendiammonium diiodide described by T. Yamamoto [14]. The IR spectra were recorded on an EQUINX 55 spectrometer in KBr matrix. ^1H and ^{13}C NMR spectra were performed on a Bruker Advance 400 MHz spectrometer. Elemental analyses were carried out with Vario EL III Elemental Analyzer, Germany. DSC and TG studies were undertaken on a HS-1 model from Beijing Henven Scientific Instrument factory and Q50 model from TA company of USA, respectively, operating at $5\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere (50 mL min^{-1}) with sample masses in the range of 1–2 mg. Migration studies were performed according to the method introduced by A. Ünver and F. Li [11,15] with modifications. The combustion catalytic properties of the ferrocene ionic compounds for thermal decomposition of main components of solid propellants were evaluated by DSC technique. The UV–vis adsorption spectra were recorded on a UV-2450 spectrophotometer of Shimadzu Corporation. Cyclic voltammograms were recorded with an CHI660C analyzer. Redox potentials were measured at a scan rate of 100 mV s^{-1} in CH_3CN containing 0.1 mol L^{-1} $n\text{-Bu}_4\text{PF}_6$ as the supporting electrolyte. An Ag/Ag^+ reference electrode and a platinum working electrode were used.

Synthesis

Since synthetic procedures for all compounds are similar, the preparation process for *N,N'*-bis[(ferrocenylmethyl)dimethyl]-1,3-propylenediammonium dinitrate (**1**) was taken as an example.

To a 50 ml Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, a 0.50 g (0.64 mmol) of *N,N'*-bis[(ferrocenylmethyl)dimethyl]-1,3-propylenediammonium diiodide was added and dissolved in 10 ml of methanol. A 0.33 g (1.95 mmol) of AgNO_3 in 15 ml of deionized water was added stepwise. Stirring was continued for 1 h. The yellow silver iodide formed was removed by filtration. The solvents were removed and the yellow residue was redissolved in acetonitrile and the insoluble powder was separated. The filtrate was evaporated to dryness and the residue was recrystallized with acetonitrile and ether. For the preparation of picrates **8–14**, sodium picrate was employed instead of AgNO_3 , the yellow precipitate formed was filtered and washed by water and then methanol for three times, and dried under vacuum at $70\text{ }^{\circ}\text{C}$ for 24 h.

Data for *N,N'*-bis[(ferrocenylmethyl)dimethyl]-1,3-propylenediammonium dinitrate (**1**)

Yellow powder, yield: 0.38 g (91.0%). M.p.: $193.1-194.6\text{ }^{\circ}\text{C}$. Anal. Found: C, 53.52; H, 6.17; N, 8.68. Calcd.: C, 53.39; H, 6.18; N, 8.59%. IR (KBr): cm^{-1} , 3095m, 3031m, 2979m, 1473m, 1382vs, 12440m, 1103m, 1043m, 999m, 837s. ^1H NMR ($\text{DMSO}-d_6$): 4.54 (m, 4H), 4.42

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