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## A COMPUTATIONAL APPROACH FOR DISTINGUISHING OF LASER-IGNITABLE AND NON-IGNITABLE ENERGETIC COORDINATION COMPLEXES (LECCs)

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In recent years, laser-ignitable energetic coordination complexes (LECCs) have attracted increasing attention, to the extent that a 2022 review questioned whether they represent merely a scientific curiosity or the future of energetic materials [1]. Today, LECCs constitute a rapidly expanding class of compounds, actively explored as lead-free primary explosives and laser-initiated energetic systems, with more than one hundred representatives already reported in the literature [2]. Despite this progress, a simple and universal descriptor capable of unambiguously classifying compounds as laser-ignitable or non-ignitable is still lacking. In this context, it is important to reconsider the fundamental criteria defining LECCs from a structural standpoint. First, the presence of a metal center is not a necessary condition, as purely organic compounds such as 4,4',5,5'-tetranitro-2,2'-biimidazole (TNBI) have been shown to undergo laser initiation at 1064 nm [3]. Second, specific electronic features of the metal ion, such as open-shell configuration or affiliation to *d*-elements, are not required, since TNBI forms laser-sensitive salts with main-group cations ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$), which are closed-shell, chemically hard species [3]. Third, the presence of components with positive energy content is also not

obligatory; for example, LECCs incorporating biuret ligands, characterized by a strongly negative enthalpy of formation and energy content ($E_c$), still exhibit laser ignitability [4]. In this context, a promising descriptor is the presence of non-zero (but not too high to prevent photochemical processes) absorption at the laser irradiation wavelength, usually diode (915 nm) or Nd:YAG (1064 nm). Thus, a relatively fast, cheap and accurate method for electronic spectrum prediction for solid forms of LECCs is of paramount importance in the field.

In this work, we studied the electronic spectra of four LECCs, namely $[(NH_2TzDMP)_3Fe][ClO_4]_2$ (**11**), $[(NH_2TzPyr)_3Fe][ClO_4]_2$ (**12**), $[(TriTzDMP)_3Fe][ClO_4]_2$ (**13**), and $[(NH_2TriTzDMP)_3Fe][ClO_4]_2$ (**15**) [5]. Experimental and predicted spectra (DFT, vacuum-isolated species) are presented in Fig. 1 (bottom) as black and red curves, respectively [5]. As can be seen, this computational approach completely fails to predict the low-energy band and shows no absorption beyond 550–600 nm. This is a known limitation of spectrum prediction for vacuum-isolated species as simplified models of crystalline systems, as weak but crucial intermolecular interactions are not taken into account. Therefore, we aimed to develop a fast, cost-effective, and accurate approach for predicting the electronic spectra of solid LECCs based on the molecular structures of their constituents; the overall workflow is schematically shown in Fig. 1 (top). The numerical values of $\lambda_{max}$ are listed in Table 1. We demonstrate that the exact crystal structure with the correct $Z'$ and space group ($\lambda_{max}$) and a simplified model cell with $P1$ symmetry and $Z' = 1$ ($\lambda_{max(P1)}$) exhibit very similar spectral behavior; thus, the latter can serve as a significantly simplified yet reliable model of real LECCs.

The final approach for electronic spectrum prediction is based on plane-wave DFT calculations using the PBE functional with D2 dispersion correction, a 1000 eV energy cutoff, and a $k$-point grid density of $0.08 \times 2\pi/Å$. The well-known systematic underestimation of excitation energies by the PBE functional was corrected using an empirical function (Eq. (1)):

$$\lambda_{corr} = 2.99\lambda^{0.833} \quad (1)$$

Table 1.

*Values of $\lambda_{max}$ for the experimental spectra of LECCs **11**, **12**, **13**, and **15**, along with calculated (uncorrected) values for both experimental and predicted crystal structures ($\lambda_{max(P1)}$), as well as corrected values and the corresponding absolute deviations*

| No | LECC | $\lambda_{max(exper)}$, nm | $\lambda_{max(calc)}$, nm | $\lambda_{max(P1)(calc)}$, nm | $\lambda_{max(corr)}$, nm | Δ, nm |
|---|---|---|---|---|---|---|
| **11** | $[(NH_2TzDMP)_3Fe][ClO_4]_2$ | 654 | 778 | 797 | 657 | 3 |
| **12** | $[(NH_2TzPyr)_3Fe][ClO_4]_2$ | 647 | 796 | 772 | 644 | -3 |
| **13** | $[(TriTzDMP)_3Fe][ClO_4]_2$ | 718 | 887 | 876 | 719 | 1 |
| **15** | $[(NH_2TriTzDMP)_3Fe][ClO_4]_2$ | 788 | 1037 | 1084 | 864 | 76 |

where $\lambda$ and $\lambda_{corr}$ are the uncorrected and corrected wavelengths, respectively. This transformation compresses the long-wavelength region more strongly than the short-wavelength region, thereby reproducing experimentally observed band positions more accurately across the full spectral range.

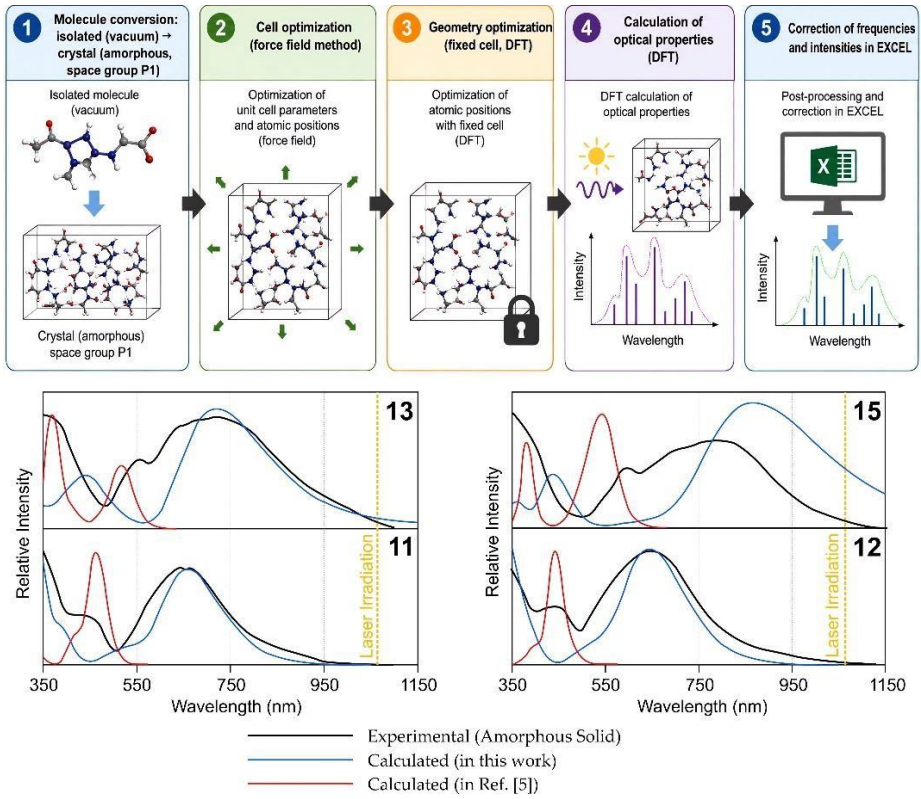


*Fig. 1. Main workflow for electronic spectrum prediction from the molecular constituents of LECCs (top); comparison of experimental and predicted absorption spectra (bottom).*

In addition to wavelength deviations, calculated spectra exhibited systematically underestimated absorption intensities in the low-frequency region corresponding to experimentally observed near-infrared absorption tails. To address this discrepancy, an empirical intensity scaling function dependent on wavelength was introduced (Eq. (2)):

$$I_{corr} = I\left(\frac{\lambda_{corr}}{350}\right)^{1.56} \qquad (2)$$

where $I$and $I_{corr}$ are the uncorrected and absorption intensities, respectively, 350 nm stands for the reference wavelength, 1.56 is the empirically determined exponent. This function increases absorption intensity progressively toward longer wavelengths while preserving relative intensity relationships in the higher-frequency region.

The absorption spectra obtained using this approach are shown in Fig. 1 (blue curves). As follows from both Fig. 1 and Table 1, the accuracy of $\lambda_{max}$ prediction is satisfactory in three out of four cases, with the exception of LECC **15**, for which a larger deviation ($\Delta$ = 76 nm) is

observed. This discrepancy can be attributed to the insufficient calibration of the empirical correction functions (Eqs. 1 and 2), which will be refined in future work. The proposed computational workflow is specifically designed to balance speed, cost, and accuracy by omitting computationally demanding steps such as crystal structure prediction, full cell relaxation, and extensive geometry optimization wherever possible. As a result, the absorption spectrum of a given LECC can be obtained within a few hours using a standard personal computer. Although this approach is not yet suitable for high-throughput screening, a significant portion of the total time is associated with manual preprocessing steps, including structure preparation and input generation. Therefore, parallelization of calculations can substantially reduce the average time per compound to the order of tens of minutes.

Despite its relatively higher computational cost compared to simple descriptor-based methods, the proposed approach currently represents one of the most reliable criteria for distinguishing between laser-ignitable and non-ignitable energetic materials. The development of faster screening tools, such as machine learning models, is presently limited by the scarcity of experimentally validated data, as this research field remains in its early stages. Nevertheless, the described method provides a physically grounded and reasonably accurate estimation of laser ignitability and can be effectively applied in the design and evaluation of new LECCs with improved ignition and sensitivity characteristics.

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## DFT-ДОСЛІДЖЕННЯ ВПЛИВУ ФТОРУВАННЯ НА ВЛАСТИВОСТІ НЕФУЛЕРЕНОВИХ АКЦЕПТОРІВ ITIC


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Нефуленові акцептори (NFA) останніми роками стали одними з найбільш перспективних матеріалів для органічної фотовольтаїки завдяки високим коефіцієнтам поглинання світла, можливості тонкого налаштування електронної структури та високим значенням ефективності перетворення сонячної енергії. Особливий інтерес викликають акцептори сімейства ITIC, які поєднують широке поглинання у видимій та ближній інфрачервоній областях спектра, високу рухливість носіїв заряду та сприятливі енергетичні характеристики.