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Influence iron-iron distance on the thermal decomposition of ammonium
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18 Keywords: bimetallic compounds, ammonium perchlorate, burning rate catalyst,19 propellant

20

#### 21 Abstract

22 Five homobimetallic compounds derived from indacene and *p*-phenylene ligands with 23 different Fe-Fe distances have been synthesized. The catalytic effect on the thermal 24 decomposition of Ammonium Perchlorate (AP) of each complex is analyzed, establishing comparisons with catocene (**Cat**) and ferrocene (**Fc**). Cyclic voltammetry 25 26 showed quasi-reversible redox potential with higher electron-transfer ability than 27 ferrocene and catocene. An anti-migration study of these compounds is carried out, 28 compared with those of Cat and Fc. Compound 5, bearing a higher molecular weight, 29 displayed a better anti-migration performance than catocene and ferrocene. In 30 addition, the synthesized compounds have shown a shift on the peak temperature to lower values as well as an increase in the released heat values during thermaldecomposition of AP.

33

#### 34 **1. Introduction**

35 Rockets constitute a very important system in all kinds of missiles, used to deliver 36 warheads to targets as well as launching satellites into orbit. There are highly effective 37 burn-rate catalysts for AP containing composite solid propellant and are excellent 38 candidates for application in rocket engines with high thrust and acceleration power 39 in comparison with Fe<sub>2</sub>O<sub>3</sub> [1]. Ferrocene derivatives have been reported to impart high rates to HTPB-based composite propellants. Within these series, the bi-ferrocene 40 complexes have better performances than the monometallic analogues, thereby 41 42 improving the performance of the composite solid propellant [2–7].

Dual-core Fc derivatives as well as dendrimer substances with iron atoms near a 43 44 ferrocene moiety have suggested as a key step the combustion of these ferrocenyl 45 derivatives initially generates Fe<sub>2</sub>O<sub>3</sub> nanoparticles [4,7–9]. These nanoparticles have a 46 larger surface area than simple hematite particles and display excellent catalytic 47 activity on the thermal decomposition of AP [8]. Besides, as mentioned in the findings 48 of X. Liu and coworkers, a decreased tendency of the catalytic effect on the thermal 49 decomposition of AP becomes evident as the non-conjugated alkylene spacers grow in 50 size in the ionic binuclear ferrocene compounds [2].

51 Even though ferrocene derivatives BR catalysts have extraordinary effects in the 52 enhancement of the burning rates of composite solid propellant, some drawbacks 53 must be thoroughly addressed, such as an undesired sublimation during curing and 54 processing, as well as migrating to the surface on the propellants after extended 55 periods of time in storage [3,10–13]. These above-mentioned deficiencies can produce 56 long-term undesirable results such as storage issues [14–16], lifespan reduction, 57 changes on the initial burning parameters [3] as well as damage to the propellant 58 system [17]. To study the previously mentioned issues even further, we have 59 synthesized and tested bimetallic compounds derived from ferrocene. Our research 60 group has designed the synthetic route to obtain a complete series of binuclear 61 organometallic complexes derived from different bridging ligands such as *s*-indacene, 62 pentalene, *p*-phenylene and naphthalene [6,18–24]. In order to understand the 63 electronic properties allowing the intermetallic communication in the mixed-valence 64 organometallic derivatives, some of these complexes have previously been reported 65 [10, 12], but were not studied as burning rate catalysts. These compounds have very 66 high molecular weights, an advantageous factor in overcoming migration and 67 sublimation issues.

68 The current work describes the catalytic activity of the neutral homobimetallic 69 complexes derived from s- and as-Indacene and p-Phenylene in comparison with 70 ferrocene (Fc) and 2,2-bis(ethylferrocenyl)propane (Catocene: Cat). Since the semi-71 rigid bridged ligands, p-Phenylene, p-Biphenylene, and p-Terphenylene and rigid 72 ligands s- and as-indacene have high molecular weights, their heavier respective 73 complexes contribute by lowering migration and sublimation losses. Additionally, 74 complexes of the respective bridging ligands have different iron-iron metal distance 75 values as well as different redox potential values. We therefore attempt to study the 76 role of the redox behavior as well as the Fe-Fe distance on the thermal decomposition 77 of AP.

78

#### 79 2. Experimental Section

#### 80 2.1. General Information of the catalysts

All manipulations were carried out under a pure nitrogen atmosphere by using a vacuum atmosphere dry box equipped with a Model HE 493 Dri-Train purifier or with the use of a vacuum line by using standard Schlenk tube techniques.

Reagent grade solvents were distilled under an atmosphere of nitrogen from sodium
benzophenone for toluene, hexane and thf (previously distilled from AlLiH<sub>4</sub>) and from

86  $P_2O_5$  for acetonitrile and dichloromethane.

87 The synthesis of the following compounds has been reported previously: Fe(acac)<sub>2</sub>;

- acac: acetylacetonate [25]; Cp\*Fe(acac); Cp\*: pentamethylcyclopentadienyl [25]; *s*-Ic':
- 89 4,8-dimethyl-2,6-diethyl-symmetric-indacene [26]; *as*-Ic': 2,7-diethyl-*asymmetric*-
- 90 indacene [27]; p-Ph': p-Bis(2,3,4,5-tetramethylcyclopentadienyl)benzene [28]; p-
- 91 BiPh': *p*-Bis(2,3,4,5-tetramethylcyclopentadienyl)biphenylene [28] [Cp\*Fe-*s*-Ic'-
- 92 FeCp\*] (1) [5]; [Cp\*Fe-*p*-Ph'-FeCp\*] (3) and [Cp\*Fe-*p*-BiPh'-FeCp\*] (4) [28]

4,4"-Dibromo-1,1':4',1"-terphenyl,
2,3,4,5-tetramethylcyclopent-2-en-1-one,
suspension of sodium pentamethylcyclopentadienyl (NaC<sub>5</sub>Me<sub>5</sub>) in THF 0.5 M and
ferrocene (purchased from Aldrich).

96 Elemental analyses (C and H) were made with a Fisons EA 1108 microanalyzer. <sup>1</sup>H and
97 <sup>13</sup>C NMR spectra were recorded on Bruker AC-400, Bruker AC-200P, and Bruker AC 80
98 Spectrometers. Chemical shifts were reported in ppm relative to residual solvents and
99 were assigned using 2D NMR tools. All peaks reported were singlets, unless otherwise

- 100 specified.
- 101

#### 102 2.2 Synthesis Organic and Organometallic Compounds

103 2.2.1 *p*-Bis(2,3,4,5-tetramethylcyclopentadienyl)terphenylene). *p*-TerPh'.

To 2.5 g (6.4 mmol) of 4,4"-Dibromo-1,1':4',1"-terphenyl dissolved in 50 mL of 104 105 anhydrous diethyl ether was added dropwise 3.0 mL (6.1 mmol) of 2.0 M n-106 butyllithium in hexanes. After the solution was stirred for 20 min, a solution of 2,3,4,5-107 tetramethylcyclopent-2-en-1-one (0.86 mL, 6.1 mmol) in 5.0 mL of diethyl ether was 108 added. The mixture was then refluxed for 1 +h. The reaction was cooled to room 109 temperature, and 3.0 mL (6.1 mmol) of 2.0 M *n*-butyllithium was added. The mixture 110 was stirred for 1 h. A solution of 0.86 mL (6.1 mmol) of 2,3,4,5-tetramethylcyclopent-111 2-en-1-one dissolved in 5.0 mL of ether was then added dropwise.

Stirring was continued for 1 h. Then, the ethereal solution was quenched with aqueous saturated ammonium chloride, the layers were separated, and the aqueous phase was extracted with 30 mL of ether. The solution was concentrated to 30 mL, and 0.5 g of *p*-toluenesulfonic acid dihydrate was added. After 2 h of stirring a precipitate formed. The solid was filtered, washed with water and then with methanol, and finally dried. The crude product (0.8 g) was recrystallized from 50 mL of hot chloroform to afford 0.65 g (21.0% yield) of yellow crystals.

- 119 Anal. Calcd for C<sub>36</sub>H<sub>38</sub>: C, 91.86; H, 8.14. Found: C, 91.83; H, 8.17.
- <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.04 (d, 6H), 1.79 (S, 6H), 1.87 (s, 6H), 2.02 (S, 6H), 3.14 (q,
- 121 2H), 7.52 (s, 4H), 7.57 (d, 4H), 7.65 (d, 4H).

<sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 142.27, 140.77, 140.72, 140.33, 140.03, 139.80, 137.67,
137.32, 136.24, 134.92, 131.66, 128.80, 128.57, 126.86, 49.87, 14.59, 12.45, 11.51,
10.68.

- 125
- 126 2.2.2 [Cp\*Fe-*as*-Ic'-FeCp\*] (2)

127 A suspension of NaC<sub>5</sub>Me<sub>5</sub> in THF 0.5 M (3.8 mL, 1.9 mmol) was added slowly to a THF 128 solution (40 mL) of Fe(acac)<sub>2</sub>, (0.48 g, 1.9 mmol) cooled to -78 °C. The reaction 129 mixture was warmed to room temperature. After 1 h the deep red solution was cooled 130 to -78 °C and a suspension of the dilithium salt of ligand 2,7-diethyl-as-indacene 131 (prepared from 2,7-diethyl-*as*-indacene (0.20 g, 0.95 mmol) and 2.0 M *n*-butyllithium 132 (0.95 mL, 1.90 mmol) in 20 mL of THF) was added. The mixture was warmed to room 133 temperature and stirred for 1 h. Then, the solvent was removed, and the product was 134 dissolved with toluene, filtered to remove the insoluble Na(acac) and Li(acac), and 135 washed three times. After removal of the solvent via vacuum, dark-red powder 136 unstable to air was obtained. Yield: 35.7 % (0.20 g).

- 137 Anal. Calcd for C<sub>36</sub>H<sub>46</sub>Fe<sub>2</sub>: C, 73.23; H, 7.85. Found: C, 73.28; H, 7.90.
- <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.15 (t, 6H), 1.76 (s, 30H), 2.26 (q, 4H), 3.21 (dd, 4H), 6.51
- 139 (s, 2H).

<sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 140.94, 132.49, 121.80, 77.74, 59.06, 29.03, 18.57, 9.94.

141

142 2.2.3 [Cp\*Fe-*p*-TerPh'-FeCp\*] (5)

143 A suspension of NaC<sub>5</sub>Me<sub>5</sub> in THF 0.5 M (2.56 mL, 1.28 mmol) was added slowly to a 144 THF solution (40 mL) of Fe(acac)<sub>2</sub>, (0.32 g, 1.28 mmol) cooled to -78 °C. The reaction 145 mixture was warmed to room temperature. After 1 h the deep red solution was cooled 146 to -78 °C and a suspension of the dilithium salt of ligand *p*-TerPh' (prepared from *p*-TerPh' (0.30 g, 0.64 mmol) and 2.0 M n-butyllithium (0.64 mL, 1.28 mmol) in 30 mL of 147 148 THF) was added. The mixture was warmed to room temperature and stirred for 2 h. 149 Then, the solvent was removed, and the product was dissolved with toluene, filtered 150 to remove the insoluble Na(acac) and Li(acac), and washed three times. After removal 151 of the solvent via vacuum, dark-red powder unstable to air was obtained. Yield: 18.4 152 % (0.10 g).

153 Anal. Calcd for C<sub>57</sub>H<sub>70</sub>Fe<sub>2</sub>: C, 78.98; H, 8.14. Found: C, 78.86; H, 8.22.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.53 (s, 30H), 1.62 (s, 24H), 7.37 (s, 4H), 7.41 (d, 4H), 7.49
(d, 4H).

- <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 142.43, 140.88, 140.48, 140.20, 137.84, 137.47, 136.40,
- 135.08, 128.73, 127.91, 127.03, 125.31, 59.87, 29.83, 19.38, 14.75, 12.61, 12.53, 11.67,
  10.76.
- 159

#### 160 **2.3 Thermal analysis**

161 DSC analysis was performed on a DSC 822e METTLER TOLEDO instrument 162 respectively at a heating rate of 5  $^{\circ}$ C·min<sup>-1</sup> under nitrogen in the range of 80–500  $^{\circ}$ C. 163 To investigate the catalytic performance of the compounds derived from indacenes 164 and *p*-phenylenes on the thermal decomposition of AP, specific amounts of the 165 complexes and AP were mixed and ground in a certain weight ratio for DSC analysis.

166

#### 167 **2.4 Electrochemical measurements**

168 A Voltalab (PGZ100) potentiostat electrochemical workstation was used to measure the electrochemical properties of the samples at ambient temperature (20 °C). A 169 170 conventional three-compartment cell was employed throughout the work. A platinum 171 disk electrode (2 mm diameter) was used as a working electrode. The counter 172 electrode was a large area coiled Pt wire, separated from the electrolytic solution by a 173 sintered glass frit. Before each experiment, the working electrode was polished to a 174 mirror finish with an aqueous alumina slurry (particle size 0.3 and 0.05 micron) on 175 micro-cloth pads, rinsed thoroughly with water and dried. All potentials are referred 176 to a Ag/AgCl (KCl,1 M) electrode. Each working solution was purged with high purity 177 argon for 15 min prior to each experiment, and a lower flow was maintained over the solution during the measurements. Tetrabutylammonium tetrafluoroborate 178 179 (Bu<sub>4</sub>N•BF<sub>4</sub>) was dried at 110 <sup>o</sup>C and kept into a dryer until used as supporting 180 electrolyte. Dichloromethane was anhydrated with phosphorus pentoxide under N<sub>2</sub> 181 atmosphere reflux. Cyclic voltammetry measurements were carried out in anhydrous 182 dichloromethane with a concentration of 0.01 M Bu<sub>4</sub>N•BF<sub>4</sub>, 5 mM analyte, at a scan 183 rate of 100 mV•s<sup>-1</sup>.

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#### 185 **2.5 Computational details**

186 Geometries were fully optimized at the density functional theory (DFT) level, as 187 implemented in Gaussian16 software [29]. The functional and basis set were selected 188 according to a previous study on ferrocenium/ferrocene system, reported by Flores-189 Leonar and coworkers [30], where the dual corrected  $\omega$ B97X-D functional [31] 190 proved to be consistent throughout the analysis of geometry, in combination with a 191 basis set SDD [32] and cc-pVTZ [33], for Fe and Cp respectively. The molecular 192 structures were fully optimized in gaseous phase and vibrational frequencies 193 calculations were performed at the same level of theory as the geometry 194 optimizations to confirm that the stationary points were minima at the potential energy surface. A tight SCF convergence criteria (10-8 a.u.) was used in all 195 196 calculations.

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#### **3. Results and Discussion**

Preparation of the complexes (**2**) and (**5**) proceeds straightforwardly by previously reported route [28,34]. Details on the thorough characterization by means NMR spectroscopy is in the supporting information file. The reaction of the dilithium ligand salts with (Cp\*)Fe(acac) affords the title compounds, which is easily separated from Na(acac) and Li(acac) byproducts. The unstable air black-red powder compounds were obtained, analytically pure, in approximately 20 % yield.

Since ferrocene-type complexes are known to be effective catalysts on the thermal decomposition of AP, the activity of the binuclear compounds (1), (2), (3), (4) and (5) as burning rate catalysts in comparison with ferrocene (Fc) and catocene (Cat) was

209 carried out. Figure 1 shows the catalysts used in this work.



Figure 1: Ferrocene (**Fc**), catocene (**Cat**), bimetallic (**1**, **2**, **3**, **4** and **5**) catalysts compared in this work.

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#### 215 **3.1 Redox properties**

The redox properties of ferrocene, catocene, and all the previously mentionedbimetallic compounds were analyzed by means of cyclic voltammetry.

Cyclic voltammetry profiles were recorded between -1.5 and 1.5 V at a sweep rate of
100 mV·s<sup>-1</sup>. The first and second oxidation potential for each compound were
obtained from the first cycle in anhydrous dichloromethane, as listed in Table 1.

Neutral compounds (1), (2), and (3) displayed two oxidation peaks associated to the oxidation of each ferrocene center in the molecule. The first and second oxidation potentials are correlating to the metal pointed in comparison with the mono- and binuclear species, as already reported [19,28,35,36]. Compounds (4) and (5) only presented one oxidation peak corresponds to the simultaneous transfer of two electrons per dimer, as observed by E. Bunel and coworkers [28] (Fig. 2).

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Figure 2: Cyclic Voltammograms of complexes (2), (4) and (5) in acetonitrile/0.1 M n-

- 232 Bu4NBF4. Scan rate 100 mV/s
- 233
- 234

- Table 1: Oxidation potentials for ferrocene, catocene and neutral complexes derived from indacenes and *p*-Phenylenes (mV vs Ag/AgCl)
- 237

| Complexes                                    | $E_{\rm ox1}(0/1+)$                        | $E_{\rm ox2}(1+/2+)$                              | $\Delta E_{ox}$ |
|--|--|---|-----------------|
| Ferrocene (Fc)                               | $500  _{Fe^{+2}/Fe^{+3}}$                  |   |                 |
| Catocene (Cat)                               | $346  _{Fe^{+2}/Fe^{+2}/Fe^{+2}/Fe^{+3}}$  | $498  _{Fe^{+2}/Fe^{+3}/Fe^{+3}/Fe^{+3}}$         | 152             |
| [Cp*Fe-s-Ic'-FeCp*][5] (1)                   | $-490  _{Fe^{+2}/Fe^{+2}/Fe^{+2}/Fe^{+3}}$ | $483  {}_{Fe^{+2}\!/Fe^{+3}\!/Fe^{+3}\!/Fe^{+3}}$ | 973             |
| [Cp*Fe-as-Ic'-FeCp*] (2)                     | $130  _{Fe^{+2}/Fe^{+2}/Fe^{+2}/Fe^{+3}}$  | $770  {}_{Fe^{+2}\!/Fe^{+3}\!/Fe^{+3}\!/Fe^{+3}}$ | 640             |
| [Cp*Fe- <i>p</i> -Ph'-FeCp*][6] ( <b>3</b> ) | $-167 _{Fe^{+2}/Fe^{+2}/Fe^{+2}/Fe^{+3}}$  | $459_{Fe^{+2}/Fe^{+3}/Fe^{+3}/Fe^{+3}}$           | 626             |
| [Cp*Fe-p-BiPh'-FeCp*] (4)                    | 91 $_{Fe^{+2}/Fe^{+2}/Fe^{+2}/Fe^{+3}}$    | -   | -               |
| [Cp*Fe- <i>p</i> -TerPh'-FeCp*] ( <b>5</b> ) | $276_{Fe^{+2}/Fe^{+2}/Fe^{+2}/Fe^{+3}}$    | -   | -               |

**Note:**  $E_{ox1}$  (0/1+) and  $E_{ox2}$  (1+/2+) are the first and second oxidation potentials (mV),  $\Delta E_{ox}$  is the subtraction between the first and second oxidation potentials in the complex  $E_{ox1}$  (0/1+) and  $E_{ox2}$  (1+/2+). (\*) According to reference [2,37] the potential oxidation was reported with Ag/AgCl as reference electrode.

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The first oxidation of compounds (1) and (3) appears at more cathodic potentials compared to compounds (2), (4) and (5). This evidences that (1) and (3) require a lower amount of energy than (2), (3) and (5), to form the respective cation.

In all cases, the first oxidation potential exhibited lower values than ferrocene andcatocene.

The thermodynamic stability of the mixed-valence species related to the electronic interactions is associated with the term  $\Delta E_{\text{ox}}$  [38]. As previously reported[5], the difference of potential between the two oxidation peaks is  $\Delta E_{\text{ox}} = 973$  mV for compound (**1**), giving a high comproportionation constant (Kc = 2.81x10<sup>16</sup>) [39], suggesting a high stability for the intervalence system (**1**+), in comparison with the compounds (**2**) (Kc = 6.6x10<sup>10</sup>) and (**3**) (Kc = 3.8x10<sup>10</sup>), corroborating the above described. In the case of the catocene (Cat), as we described [5,6] the difference of potential between the two oxidation peaks is small ( $\Delta E_{\text{ox}} = 151 \text{ mV}$ ) and low comproportionation constant (Kc =  $3.57 \times 10^2$ ), which is indicative that the metals are noninteracting either because the ligand does not provide an electronic coupling pathway.

258 The  $\Delta E_{\text{ox}}$  value of zero for the compounds (**4**) and (**5**), indicates a reduced 259 delocalization due to the increased distance between the iron centers.

Additionally, the redox properties may help us in better understanding the electrontransfer mechanism of the compounds and its effect on the catalytic performance on the thermal decomposition of AP.

263

#### 264 **3.2. Computational characterization**

265 Given the fact that both moieties may lie on the same side of the bridging ligand plane 266 (syn) or on different sides (anti), two different molecular configurations are possible. 267 The geometry optimization of *anti*-configuration of the neutral bimetallic complexes 268 has been performed considering that the metal atoms coordinate the C<sub>5</sub> rings, as 269 usually observed experimentally [36,40,41]. As expected and for sterically related 270 effects [42], the *anti*-configuration was always found to be slightly more stable than the syn isomer; therefore, we have focused our theoretical calculations on the anti-271 272 configuration (Figure 3).

All complexes in the neutral state were optimized in a vacuum with the  $\omega$ B97X-D functional in combination with a basis set SDD[43] and cc-pVTZ[44] for Fe and Cp, respectively. Frequency analysis in gas phase was performed on each optimized structure to verify the existence of a minimum in the potential energy surface. Performing single point calculations on the gas phase optimized structures. Figure 2 shows the optimized structures in gas phase, in order to determine the distance between the metallic iron centers.

- 280
- 281



(Cat)







(2)

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Figure 3: Optimized structures at  $\omega$ B97X-D/SDD/cc-pVTZ level in gas phase.

Table 2 (*vide infra*) shows that the compound (**2**) has the shortest distance between the metal centers iron (5.08 Å), even less than catocene (5.68 Å) and its analog compound *s*-indacene derivate (**1**) (5.73 Å). Regarding the compound (**3**) (8.74 Å) has a greater distance than compounds (1), (2) and (Cat); and as expected a shorter
distance to the compounds (4) and (5), 13.11 Å and 17.27 Å, respectively.

Furthermore, these iron-iron distances would help us in better understanding the reaction mechanism of the compounds and of the catalytic performance on the thermal decomposition of AP.

302

#### 303 3.3 Anti-migration studies

Solid propellant samples were prepared in order to explore anti-migration behavior of the bimetallic compounds. Detail of the samples preparation is shown in Table S1 supplementary information. The samples were first filled in glass tubes and put for the curing process at 65 °C for seven days. Then blank simulative solid propellant was filled in the end of the tubes. Anti-migration studies were carried out in an oven at 65 °C for 21 days.

310 Figure 5 shows the results of anti-migration studies. Ferrocene showed the maximum 311 migration with a value of 4.0 cm in 21 days. Samples of catocene and bimetallic compounds showed anti-migration behavior comparable with ferrocene (Figure 4, 312 313 Figure S2.1 and S2.3). On long-term storage, ferrocene inevitably reached the ends of 314 the tube (Supplementary Material Figure S2.2), while indacenes and *p*-phenylenes 315 derivatives moved to a lesser extent. The migration distances of these samples are plotted in Figure 5. It can be seen that compound (5) has the best anti-migration 316 317 property among the samples, due to its high molecular weight (866 g/mol). In general, 318 the neutral compounds present anti-migration behavior mostly because of its higher 319 molecular weight (590 - 866 g/mol) than ferrocene (186 g/mol) and catocene (484 320 g/mol). Higher molecular weight leads to stronger van der Waals forces. However, 321 this force is not strong enough to prevent migration on long-time storage for 322 compounds (1), (2), (3), and (4).



### 

Figure 4: Anti-migration studies photos of compound (5) on days a) 7, b) 14 and c) 21



Figure 5: Evaluation of the migration tendency of (1), (2), (3), (4) and (5) along
migration distance and for different aging time (the bars in each parallel row from left
to right represent a compound was aged for 7, 14 and 21 days, respectively at 65 °C).

#### 334 **3.4 Catalytic Effects on thermal decomposition of ammonium perchlorate**

The catalytic effects of the bimetallic compounds on the thermal decomposition of AP 335 336 were investigated by DSC measurements with a heating rate of 5 °C·min<sup>-1</sup> in N<sub>2</sub> 337 atmosphere in the range of 140-450 °C. Figure 6 (Fig S3.1-S3.5 supporting 338 information) shows the DSC curves of both AP and the mixture of AP with the title 339 compound. In general, the catalytic activity of a BR catalyst in solid propellant can be 340 assessed by studying its effect on the thermal degradation of AP by DSC instrument. 341 The weight percentage of ferrocene-based BR catalysts used in AP were 2, 4 and 6 342 wt%.



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Figure 6: DSC curves of AP with different percentage (wt%) of compound (4).

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The fact that the endothermic process of AP peaked at 249 °C is due to the crystal transformation from orthorhombic to cubic phase, displaying almost no shift (max. ca. 4 °C) and exhibited a similar shape with 2–6 wt% of (1), (2), (3), (4) and (5) as additives. Both exothermic stages are evidenced firstly by the low-temperature 350 decomposition (LTD) (peak temperature at 320 °C), and secondly by the high-351 temperature decomposition (HTD) (peak temperature at 418 °C) of AP. Each of these 352 phases is respectively attributed to a partial decomposition of AP to form some 353 intermediate product, to a later and eventual complete decomposition to volatile 354 products. The exothermic processes are significantly affected by the addition of the 355 catalysts derived from indacenes and *p*-phenylenes, where the wide decomposition 356 temperature range of AP was considerably narrowed and the released heat of AP 357 increased. DSC curves of pure AP and AP with 2 wt% of the bimetallic catalysts are 358 almost the same (Figure 6 and S3.1-S3.5 supplementary material).

The exothermic process suggests that the high temperature decomposition (HTD) of AP with the bimetallic compounds occurs predominantly via the thermal decomposition. This implies that the additives have a greater catalytic effect on the HTD of AP than on the earlier stage. However, when wt% of bimetallic complexes was further increased, from 2% to 6%, the catalytic effect did not improve, with the exception of compound (**1**), obtaining the best catalytic effects at 4 w%.

Therefore, 4 wt% was chosen as the optimum amount of each compound for the evaluation of their catalytic effects. After adding 4 wt% of the compounds (1), (2), (3), (4) and (5), the highest thermal decomposition temperatures are 321, 320, 319, 330 and 340 °C respectively, decreased by 97, 98, 99, 88 and 78 °C compared with pure AP, which indicates the additives have an evident catalytic effect on the thermal decomposition of AP.

371 It is noted that all the DSC curves displayed a similar shape with one peak, except that
372 of compound (4) (Figure 6), suggesting that an identical decomposition mechanism of
373 the mixture systems should be expected.

When comparing the monometallic compound ferrocene with all the bimetallic complexes the heat released is greater. In fact, the heat released of compound (4) (2122 J·g<sup>-1</sup>) is almost similar to the catocene (2472 J·g<sup>-1</sup>) (see Table 2).

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# 381 3.5 Possible burning rate catalytic mechanism of ferrocene-based compounds 382 on the thermal decomposition of AP

Four catalytic mechanisms have been proposed: electron transfer mechanism, proton
transfer mechanism, forming transition materials mechanism and acid-base
interaction mechanism. [45–47]

In order to clarify the possible type of reaction mechanism and considering that combustion is a drastic oxidation-reduction process, our research group has suggested a relationship between the oxidation potential and the catalytic effect on the AP thermal decomposition, as summarized in Table 2. In each case, compounds Fc, **Cat** and the bimetallic substances, behave whether by lowering the HTD temperature value and/or a higher heat release.

392 As it is accepted by other authors[48], the low temperature decomposition (LTD) is 393 governed by the electron transfer process. This decomposition is the most important factor governing the decomposition of NH<sub>4</sub>ClO<sub>4</sub>, followed by exothermic peak (HTD) 394 395 associated with the further decomposition of HClO<sub>4</sub>, which gets converted into small 396 molecules, such as H<sub>2</sub>O, HCl, N<sub>2</sub> and O<sub>2</sub>. In this context, bimetallic compounds play a 397 vital role in accelerating the electron transfer process, initiating the decomposition 398 process. Therefore, there is a clear relationship between oxidation potential and 399 catalytic effect. Regarding Fc, Cat and bimetallic compounds, it is possible to 400 appreciate a general tendency associated to oxidation potentials versus shifting of the 401 HTD peak of AP to lower temperatures. All these compounds present low oxidation 402 potential in comparison with AP, which could be the key for the candidates as BR 403 catalysts. These results suggest that the addition of bimetallic catalyst leads probably 404 to the decomposition of AP through electron transfer mechanism. However, in 405 relation to the bimetallic compounds (1) and (2), it is not possible to see a clear 406 tendency with the oxidation potential versus the shift of the HTD peak of AP to the 407 left, because, probably, another important factor is affecting the catalytic effect (vide 408 *infra*). But if we look at compounds (3), (4) and (5), it is possible to see a tendency 409 with oxidation potential versus the shift of the HTD peak of AP. Furthermore, it is not 410 possible to clarify a tendency with the heat released for each compound, indeed the 411 heat released by **Cat** is still higher than the others catalysts reported here.

| Compounds       | <i>E</i> <sub>ox1</sub> vs<br>Ag/AgCl (mV) | HTD of AP<br>(ºC) | Heat released<br>(J·g <sup>-1</sup> ) | Distance<br>(Å) |
|-----------------|--|-------------------|---------------------------------------|-----------------|
| $NH_4ClO_4(AP)$ | 825  | 418               | 943                                   | -               |
| (Fc)            | 500  | 360               | 1313                                  | -               |
| (1)             | -490                                       | 321               | 1594                                  | 5.73            |
| (2)             | 130  | 320               | 1870                                  | 5.08            |
| (3)             | -167                                       | 319               | 1560                                  | 8.74            |
| (4)             | 91   | 330               | 2122                                  | 13.11           |
| (5)             | 276  | 340               | 1212                                  | 17.27           |
| (Cat)           | 346  | 346               | 2472                                  | 5.68            |

Table 2: Summary table, relationship between the oxidation potential and the catalytic

effect (4 wt%) on AP thermal decomposition of the ferrocene derivatives

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It can be also noted that the final decomposition temperatures of AP with complex (3)
as additive is lower than the other complexes, implying that the effects of the
bimetallic compound on the thermal degradation of AP are greater than catocene.

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419 Regarding transition materials mechanism, it has been widely accepted that 420 ferrocenyl-bimetallic derivatives tend to form Fe<sub>2</sub>O<sub>3</sub> particles [4,7-9]. The systems 421 having a higher content of iron per molecule, greater number of electron donor 422 groups and the Fe atoms closer to one another, could better promote the formation of 423 nanoscale hematite particles [9]. If we compare the iron-iron distances in the family of 424 the rigid bridging ligands, s- and as-indacene, we could see a tendency in their Fe-Fe 425 distance and the catalytic effect on the thermal decomposition of AP,  $(2) \ge (1)$ . In the 426 same way, the complexes derived from semi rigid bridging ligands, p-phenylene, p-427 Biphenylene and *p*-Terphenylene display a marked catalytic tendency of the effect on 428 the thermal degradation of AP, (3) > (4) > (5).

This could confirm the mechanism proposed about Ferrocenyl-bimetallic derivatives
during the burn-up phase, responsible for generating high surface area Fe<sub>2</sub>O<sub>3</sub>
nanoparticles, more effective in comparison with common powdered Fe<sub>2</sub>O<sub>3</sub>. Zain-ul et

432 al. and Gao et al. [8,49] gave a more visual description of the burning process. This promotion stems from the unique structure of the bimetallic complexes (Figure 7). 433



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- 436 Figure 7: Possible formation mechanism of nanoscale Fe<sub>2</sub>O<sub>3</sub> from the bimetallic
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#### 439 4. Conclusion

440 All compounds showed much slower migration rates than that of catocene, mostly due 441 to their molecular weights. In addition, the bimetallic complexes showed 442 quasireversible redox potential values displaying lower energy charge-transfer in a 443 similar situation to that of ferrocene and catocene, which may come in handy to 444 further study how redox processes may affect the decomposition of AP.

molecule.

The catalytic results by means of DSC techniques confirmed that the bimetallic complexes derived from rigid bridging ligands, *s*- and *as*-indacenes; and semi rigid bridging ligands, *p*-phenylene, *p*-Biphenylene and *p*-Terphenylene, have high catalytic activity for the thermal decomposition of ammonium perchlorate. Catalytically, compound (**3**) is the most active despite the fact its released heat is somewhat lower.

- From the results obtained, we can state that for the fine-tuning of catalyst design on the thermal decomposition of AP, it is indeed necessary to consider Fe-Fe distance factors and the oxidation potential values, perhaps opening fields on further research for newer molecules based on intrametallic distance values. Despite the effect that BR catalysts cannot be uniquely analyzed upon the influence on the thermal decomposition of AP, the results confirm the bimetallic compounds could have promising applications as burning rate catalysts in composite solid propellants.
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#### 465 **Supplementary material**

466 NMR characterization, Migration studies and DSC curves to different wt% for all467 compounds related to this article can be found at supplementary data.

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#### HIGHLIGHTS

Influence iron-iron distance on the thermal decomposition of ammonium perchlorate. New catalysts for the highly efficient combustion of solid rocket propellant

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- Complexes show catalytic activity on thermal decomposition of AP.
- These compounds show a shift on the peak temperature of AP to left.
- These compounds increase released heats during thermal decomposition of AP.
- Catalytic activities are examined by DSC techniques.
- Theoretical calculations are carried out to gain further understanding.

#### **Declaration of interests**

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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