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Insights into the Nature of Self-Extinguishing External Donors for Ziegler-Natta Catalysis: A Combined Experimental and DFT Study

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Abstract: Developing donors for Ziegler-Natta (ZN) catalysis to control the polymerization reaction and produce polymers with desirable properties has always been challenging due to the multi-component nature of the catalytic systems. Here, we have developed a new synthetic protocol for making two external donors, **D**₁ (2,2,2-trifluoroethyl myristate) and **D**₂ (2,2,2-trifluoroethyl palmitate) that show self-extinguishing properties, followed by a systematic DFT study to understand this peculiar property of these donors. **D**₁ and **D**₂ can undergo parallel reactions with aluminum and titanium species present in the system to produce ketones and aldehydes, which are poisons for ZN catalytic systems, thus explaining their self-extinguishing nature. The non-covalent interaction between the long alkyl chain of the donors with the surface plays a vital role in determining the donors' self-extinguishing nature. There is a significant thermodynamic preference for the binding of the donor with the longer alkyl chain at the titanium center. The current work, therefore, provides interesting insights into how self-extinguishing donors function in ZN catalytic systems.

Introduction

Ziegler-Natta (ZN) catalysis is one of the most important catalytic processes, which produces around 150 million tons of polyolefins/year, and has a billion dollar market.^[1] Since its discovery in the 1950s by Karl Ziegler and Giulio Natta, for which they received the Nobel prize in 1963,^[2,3] continuous efforts to improve the performance of the ZN systems, concerning their activity and the selectivity, have been undertaken, along with understanding at the molecular level, by employing various experimental^[4–11] and computational tools.^{[12–}

^{34]} The main components of the ZN system are (i) MgCl₂ as a catalyst support, (ii) TiCl₄ as precatalyst, (iii) triethylaluminum (*teal*) as an alkylating agent, and (iv) Lewis base donors (e.g. oxygen-containing molecules and nitrogen-containing polymers^[35]). Donors are generally classified into (i) internal donors (**D**_i) that are added during the catalyst preparation, such as ethyl benzoate,^[26,36–41] diethers,^[13,27,38,42–44] phthalates,^[13,22,38,45,46] tetrahydrofuran,^[29,47] and succinates,^[27,38,48] and (ii) external donors (**D**_e) that are added along with the alkylating agent, such as alkoxysilanes^[38,46,49] and *p*-ethoxyethylbenzoate.^[38]

Donors are vital components of the ZN polymerization process that can enhance the stereo- and regioselectivity of the product by coordinating in the vicinity of the active titanium center.^[9,42,43,46] It can influence the kinetics of the activation, insertion and termination steps in the polymerization reaction, and can also help the titanium to coordinate to the (104) MgCl₂ surface, which is otherwise unutilized.^[30,31,33] It is interesting to note that tuning the structure of existing donors and developing new donors has always been challenging and a prominent area of research in ZN catalysis, because of their potential to produce polyolefins with desirable properties.

Olefin polymerization is an exothermic process that releases heat, and an increase in the temperature inside the reactor results in increase in the rate of the polymerization reaction, and vice versa. The reaction temperature is a crucial factor for polymerization as the heat generation causes polymer melting, which leads to the agglomeration of polymer particles that further causes lump formation. Such situations are detrimental to the continuous production of polymer resin. There is, therefore, considerable incentive to develop new ways over the existing ones to overcome this problem without affecting the

desirable properties of the polymerization reaction. One of the promising ideas is to use one of the components itself to “self-extinguish” the process at a higher temperature. There are several patents regarding the use of long-chain fatty acid external donors as activity limiting agents and bringing self-extinguishing behavior in the catalyst system.^[50–55] However, to the best of our knowledge, there are no detailed studies available about such systems that can shed light into the underlying reasons leading to the self-extinguishing of the donors, which can help to modify them to eliminate reactor fouling.

In the current work, we report the synthesis, polymerization studies, and a systematic density functional theory study (DFT) of a new class of self-extinguishing molecules **D₁** and **D₂** (see Figure 1) that can be used as self-extinguishing donors in ZN polymerization. **D₁** and **D₂** are fluorine-containing ester derivatives of myristic acid and palmitic acid, respectively. These compounds, when employed as donors (as **D_{ES}**), reduce the activity at elevated temperatures. The most probable reason for the lowering of the activity is parallel reactions in the ZN system. In 2014, the parallel reactions of various ester donors with Al_2Et_6 and TiCl_2Et on the MgCl_2 surface was investigated.^[34] We have now performed a systematic study using DFT to develop an understanding of this peculiar behavior of these **D_{ES}**.

Figure 1. Structures of the two self-extinguishing donors **D₁** and **D₂**.

Results and Discussion

(A) Synthesis of **D₁** and **D₂**

The synthesis of 2,2,2-trifluoroethyl fatty esters has been done by an entirely new strategy, which is significantly superior to the methods reported in the literature (see Scheme 1). Our approach involves only a single step, which is free from a base and chlorinated solvent, and, additionally, also occurs without the formation of any by-product. The eco-benign and economically favourable synthesis of such donors for ZN systems opens up a new area for deep exploration.

In 1993, Liu *et al.* reported the synthesis of the trifluoromethylated ester of fatty acids.^[56] The synthesis involved

conversion of fatty acids into the corresponding acid chlorides, followed by treatment with trifluoroethanol in the presence of base. However, a purification method was required and yielded the desired product up to 89 % yield. Monteiro *et al.* reported the synthesis of the trifluoromethylated ester of fatty acids using a similar strategy (*via* acid chloride method) and employed reusable acylating agents in the enzyme-catalyzed transacylation reactions.^[57]

Scheme 1. Synthesis of **D₁** and **D₂**.

(B) Polymerization Studies

Slurry phase propylene polymerization studies have been done using non/fluorinate myristic and palmitic derivatives as external donors. During the polymerization, the MgCl_2 supported TiCl_4 catalyst and triethyl aluminium were used as catalyst and co-catalyst respectively. In a preheated, 4L CSTR moisture free stainless-steel jacketed reactor having a stirrer, 2L n-hexane was added as a medium. During polymerization, a molar ratio of 250 of cocatalyst and precatalyst were maintained. 300 ml of hydrogen used as a chain transfer agent was added into the reactor under ambient conditions. The polymerization was carried out at 5.0–5.5 kg/cm^2 pressure and 70°C temperature. During polymerization, the reactor temperature increased to a maximum temperature due to the exothermicity of the reaction and then subside depending on the catalyst system. After 2 hours, propylene supply was cut off and the reactor was degassed slowly to atmospheric pressure. The hexane was removed and the polymer resin was collected and dried. A free-flowing polymer resin was found without lump formation, which indicated the absence of runaway reactions and the polymerization was self-extinguished in the presence of different catalyst systems. The self-limiting temperature for the isopropyl myristate (**D₃**), 2,2,2-trifluoroethyl myristate (**D₁**) and 2,2,2-trifluoroethyl palmitate (**D₂**) were observed to be 87.1°C , 81.9°C and 77.5°C respectively. These polymerization results suggest that the fluorinated donor showed a good self-extinguishing property in comparison to the non-fluorinated one (see Figure 2). The results also show that the length alkyl chain is an important factor, because **D₂**, having the longest alkyl chain, has the lowest self-extinguishing temperature.

Figure 2. The self-extinguishing temperature for **D**₁, **D**₂, and **D**₃.

(C) DFT Studies

In order to understand the reason for the difference in the self-extinguishing property of **D**₁ and **D**₂, we have performed a systematic full quantum mechanical study at the PBE-D3/TZVP//PBE0-D3/TZVP level of theory using density functional theory (for further information, please see the Computational Details section). Since **D**₁ and **D**₂ both have a long alkyl chain attached to the carbonyl carbon (see Figure 1), they can exist in different conformations. Before starting the study of the interaction of these **D**_{ES} with aluminum and titanium, we have performed a conformational analysis using the HyperChem software package.^[58] Our calculations indicate that the linear chain conformation of the alkyl chain is preferable among the other possible structures, and therefore, these most stable conformations of **D**₁ and **D**₂ have been used for further computational studies.

(i) Decomposition reaction of **D**₁ and **D**₂ with Al₂Et₆

D₁ and **D**₂ can react with Al₂Et₆, and lead to two different products. It can either form a dimer-donor adduct (Al₂Et₆-**D**₁/**D**₂) or two monomer-donor adducts (2AlEt₃-**D**₁/**D**₂). Our calculations indicate that the formation of two monomer-donor adducts is more favorable than the formation of a dimer-donor adduct (see below). We have taken the monomer-donor adduct (AlEt₃-**D**₁/**D**₂) as the reference energy for further calculations of the formation of ketone and aldehyde.

(a) Ketone pathway (KP)

Once the monomer-donor adduct formation takes place, it can pass through a six-membered transition state with the help of one more molecule of AlEt₃ (TS_{1KPM} and TS_{1KPP} for **D**₁ and **D**₂ respectively), in which one ethyl group from aluminum is transferred into the carbonyl carbon of the donor (see Figures 3 and 4). The barriers are 23.6 kcal/mol and 23.7 kcal/mol for **D**₁ and **D**₂, respectively. The second transition state is also six-membered, which involves the transfer of one ethyl group from AlEt₃ to AlEt₂, which is already bonded with the carbonyl O of

the donor, along with the breakage of the C-O bond and the formation of the Al-O bond, leading to the formation of the ketone. The corresponding barriers are minimal for **D**₁ (5.0 kcal/mol) and **D**₂ (4.9 kcal/mol). Our calculations therefore suggest that the formation of ketone by the reaction of **D**₁ and **D**₂ with Al₂Et₆ is thermodynamically and kinetically favourable. It should also be noted that since the corresponding barriers for the **D**₁ and **D**₂ cases are almost the same, the results also indicate that there is no difference in the reactivity of **D**₁ and **D**₂ in this particular reaction.

(b) Aldehyde pathway (AP)

Another possible pathway for the donor-AlEt₃ adduct to proceed is the AP, in which the first transition state (TS_{1APM} and TS_{1APP}) is the rate-determining one for both **D**₁ and **D**₂. The transition state involves the transfer of a hydride ion and the elimination of an ethylene molecule in the presence of one more molecule of AlEt₃, with a barrier of 21.2 kcal/mol for **D**₁ and 21.3 kcal/mol for **D**₂ (see Figure 3 and 4). It is interesting to note that the extra AlEt₃ molecule is not covalently interacting like in the case of KP. The second transition state is different from KP because the AP has a new stable intermediate (Int_{2APM} and Int_{2APP} for **D**₁ and **D**₂, respectively). We were not able to optimize such an intermediate for KP, probably due to the electron-donating effects of the ethyl group, which facilitates the C-O bond breakage and leads to the formation of the final product. The second transition state involves the formation of the Al-O bond alone, with a barrier of 2.6 kcal/mol for **D**₁ and 3.3 kcal/mol for **D**₂. Subsequent to this, the intermediate surmounts a barrier of 3.6 kcal/mol for **D**₁ and 4.5 kcal/mol for **D**₂, which leads to the formation of aldehyde.

Figure 3. The free energy profile for the decomposition reaction of **D**₁ (R = (CH₂)₁₂CH₃) with Al₂Et₆. The values are in kcal/mol. Blue indicates the ketone pathway (KP) and red indicates the aldehyde pathway (AP).

Our calculations therefore suggest that the AP is less favorable compared to the KP, thermodynamically and kinetically, which corroborates with NMR studies. However, like KP, **D**₁ and **D**₂ do not show any considerable difference for the AP as well.

Figure 4. The free energy profile for the decomposition reaction of **D**₂ ($R = (CH_2)_{14}CH_3$) with Al_2Et_6 . The values are in kcal/mol. Blue indicates the ketone pathway (KP) and red indicates the aldehyde pathway (AP).

(c) The effect of the $-CF_3$ group and the length of alkyl chain on the decomposition with Al_2Et_6

In order to understand the effect of the $-CF_3$ group and the length of the alkyl chain in the decomposition reactions, we have chosen three donors; **D**₃, **D**₄, and **D**₅ (see Figure 5 below). Experimental studies with **D**₃ (where trifluoroethyl group is replaced with isopropyl group), as reported above, indicate that it is less reactive than **D**₁ and **D**₂. On the other hand, **D**₄ and **D**₅ are two model donors that we considered here for computational purposes, in which the $-CF_3$ group has been replaced with $-CH_3$, and a long alkyl chain has been replaced with a $-CH_3$ group, respectively. Since the rate of the reaction depends on the slowest step in a reaction profile, we have calculated barriers for only the rate-determining steps for both KP and AP and compared the same with the barriers of **D**₁ (see Figure 6). It was found that the alkyl chain has a small effect on the barriers (for **D**₅, the barriers were 21.7 kcal/mol and 23.8 kcal/mol for KP and AP, respectively), but replacing the $-CF_3$ group with other alkyl groups had a significant impact on the barriers (the barriers increased by around 2.1 to 3.2 kcal/mol in both **D**₃ and **D**₄, see Figure 6). These calculated values indicate that a long alkyl chain would not help significantly to facilitate the decomposition reaction of a donor with Al_2Et_6 , but having an electron-withdrawing group attached to it (such as $-CF_3$) can increase the rate of decomposition reactions with Al_2Et_6 .

It is interesting to note that **D**₁ and **D**₂ did not show any considerable difference in their reactivity towards Al_2Et_6 , either thermodynamically or kinetically. However, there is a difference in their self-extinguishing properties, according to experimental observations.

Figure 5. Structures of **D**₁ and **D**₃, and the two model donors **D**₄ and **D**₅.

Figure 6. Barriers (values in kcal/mol) for the rate determining step for the decomposition donors **D**₁ (green), **D**₂ (orange), **D**₃ (blue), **D**₄ (purple), and **D**₅ (red), in the decomposition reaction with Al_2Et_6 .

(ii) Decomposition reaction of **D**₁ and **D**₂ with titanium on the (110) $MgCl_2$ surface

As mentioned in the Introduction, a donor can interact with titanium as well. We have calculated the binding energy of **D**₁ with titanium on the (110) $MgCl_2$ surface, where the choice of $MgCl_2$ model is based on work reported earlier (for further information, please see the Computational Details section).^[34] Here, one important thing to be noted is the orientation of the alkyl chain concerning the (110) $MgCl_2$ surface. We have considered two extreme cases: (i) the alkyl chain oriented away from the $MgCl_2$ surface and (ii) the alkyl chain oriented just above the $MgCl_2$ surface (see Figure 7). The calculated values indicate that the structure in which the alkyl chain is oriented just above the $MgCl_2$ surface is more stable than the other possibility by 21.0 kcal/mol. This vast difference in the binding energy is due to the favorable non-covalent interactions between the alkyl chain and the $MgCl_2$ surface. In other words, the long alkyl chain helps the donor to bind to the titanium more strongly. If the above hypothesis is correct, then there should be a considerable difference in the binding energies of **D**₁ and **D**₂ with titanium on the (110) $MgCl_2$ surface, because there is a difference of the alkyl chain length (by two carbon units) among these **D**_{ES}. However, our results do not show any significant difference in the binding energies, due to the limitation of our chosen small $MgCl_2$ surface model. The use of a sizeable $MgCl_2$ surface model that can completely interact with the long alkyl chain of **D**₁ and **D**₂ can provide the exact difference between the binding energies of **D**₁ and **D**₂, but such a computationally expensive

approach is beyond the scope of the current work. However, another way to proceed forward is to use the same MgCl_2 surface model but choose new donors in such a way that the difference between them is the same as between D_1 and D_2 . We have chosen three model donors D_6 , D_7 , and D_8 (see Figure 8) with small alkyl chains so that complete interaction is possible between the alkyl chain and the (110) MgCl_2 surface. The binding energy values obtained (-11.5 kcal/mol for D_6 , -14.5 kcal/mol for D_7 and -16.6 kcal/mol for D_8) for these new model donors clearly show an increase in the binding energy around 2.0 to 3.0 kcal/mol per addition of an extra CH_2CH_3 group in the structure of the donor. It is reasonable to assume that the same would be true for the case of D_1 and D_2 , which means that D_2 has a thermodynamic preference over D_1 to bind with titanium on the (110) MgCl_2 surface.

Figure 7. The relative binding energies (for D_1) of two possible orientations of the alkyl chain concerning the MgCl_2 surface (values are in kcal/mol); (A) the alkyl chain is oriented just above the (110) MgCl_2 surface, and (B) the alkyl chain is oriented away from the (110) MgCl_2 surface.

Figure 8. Structures of new model donors D_6 , D_7 , and D_8 with small alkyl chains compared to D_1 and D_2 .

In order to obtain more insights into the interaction between the alkyl chain and the (110) MgCl_2 surface, we have done non-covalent interaction (NCI) plots^[59] for the binding of D_6 , D_7 , and D_8 . The NCI plots indicate that there is a weak attractive interaction (the area colored in green between the alkyl chain and the MgCl_2 surface, see Figure 9) between the alkyl chain and the (110) MgCl_2 surface and, more importantly, the area of attraction increases with increase in the length of the alkyl chain.

Figure 9. The non-covalent interaction (NCI) plots for D_6 , D_7 , and D_8 binding to titanium, with the alkyl chain interacting with the MgCl_2 surface (the area of interest encircled in red). The color code for the NCI plots is as follows: blue - strongly attractive, green - weakly attractive, and red - strongly repulsive.

Once the donor binds with titanium, it can undergo decomposition through KP and AP. It is already reported that the first step, involving ethyl transfer in KP and hydride transfer in AP, are the rate-determining transition states. We have, therefore, calculated the barriers for both D_1 and D_2 (see Figure 10), and our calculations suggest that KP is much more favorable than AP, both in cases of D_1 and D_2 . However, the alkyl chain length does not have any influence on the barriers. It is important to note here that for D_1 and D_2 , the alkyl chain does not entirely interact with the (110) MgCl_2 surface. Therefore, in order to make sure that the alkyl chain length is not affecting the barriers, we have calculated the barriers for AP for D_6 (29.0 kcal/mol), D_7 (29.1 kcal/mol), and D_8 (29.3 kcal/mol), and found that there is no difference in the barriers. Our study also indicates that among various possibilities of decomposition reactions of D_1 and D_2 with AlEt_6 and titanium, the KP with the help of titanium is the most preferred pathway for both D_1 and D_2 .

Figure 10. The free energy profile for the rate determining steps for the decomposition reaction of D_1 ($\text{R} = (\text{CH}_2)_{12}\text{CH}_3$) and D_2 ($\text{R} = (\text{CH}_2)_{14}\text{CH}_3$) with titanium. The values are in kcal/mol. Blue indicates the ketone pathway (KP) and red indicates the aldehyde pathway (AP).

Our calculations indicate that difference in the reactivity of D_1 and D_2 is due to the difference in the chain length. However, in the slurry phase polymerization, there could be a competition between the alkyl chain of the donor and the n-hexane

molecules for the MgCl_2 surface. We have calculated the free energy required to displace the alkyl chain from the MgCl_2 surface by the *n*-hexane molecule (we have used an *n*-hexane molecule explicitly; see Figure S1 in ESI). For **D**₁ and **D**₂, the values are found to be the same (17.6 kcal/mol and 17.4 kcal/mol, respectively), which is due to the reason discussed earlier: our surface model is not big enough to quantify the complete interaction of alkyl chain with the MgCl_2 surface. Hence, we have calculated the corresponding free energy for **D**₆ (-4.7 kcal/mol), **D**₇ (-3.1 kcal/mol), and **D**₈ (-0.9 kcal/mol). Results indicate that with an increase in the alkyl chain length, it is difficult for the *n*-hexane molecule to displace the alkyl chain from the MgCl_2 surface, which is applicable for the case of **D**₁ and **D**₂ donors as well.

Conclusion

Reactor fouling is a significant issue in ZN catalyst systems, caused by overheating of the reactor vessel during the exothermic polymerization process. An interesting means of avoiding this problem is to employ donors with the ability to stop the polymerization process if the temperature were to exceed a certain value. In the current work, we report the synthesis and performance of two new donors and demonstrate their ability to self-extinguish under polymerization conditions. The two donors, **D**₁ (2,2,2-trifluoroethyl myristate) and **D**₂ (2,2,2-trifluoroethyl palmitate), have been made with an entirely new synthetic strategy, which is both eco-benign and economical. These donors can be employed as self-extinguishing in ZN catalyst systems, and polymerization studies that we have conducted show that **D**₂ self-extinguishes the reaction progress at 77.5°C, while **D**₁ does the same at 81.9°C. We have further explored the reason behind this difference in the self-extinguishing property between the two donors using density functional theory (DFT). A systematic study of the decomposition reaction of **D**₁ and **D**₂ with Al_2Et_6 and titanium attached on the (110) MgCl_2 surface has been done. With Al_2Et_6 , both **D**₁ and **D**₂ show a tendency to form monomer-donor adducts, and these adducts can undergo decomposition reactions with the help of another AlEt_3 molecule, either through the ketone pathway (KP) or the aldehyde pathway (AP), leading to the formation of a ketone or an aldehyde respectively. Such species are known to act as poisons in ZN systems, thereby explaining why **D**₁ and **D**₂ have the self-extinguishing property. Both donors have similar barriers for KP and AP, and among the two possible pathways, KP is more favorable, which corroborates with experimental observations. With titanium, both **D**₁ and **D**₂ bind strongly compared to Al_2Et_6 , and KP is a significantly more facile pathway. It is also interesting to note that the alkyl chain plays a significant role in making the binding stronger through non-covalent interactions. Even though the barriers are similar for both **D**₁ and **D**₂ for the decomposition reactions (both KP and AP) with titanium, the thermodynamic binding preference of **D**₂ over **D**₁ makes **D**₂ a better self-extinguishing donor, which agrees with the polymerization studies.

In summary, our work encompasses novel donor synthesis, polymerization studies that demonstrate their peculiar ability to self-extinguish during ZN catalysis, and careful and comprehensive computational studies that provide insight into how the donors interact with Al_2Et_6 , TiCl_4 and, importantly, also

the MgCl_2 surface in order to undergo the self-extinguishing process.

Experimental Section

Computational Details

The Turbomole 7.0 suite of program^[60] has been employed to optimize all the structures including intermediates and transition states using density functional theory (DFT). Geometry optimizations have been performed using the Perdew, Burke, and Ernzerhof (PBE) functional^[61] and TZVP basis set^[62]. The dispersion correction (DFT-D3) developed by Grimme et al. has been used to increase the accuracy of the calculations.^[63] The resolution of identity (RI)^[64] and the multipole accelerated resolution of identity (marij)^[65] approximations were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations. Closed-shell calculations were done for the Al_2Et_6 -donor model system cases, while open-shell calculations have been considered for the TiCl_2Et -donor model system cases. For better accuracy, we have performed single point calculations using PBE0 functional,^[66] TZVP basis set,^[62] and dispersion correction (DFT-D3).^[63] Our choice of the PBE-D3/TZVP//PBE0-D3/TZVP level of theory is based on benchmarking and computational studies.^[67,68,34] For the calculations that we have performed, the energy convergence criteria was 10^{-6} H, and the norm for the cartesian gradients was 10^{-3} . And the second-order derivatives of the potential energy obtained numerically. Further, to check whether our chosen level of theory is adequate to address the interactions in the system, especially in alkyl aluminum species (many functionals are known to underestimate the dimerization energy of bridged alkyl aluminum species),^[69] we have calculated the dimerization energy of AlEt_3 . Our calculations indicate that dimeric Al_2Et_6 is more favorable by 8.7 kcal/mol over monomeric AlEt_3 , suggesting that the chosen level of theory is sufficient to address the interactions. We have employed a 15 molecule MgCl_2 cluster (see Figure S2 in ESI) and have not employed any periodic boundary conditions. This model is chopped from the MgCl_2 model proposed by Cavallo and co-workers.^[27] The values reported are ΔG values, with zero point energy, internal energy, and entropic contributions (including translational, rotational, and vibrational entropy contributions) included through frequency calculations on the optimized minima and transition state structures, with the temperature taken to be 298.15 K. This was done in order to ensure that all of the reported transition state structures contained only one imaginary frequency corresponding to the correct normal mode. IRC calculations have been considered for the confirmation of the transition states. In every case, the IRC calculations have yielded the correct reactant and product structures.

General information for synthesis

¹H, ¹³C, and ¹⁹F NMR spectra were recorded either with JEOL 400 MHz, or BRUKER 500 MHz. ¹H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CHCl_3 at 7.27 ppm, integration, multiplicities (s = singlet, d = doublet, q = quartet, t = triplet, m = multiplet), and coupling constants (Hz). ¹³C NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77.0 ppm. $\text{CF}_3\text{CO}_2\text{H}$ used as external standards for ¹⁹F NMR. Myristic acid, Palmitic acid and Trifluoroethanol was purchased from Sigma-Aldrich and used without further purification. HPLC grade cyclohexane was purchased from Merck and used as received. Other organic solvents and conc. H_2SO_4 was purchased from local suppliers and used as received.

Procedure for preparation of **D**₁

To a solution of myristic acid (50.0 mmol, 1.0 equiv., 11.4 gm.) and 2,2,2-trifluoroethanol (50.0 mmol, 1.0 equiv., 5.0 gm) in 50 mL cyclohexane, was added conc. H_2SO_4 (30.0mol %) at ambient temperature and heated

to reflux (at 100°C) for 12 h. The mixture was cooled to room temperature, added saturated NaHCO₃ solution to neutralize excess H₂SO₄, and then was extracted three times with CH₂Cl₂ (100 mL each time). The combined organic phases were washed with brine solution, dried over anhydrous Na₂SO₄, and concentrated *in vacuo* to give the desired 2,2,2-trifluoroethyl myristate.

Colourless liquid at 300 K. Isolated Yield: 15.3 gm, 99.0 %. ¹H NMR (500 MHz, CDCl₃): δ = 4.46 (q, *J* = 8.5 Hz, 2H), 2.41 (t, *J* = 7.6 Hz, 2H), 1.66 (quin, *J* = 7.4 Hz, 2H), 1.35–1.24 (m, 20H), 0.88 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 172.11, 126.33, 124.12, 121.92, 119.72, 60.51, 60.22, 59.93, 59.64, 33.61, 31.93, 29.68, 29.64, 29.57, 29.42, 29.37, 29.18, 28.97, 24.69, 22.69, 14.06. ¹⁹F NMR (376 MHz, CDCl₃): δ = -74.02. GC data (Rt): 8.356 min (GC Programme: Column HP 5; Method: 80°C hold 1min; 20°C ramp up to 280°C; at 280°C Hold for 10 min; Inlet temp. 300°C, Detector temp. 300°C, H₂ Flow 40 mL, Air Flow 400 mL, N₂ Flow 25 mL per minute, Constant Flow mode).

Procedure for preparation of D₂

To a solution of palmitic acid (50.0 mmol, 1.0 equiv., 12.82 gm.) and 2,2,2-trifluoroethanol (50.0 mmol, 1.0 equiv., 5.0 gm) in 50 mL cyclohexane was added conc. H₂SO₄ (30 mol %) at ambient temperature and heated to reflux (at 100°C) for 12 h. The mixture was cooled to room temperature, added saturated NaHCO₃ solution to neutralize excess H₂SO₄, and then was extracted three times with CH₂Cl₂ (100 mL each time). The combined organic phases were washed with brine solution, dried over anhydrous Na₂SO₄, and concentrated *in vacuo* to give the desired 2,2,2-trifluoroethyl palmitate.

Colourless solid at 300 K. Isolated Yield: 16.5 gm, 98 %. ¹H NMR (500 MHz, CDCl₃): δ = 4.46 (q, *J* = 8.5 Hz, 2H), 2.41 (t, *J* = 7.8 Hz, 2H), 1.66 (quin, *J* = 7.4 Hz, 2H), 1.35–1.22 (m, 24H), 0.88 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 172.11, 126.32, 124.12, 121.92, 119.71, 60.51, 60.23, 59.93, 59.64, 33.61, 31.94, 29.70, 29.67, 29.64, 29.57, 29.42, 29.38, 29.18, 28.97, 24.68, 22.70, 14.07. ¹⁹F NMR (376 MHz, CDCl₃): δ = -73.99. GC data (Rt): 9.359 min (GC Programme: Column HP 5; Method: 80°C hold 1min; 20°C ramp up to 280°C; at 280°C Hold for 10 min; Inlet temp. 300°C, Detector temp. 300°C, H₂ Flow 40 mL, Air Flow 400 mL, N₂ Flow 25 mL per minute, Constant Flow mode).

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Entry for the Table of Contents

We have synthesized two new external donors **D₁** and **D₂**, for Ziegler-Natta catalysis that show the ability to self-extinguish, followed by a DFT study to shed light on this interesting property. **D₁** and **D₂** can produce ketone and aldehyde, which are considered poisons for the system, by reacting with the aluminum and titanium species. The binding of a donor with titanium will be more favourable if it has a higher alkyl chain length.

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