

Probing the Impact of Solvent on the Strength of Lewis Acids via Fluorescent Lewis Adducts

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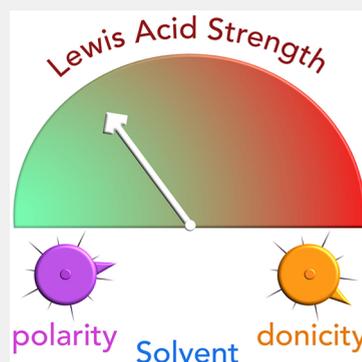
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ABSTRACT: Various methods have been developed to measure the strength of a Lewis acid. A major challenge for these measurements lies in the complexity that arises from variable solvent interactions and perturbations of Lewis acids as their reaction environment changes. Herein, we investigate the impact of solvent effects on Lewis acids for the first time as measured by the fluorescent Lewis adduct (FLA) method. The binding of a Lewis acid in various solvents reveals a measurable dichotomy between both polarity and donor ability of the solvent. While not strictly separable, we observe that the influence of solvent polarity on Lewis acid unit (LAU) values is distinctly opposite to the influence of donor ability. This dichotomy was confirmed by titration data, illustrating that solvation effects can be appropriately and precisely gauged by the FLA method.



KEYWORDS: Fluorescence, Fluorescent Lewis adducts, Lewis acids, Effective Lewis acidity, Solvent polarity, Solvent donor strength

INTRODUCTION

Lewis acids have become essential throughout the chemical sciences, particularly in the fields of catalysis^{1–3} and organo-electronics.^{4–6} Catalysis, in particular, has seen great benefit from the emergence of frustrated Lewis pairs (FLPs) and other metal-free transformations.^{2,7–9} As Lewis acid chemistry begins to permeate other disciplines, the need for correlating the acceptor strength of a Lewis acid with their efficacies becomes vital. However, determining the reactivity of specific Lewis acids remains ambiguous, creating challenges in selecting reaction conditions and an appropriate Lewis acid to achieve a desired reaction.¹ Currently, Lewis acidity cannot be described by a single measured property, and several parameters must be considered jointly in order to select a potent Lewis acid catalyst.^{10–12} As such, models based on spectroscopic and computational methods have been developed to quantitatively distinguish Lewis acidity, such as the Gutmann–Beckett method, the Childs method, ion affinity, and the global electrophilicity index (Scheme 1).^{13–20} However, these approaches may sometimes lead to inconclusive results depending on the applied method and rarely account for chemical environment, such as additional species in solution, solvents, or solvated species. Further, these methods neglect the *effective* or *reactive* nature of the Lewis acid in favor of measuring an *absolute* Lewis acid strength, reducing their utility to predict reactivity, as emphasized by Erdmann and Greb.²¹ Absolute Lewis acid measurements, such as the commonly used, aforementioned methods, are established under static conditions and may not accurately predict the utility of a Lewis

acid under the dynamic conditions of a reaction. To better describe the reactivity of a Lewis acid under the varied range of conditions (i.e., as a catalyst), a methodology to precisely measure *effective* Lewis acidity is required. A method that measures effective Lewis acidity must be variable enough to be utilized with changing reaction conditions, sensitive enough to discern the impact of the changes, and precise enough to be consistent across varied Lewis acids and reaction conditions.

We recently established a new methodology based on fluorescence spectroscopy to quantify Lewis acidity, termed fluorescent Lewis adducts (FLAs).^{22,23} This method utilizes a series of fluorescent dithieno[3,2-*b*:2',3'-*d*]phosphole oxide Lewis base probes^{24–26} that, when bound to a Lewis acid in solution, lead to a bathochromic shift of their optical properties (Scheme 1).²²

The degree of the bathochromic shift is generally proportional to the Lewis acid strength, as the Lewis acid coordination alters the polarity of the exocyclic P=O bond, leading to a lowered LUMO energy level, i.e., the π^* -system of the probe.^{22,27} However, instead of relying on emission maxima, the FLA method utilizes chromaticity for a measure

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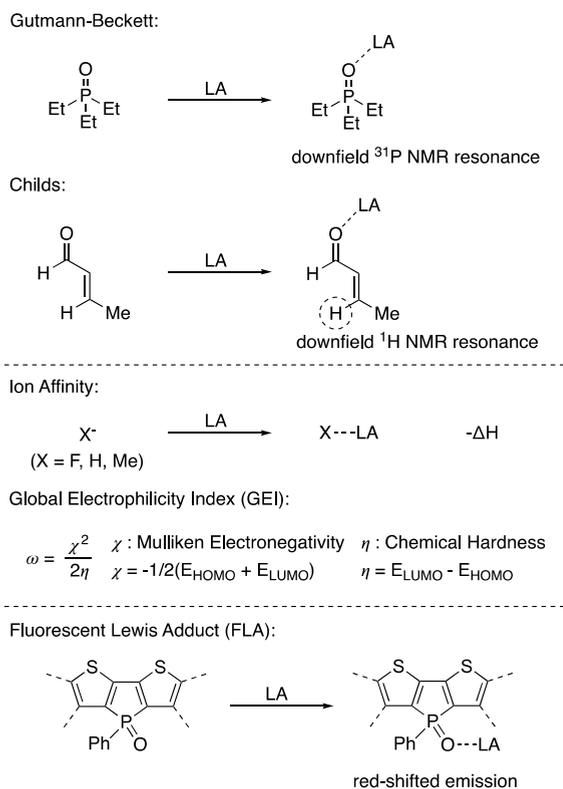
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Scheme 1. Multiparameter Methods for Measuring Lewis Acidity (LA = Lewis Acid)



of the emissive properties of the solution as a whole, incorporating all emissive species present. This allows for a true “solution-state” measurement that is more consistent with the *effective* nature of the Lewis acid in solution than simply the measure of the impact to an isolated “naked” Lewis base on the Lewis acid (i.e., *absolute* Lewis acidity).

The FLA method differs from typical (absolute) Lewis acid measurements in that it leverages the impact of the Lewis acid on several Lewis base probes.^{22,23} This affords the system high versatility, while the use of fluorescence and chromaticity affords a high sensitivity. By using chromaticity, Lewis acids that persist in solution in multiple forms are evaluated incorporating all adduct permutations to the emission spectrum. This includes structural changes to the Lewis acid itself, such as the formation of solvates, coordination complexes, or other such permutations of the (hypothetical) monomeric structure. A representative example is AlCl_3 , which can exist as oligomeric, charge-separated salts or even octahedral species in solution. The method can account for the statistical distribution of these structural permutations in solution, allowing a “solution-state” measurement. Our initial proof-of-concept for the FLA method demonstrated its simplicity, precision, and sensitivity,²² whereas in our subsequent paper, the robustness and broad scope were highlighted by expanding the library of measured Lewis acids to over 50 species, including both common and unique compounds that could not be measured by pre-existing methods.²³ The FLA method provides a simple scale in Lewis acid units (LAU) to compare all measurements universally, theoretically ranging from 0 to ∞ , with values currently reported between 5 and 50 LAU, and a margin of error of less than 0.25 LAU.²³ These foundational contribu-

tions have provided a considerable step forward in developing the FLA method, allowing the exploration of a variety of inherently dissimilar Lewis acids in an otherwise identical chemical environment. Previously, the FLA method had been solely performed in toluene for its benign reactivity and to allow the sufficient solvation of the probes and the many measured substrates. However, to truly demonstrate the utility of the FLA method as a means to measure effective Lewis acidity, the method must also show robustness across varied chemical environments, which we aim to address in this study.

The solution-state nature of the FLA method, along with the high sensitivity of the fluorescence measurement, affords the unique potential to precisely measure how Lewis acids may differ under environmental changes, such as in the presence of additional donor species (including solvents) or varied polarity. We propose that this process will provide further insight into an effective Lewis acidity, allowing the comparison of species as they would be used in a chemical reaction environment. We now report the impact of solvent effects on a panel of representative Lewis acids using the FLA method, which showcases different solvent environments and the influence of varied environments on their effective Lewis acidity.

RESULTS AND DISCUSSION

The FLA method uses multiple probes with emission chromaticities that span the commission internationale de l'éclairage (CIE) diagram (Figure 1).²³ In the context of this

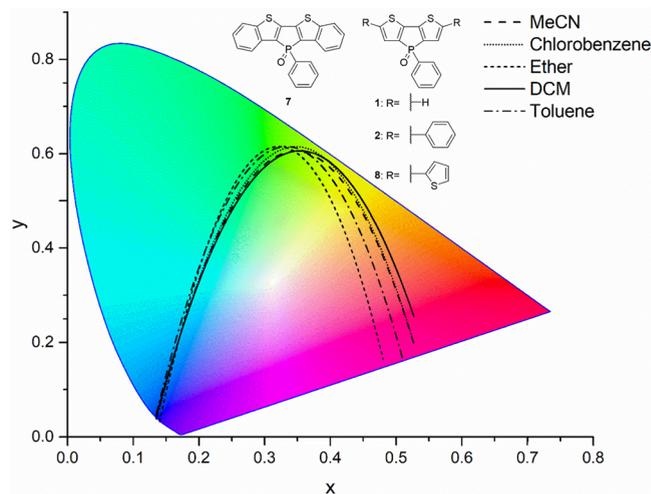


Figure 1. Probe fit functions in solvents of varied polarity and donor potential over CIE space, with probes 1, 2, 7, and 8.

study, four probes (1, 2, 7, and 8)²⁸ were used to measure their respective emission profiles in varying polar solvents.^{24–26} The selected solvents ranged in polarity from nonpolar to polar, based on the Dimroth–Reichardt $E_{\text{T}}(30)$ parameter scale: toluene (Tol, 33.9 kcal/mol), diethyl ether (Et_2O , 34.6 kcal/mol), chlorobenzene (PhCl, 37.5 kcal/mol), dichloromethane (DCM, 41.1 kcal/mol), and acetonitrile (MeCN, 46.0 kcal/mol).²⁹ It should be noted in this context that $E_{\text{T}}(30)$ values are determined by the solvatochromism of betaine dye 30 and correlating it to free energies.²⁹ We also refer to the donor number introduced by Gutmann et al.; this donor number measures the ability of a solvent to solvate the Lewis acid standard, SbCl_5 .³⁰ The selected solvents used in the present

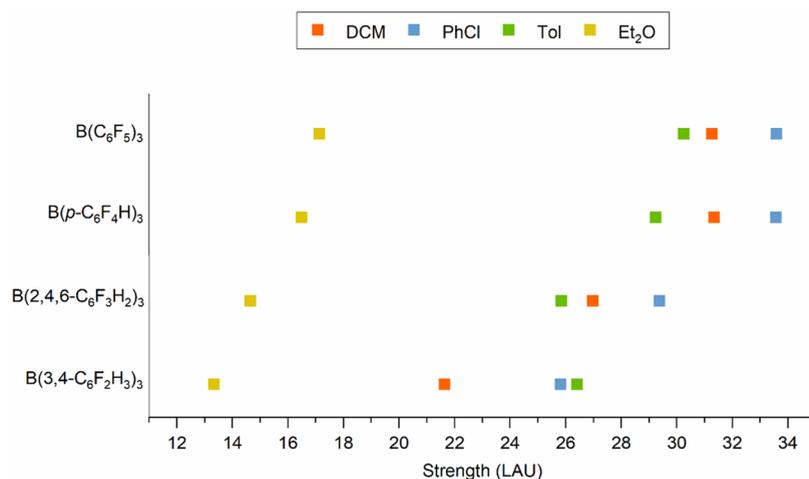


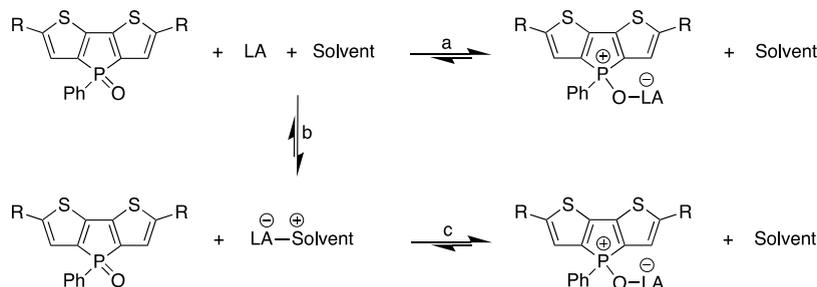
Figure 2. LAU values in various solvents of fluorinated arylborane Lewis acids with varied degree of fluorination. Values in toluene are from previous measurements.^{22,23}

study range in donor ability from noncoordinating to coordinating: toluene (Tol, 0.1 kcal/mol), dichloromethane (DCM, 1.0 kcal/mol), chlorobenzene (PhCl, 3.0 kcal/mol), acetonitrile (MeCN, 14.1 kcal/mol), and diethyl ether (Et₂O, 19.2 kcal/mol). While the chosen dithienophosphole oxide probes do not exhibit solvatochromism, each individual solvent afforded a unique trend in chromaticity space for the precise fit of the Lewis base emissions with a parabolic function (Figure S1). The resultant fit data (within the CIE space) are then used to calculate the LAU values (Table S1) in the respective solvent. As such, each solvent generates a unique fitting function for the emissions of the base probes, which is to be used when determining the LAU values of a Lewis acid measured in that solvent. Notably, the fit functions remain similar enough that when accurate measurement is not strictly needed, the original toluene fit function may provide a general estimate Lewis acid measure. Additional solvent–fit functions can thus be generated for any solvent viable for fluorescence measurements.

At the core of the FLA method is the correlation of chromaticity of the adduct emission with the binding constant of the Lewis acid/base adduct at emission saturation, not dissimilar to the determination of $E_T(30)$ values. To determine if this correlation is sustained across chemical environments, titration studies of B(C₆F₅)₃ against the probes **1**, **2**, **7**, and **8** were conducted in the select solvents. The binding constants were determined from the concentration and the ratio of the adduct and the dithienophosphole oxide emission intensities at equilibrium using eq S1, and the calculated values are presented in Table S8.³¹ These data suggest that the FLA method retains the correlation between chromaticity and binding constant across solvent environments. However, from this study, distinct trends in the binding constants emerged based on the nature of the solvent employed. In toluene, the binding constant of probe **1** with B(C₆F₅)₃ was relatively large, $1 \times 10^5 \text{ M}^{-1}$, suggesting a strong interaction between the phosphoryl oxygen atom and the boron center. Upon introducing weakly coordinating solvents, such as DCM and PhCl, the binding constant decreased by nearly an order of magnitude to $\sim 3 \times 10^4 \text{ M}^{-1}$. By employing an even stronger donating solvent, such as Et₂O, the binding constant decreased by another order of magnitude, $\sim 3 \times 10^3 \text{ M}^{-1}$. In MeCN, however, no binding was observed, and the emission consisted

entirely of free dithienophosphole oxide probe. The incorporation of a competing donor had the anticipated impact on the determined binding constant, and the chromaticity of the emission appropriately correlated to that change. Therefore, the data show that in an environment with a more donating solvent, the Lewis acid and base have a reduced propensity to generate the corresponding adduct. This result itself is rather intuitive, but the FLA method afforded a simple and accessible direct measure of this observation for the first time, confirming that it is sufficiently sensitive and precise for measuring the variations in Lewis acidity due to solvent effects.

In contrast to the direct association of the binding constant to chromaticity, the LAU value results from an aggregate of data from several different Lewis bases, and as such loses the specificity of any specific acid/base binding (i.e., *absolute* Lewis acidity). This property arises from the use of both chromaticity and multiple probes to determine a single LAU value. Thus, the true power of the FLA method lies in the measurement of the solution state (i.e., *effective* Lewis acidity), since it uses an aggregate of binding data instead of a single (absolute) measurement/calculation for Lewis acid/base adduct. Thus, to establish a quantifiable relationship between solvent properties and Lewis acidity, the LAU values in the new solvent environments were determined using the previously reported method.²³ Appropriately, the stronger the coordination of the solvent, the weaker the binding constant for the Lewis acid adduct, and the lower the LAU value. For example, B(C₆F₅)₃ presented a LAU of 31.27 in DCM, 17.14 in Et₂O, and was unmeasurable in MeCN, even with a large excess of Lewis acid, due to the strong Lewis acid–base adduct formed between acetonitrile and B(C₆F₅)₃.³² While these data utilize chromaticity to afford a measure of all acid–base interactions in solution, it should be noted that the emission maxima undergo a blue shift in emission, indicating that the primary acid–base interaction, or the idealized B(C₆F₅)₃·probe adduct, is less prevalent in donating solvents than the original study in toluene (Tables S4–S7). While this coincides with the binding data, it is fundamentally different. By using both chromaticity and an aggregate of multiple probe measurements, the LAU value represents a direct measure of the Lewis acid as it persists in solution, the effective Lewis acidity. Therefore, the *effective Lewis acid strength of the solution* (as indicated by the LAU value) is ultimately reduced with respect to increasing

Scheme 2. Proposed Competing Equilibria during the Formation of the Fluorescent Lewis Adduct (FLA)^a

^aA stronger Lewis base (i.e., P=O) increases the forward rate of (a), while a stronger donor solvent (acetonitrile) increases the forward rate of (b). With a mild Lewis base and a mildly coordinating solvent such as Et₂O, (a) and (c) can both be seen and measured independently in part due to the slow rate of (b).

Gutmann donor number. With both the binding and LAU data together, it can be demonstrated that B(C₆F₅)₃ is *both weaker and less accessible* in a solution with a stronger donor solvent.

Next, we attempted to correlate the titration data of B(C₆F₅)₃ with probes **1**, **2**, **7**, and **8** with the polarity of the solvents used. Interestingly, however, we noticed that polarity afforded the opposite effect among solvents of similar donor potential. Increasing binding constants were observed in the more polar solvents when comparing solvents of similar donor potential. While slightly less intuitive than the above result, these data demonstrate that the FLA method can also distinguish between the influence of polarity and donor potential of a solvent by selective experimental design. Again, generation of LAU values allows for the comparison of the effective Lewis acidity, and when looking at solvent polarity, an increase in polarity led to higher LAU values. For example, when comparing PhCl (3.0 kcal/mol) and DCM (1.0 kcal/mol), the LAU value increases in the more polar solvent, and as such, polar solvents increase the *effective Lewis acid strength of the solution* (Figure 2).

In addition, during the titration experiments conducted in diethyl ether, the FLA method afforded an intriguing perspective into the dynamics of Lewis acidic solutions. Originally appearing as anomalous, in the moderately coordinating solvent, a two-step equilibrium process was observed (Figure S163). Since the FLA method involves three components, a Lewis acid, a Lewis base, and the solvent,²² it is reasonable to propose that the observed interactions reflect the difference in the binding of the Lewis base probe with a free Lewis acid or a solvated Lewis acid species (Scheme 2).³³ The two-step equilibrium process was observed in the titration curves as two distinctly separate equilibria, specifically when using the relatively weaker Lewis base **8**.^{22,23} Upon increasing the relative donor strength of the dithienophosphole probe (via modification of the conjugated backbone), the rate of (a) increases (Scheme 2), resulting in an overlap in the measure of the two competing equilibria. Thus, utilizing the relatively stronger Lewis base probe **1**,^{22,23} the two equilibria cannot be distinguished by the titration data alone. Although the competing reaction is likely occurring in solution, the rates have become so similar that they are nearly impossible to separate via these experiments (Figure S163). These competing equilibria likely also occur with other Lewis acids and solvent combinations; however, it may require highly specific experimental design to separate them and allow for the independent measure of (a) and (c). This specificity does not impact the resultant LAU values determined during any

specific experiment, a benefit of the solution-state measurement. Instead, these data demonstrate the high sensitivity of the FLA method and allow for a deeper study into the complexity of even relatively simple Lewis acids in a route that has yet to be thoroughly investigated.

The study of B(C₆F₅)₃ in varied solvents demonstrates that the FLA method can provide a direct measurement of effective Lewis acidity, which with previous models have challenges.²³ The LAU values provide a scale for comparing effective Lewis acidity across these varied environments. Additionally, a dichotomy between polarity and donor potential of a solvent can clearly be measured, revealing the complexity of Lewis acid states in solution, and underscoring the importance of solvent effects when choosing a Lewis acid and reaction conditions.

Having shown that the precision of the FLA method is retained across changes in chemical environment, we sought to expand this approach to a broader scope. More specifically, we aimed to determine if any general trends changed or persisted across a panel of select Lewis acids and to ensure that the LAU measurements remained viable across varied environments. We began this study with a series of triaryl boranes with decreasing fluorination (Figure 2); this series behaves similarly and consistently. All these Lewis acids followed the same general trends with respect to influence of solvent polarity and donor ability as with B(C₆F₅)₃ and largely retained their relative rank across the differing solvent environments. However, the degree to which polarity and solvent donor potential impact the Lewis acids varies, in part by the strength of the Lewis acid, as these boranes remain monomeric in solution, and structural permutations are minimal. It becomes clear that the impact of solvent polarity dominates in solutions of stronger Lewis acids. B(C₆F₅)₃ and B(*p*-HC₆F₄)₃ show a significant increase in effective Lewis acidity, even in dichloromethane and chlorobenzene, over that previously reported in toluene, while B(3,4-C₆F₂H₃)₃ and B(2,4,6-C₆F₃H₂)₃ show a significantly lesser increase in those solvents. While the impact of solvent donor strength or polarity on a Lewis acid solution in general may seem intuitive, these results demonstrate that the degree to which those properties impact a Lewis acid solution are not. These data suggest that the nature of the Lewis acid determines how the solvent properties alter the effective Lewis acidity of the corresponding solution. This underlines the necessity for effective Lewis acid measurements. In other words, no standardized list of modifiers can adjust an absolute Lewis acid measurement to predict an effective Lewis acid measurement. In fact, B(C₆F₅)₃ is definitively a stronger Lewis acid than B(*p*-HC₆F₄)₃ in toluene; in the other solvents,

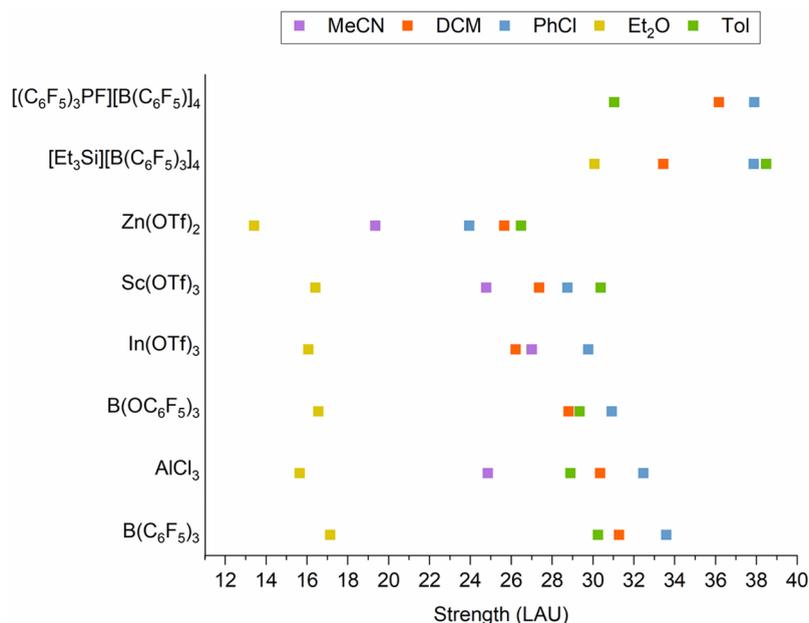


Figure 3. LAU values of main group, metallic, and cationic Lewis acids plotted by solvent. Values in toluene are from previous measurements.²³

however, the adjusted LAU values are within the margin of error, potentially leading to the common discrepancy in the measure of these two species. In addition, we measured the related borate $B(OC_6F_5)_3$, as the aryloxy functionality may afford a different relationship between donor and polar solvent environments. Indeed, the borate species showed similar LAU values in noncoordinating solvents as were measured in toluene, with solutions corresponding to Lewis acid strengths consistently falling between the trifluorophenyl- and tetrafluorophenyl-based boranes. Notably, in ether, the borate solution is marginally stronger than $B(p-HC_6F_4)_3$, yet in DCM and PhCl, the borate solution is weaker. The impact of donor potential and polarity is altered; however, the dichotomy between the two properties is notably retained.

Since the effective Lewis acidity is clearly reliant on the specific Lewis acid present, we then expanded the study beyond boranes to other pertinent Lewis acids: $AlCl_3$, $In(OTf)_3$, $[SiEt_3]^+$ (as $[SiEt_3]^+ [B(C_6F_5)_4]^-$), $Sc(OTf)_3$, $Zn(OTf)_2$, and $[(C_6F_5)_3PF]^+$ (as $[(C_6F_5)_3PF]^+ [B(C_6F_5)_4]^-$). These Lewis acids were chosen for their differences in type, strength, and/or common utility in catalysis.^{22,34–39} The LAU values of these Lewis acids were again determined using the previously reported procedure,²³ and overall, we observed the same trends as seen with the borane-based Lewis acids in the different solvents. In general, LAU values increase relative to the solvent polarity; however, the donor potential of the solvent can lower the LAU value, as shown in Figure 3 and Table S3, but this was not always explicitly the case. Notably, as seen above, some solutions in Et_2O (19.2 kcal/mol) and CH_3CN (14.1 kcal/mol) inhibit the formation of the fluorescent Lewis adduct.

While it remains clear that the specific Lewis acid has a strong influence on the impact of solvent effects, some general trends could nonetheless be observed across the studied Lewis acids. The cationic Lewis acid species in the series are some of the strongest measured by the FLA method, and often present difficulties with other methods, both spectroscopic and computational. Both $[SiEt_3]^+$ and $[(C_6F_5)_3PF]^+$ were successfully measured in several solvents and provided the highest yet

measured LAU values in DCM, PhCl, and ether. Unfortunately, the phosphonium cation provided inconsistent results over multiple measures in ether, due to poor solubility.⁴⁰ But the cationic Lewis acids acted similarly to one another when comparing impact of polarity or donor ability; they specifically showed strong reliance on donor ability.

$[SiEt_3]^+$ exhibits the highest measured LAU value in this study in toluene. This is not the result of solvent polarity or donor ability, but instead, demonstrates the precision of the FLA method. In toluene, and other non-halogenated arenes, $[SiEt_3]^+$ generates a highly reactive π -arene complex.^{41,42} The absolute Lewis acid strength of this complex has not been determined, however, the LAU value of $[SiEt_3]^+$ in toluene incorporates the Lewis acidity of this reactive intermediate. The LAU value still precisely depicts the Lewis acid strength of the solution, as this species will be generated in any typical toluene solution of $[SiEt_3]^+$.

Similarly, the metallic Lewis acids appear to exhibit a strong increase in LAU values in polar solvents, with strong donor solvents significantly reducing the LAU values, however, nonpolar solvents lead to the largest observed LAU values demonstrating that the donor strength has a very strong influence on their effective Lewis acidity. For $Sc(OTf)_3$ and $Zn(OTf)_2$, nonpolar weak donor solvents generate the strongest Lewis acid solutions. However, it remains clear that across all measured Lewis acids, the influence of donor strength and polarity were strictly opposite.

It is important to note that separating solvent polarity and donor potential is not trivial, as the two solvent properties are interconnected. Ideally, the influence of one property would be most clearly measured over a panel of solvents with identical polarity and varied donor potential or the opposite. As such, the impact of one specific property is determined by comparing environments in which there is a significant change in one property and a minimal change in the other. For example, the polarity of toluene and diethyl ether are relatively similar; however, the Gutmann donor number is significantly different. Therefore, comparing the LAU results between the two is more indicative of the impact of solvent donor ability on

Table 1. Select LAU Values of Lewis Acid and Solvent Combinations Demonstrating the Impact on Changing Polarity or Donor Potential of the Solvent^a

Lewis acid	solvent	polarity (kJ/mol)	donor potential (kcal/mol)	LAU	dominant influence
BPh ₃	toluene	33.9	0.1	11.31	polarity
	MeCN	46.0 ↑	14.1 ↑↑↑	14.02 ↑	
[SiEt ₃] ⁺	toluene	33.9	0.1	38.48	polarity
	PhCl	37.5 ↑	3.0 ↑	37.87 ↓	
	DCM	41.1 ↑	1.0 ↓	33.44 ↓	
[(C ₆ F ₅) ₃ PF] ⁺	DCM	41.1	1.0	36.16	polarity
	toluene	33.9 ↓	0.1 ↓	27.85 ↓	
B(C ₆ F ₅) ₃	toluene	33.9	0.1	30.25	donor potential
	DCM	41.1 ↑	1.0 ↑	31.27 ↑	
	PhCl	37.5 ↓	3.0 ↑	33.59 ↑	
B(<i>p</i> -C ₆ F ₄ H) ₃	toluene	33.9	0.1	29.23	donor potential
	Et ₂ O	34.6 ≈	19.2 ↑↑↑	16.49 ↓↓↓	
Zn(OTf) ₂	MeCN	46.0	14.1	19.34	polarity
	DCM	41.1 ↓	1.0 ↓↓↓	25.66 ↑	
	toluene	33.9 ↓↓↓	0.1 ↓	26.99 ↑	
Sc(OTf) ₃	toluene	33.9	0.1	30.37	polarity
	DCM	41.1 ↑	1.0 ↑	25.66 ↓	
	MeCN	46.0 ↑	14.1 ↑↑↑	24.77 ↓	

^aThe difference and magnitude of change in a property is represented by arrows, and a summary of the more influencing property is established.

the Lewis acid. Using several such comparisons allows for determining which property demonstrates a stronger influence on the effective Lewis acidity. Nonetheless, any observed changes in one property occur with at least minor changes in the other. This can lead to occasionally counterintuitive results in LAU values, such as when there is a large change in both solvent polarity and donor potential leading to only a minor change in LAU value overall. This is a result of polarity and donor ability acting in opposition toward Lewis acid strength; the dichotomy of these properties remains true, yet they are not independent variables. Nonetheless, trends observed across the measured set of Lewis acids, with the exception of the dichotomy between polarity and donor potential of a solvent, can not necessarily be extended to any given Lewis acid but may still prove beneficial in predicting reactivity.

To more deeply explore this dichotomy between solvent polarity and donor potential, we highlight the impact of acetonitrile on the neutral boranes. Acetonitrile solutions of strongly Lewis acidic boranes completely shut down FLA formation due to the coordination of the nitrile (*vide supra*). However, AlCl₃ still generated a solution of measurable (and moderate) Lewis acid strength, as did all three triflate species, including the group 13 species In(OTf)₃. We sought to explore if the donor potential of acetonitrile was uniquely shutting down access to borane Lewis acids, or if this too was strongly influenced by the nature of the Lewis acid. In our previous work, BPh₃ was used as a basis for non- to low-strength Lewis acidity and again acts as an essential comparison to the perfluorinated phenylboranes. In acetonitrile, BPh₃ generates a solution of 14.02 LAU, an increase over the measurement in toluene. The Lewis acidity was not quenched due to coordination to the boron center, and in fact the LAU value increased over toluene signifying the increase as a result of the more polar solvent. This suggests that the dichotomy of polarity versus donor potential does strongly favor polarity with weaker Lewis acids, and that the neutral boranes are not unique in their reactivity with acetonitrile.

While these results demonstrate that *effective* Lewis acidity is a complex entity and it incorporates many individual properties

of the environment the Lewis acid is in, it can still be measured precisely. Table 1 summarizes the results and trends across the select Lewis acids measured in this study. The dichotomy of solvent polarity and donor potential in measured Lewis acid solutions can clearly be seen. The select Lewis acidic solutions are presented in comparison to a nonpolar, weakly donating toluene solution. The influence of the new solvent on LAU values, and as such effective Lewis acidity, as well as the primary property (polarity or donor potential) that afforded the change are presented. The primary influence can be determined by the degree of change in LAU value that occurs, although it should be noted that both properties are always acting in opposite effect of one another. It is clear that the Lewis acid choice greatly influences the solvent impact, but some trends remain. Neutral group-13 Lewis acids experience a strong influence from donor solvents that reduces their Lewis acidity, cationic Lewis acids can be strengthened by stabilizing the cation in a polar solvent, but have a strong influence from donor solvents that can coordinate to the cation, and weaker Lewis acids show the weakest influence from donor solvents due to the weak Lewis acid/base interaction, and are more strongly influenced by solvent polarity. These influences from the Lewis acid itself as to how the interaction with solvent properties alters Lewis acidity emphasizes the need for effective Lewis acid measurements, for which the FLA method has shown itself to be a precise tool.

CONCLUSIONS

In conclusion, using the FLA method, we have provided insights into how solvents impact *effective Lewis acidity*. Two significant factors influencing the measured Lewis acidity in the FLA method are the polarity and donating potential of the solvent. Specific Lewis acids, however, dictate the degree to which donor potential and polarity each effect Lewis acidity. It should be stated that while no universal correlation for solvents can be established for all Lewis acids, several generalizations could clearly be established across the select group of Lewis acids studied. The FLA method records the binding of all potential Lewis acid species in solution to a theoretical probe;

however, depending on the coordinating ability of the solvent, a complex equilibrium with the solvent may be observed. Within a specific range of Lewis acidity and solvent choice, that complexity can be observed as two distinct equilibria. We hypothesize that the first equilibrium involves the free Lewis acid, and the second equilibrium the solvated Lewis acid. This likely occurs in any donating solvent but was not always strictly separable in our measurements. Nonetheless, the results of the binding of a Lewis acid, even as impacted by solvent, via both polarity and donor potential, and solvation can be accurately gauged by the LAU value determined from the FLA method, further solidifying the FLA method as a measure of *effective Lewis acidity*. To demonstrate the utility of these results, we are currently systematically investigating Lewis acid-catalyzed reactions against which these data can be compared.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/prechem.2c00009>.

Experimental details, chromativity data of all FLAs, emission and excitation data of all FLAs, and binding constants (PDF)

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Author Contributions

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Notes

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