Electronic and Optical Properties of Eu$^{2+}$-Activated Narrow-Band Phosphors for Phosphor-Converted Light-Emitting Diode Applications: Insights from a Theoretical Spectroscopy Perspective

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ABSTRACT: In this work, we present a computational protocol that is able to predict the experimental absorption and emission spectral shapes of Eu$^{2+}$-doped phosphors. The protocol is based on time-dependent density functional theory and operates in conjunction with an excited-state dynamics approach. It is demonstrated that across the study set consisting of representative examples of nitride, oxo-nitride, and oxide Eu$^{2+}$-doped phosphors, the energy distribution and the band shape of the emission spectrum are related to the nature of the 4f−5d transitions that are probed in the absorption process. Since the 4f orbitals are very nearly nonbonding, the decisive quantity is the covalency of the 5d acceptor orbitals that become populated in the electronically excited state that leads to emission. The stronger the (anti) bonding interaction between the lanthanide and the ligands is in the excited state, the larger will be the excited state distortion. Consequently, the corresponding emission will get broader due to the vibronic progression that is induced by the structural distortion. In addition, the energy separation of the absorption bands that are dominated by states with valence 4f−5d and a metal to ligand charge transfer character defines a measure for the thermal quenching of the studied Eu$^{2+}$-doped phosphors. Based on this analysis, simple descriptors are identified that show a strong correlation with the energy position and bandwidth of the experimental emission bands without the need for elaborate calculations. Overall, we believe that this study serves as an important reference for designing new Eu$^{2+}$-doped phosphors with desired photoluminescence properties.

INTRODUCTION

Over the last few decades, light-emitting diode (LED) phosphors have been widely used in applications in the field of modern lighting and display technologies. In particular, phosphor-converted LED (pc-LED) materials provide lighting sources that (1) show high luminous efficacy and (2) operate under low power consumption and (3) they are environmentally friendly. Due to these reasons, pc-LEDs are considered as the next-generation solid-state lighting technology with the potential to substitute traditional lighting sources ranging between incandescent, fluorescent, and halogen lamps to backlights of liquid crystal displays (LCDs).

Successful design of innovative materials featuring pc-LED phosphors requires (1) a high degree of tunability of the emission band position in the range between red and blue light, (2) a narrow band width of the emission band, and (3) thermal stability. In fact, a high degree of tunability implies that the targeted pc-LED phosphors show systematic geometric and electronic structure properties. Hence, identification of such systematic descriptors is of paramount importance for the design of pc-LED phosphors with desired luminescence properties.

This has led to the development of combined experimental and theoretical protocols that are aiming to establish at least semiquantitative rules that relate the geometric and electronic structure of the system under investigation to the desired spectroscopic properties of such materials. A number of correlations have been attempted on the basis of density functional theory (DFT) calculations that relate properties such as the crystal field strength or the band gap to the Stokes shift of classes of pc-LED phosphors. Machine learning techniques have also been employed in an effort to provide predictions of novel materials with the desired properties summarized above. While the usefulness of DFT or machine learning-based approaches alongside empirical correlations is undeniable, they also suffer from some
significant shortcomings that will be elaborated on below. In fact, to date, most promising phosphors are still discovered by an elaborate trial-and-error process. Thus, there is a continued desire to improve the predictive power of the theoretical protocols to better aid the design of new phosphors with tailored properties. This paper represents an attempt in this direction.

Combining a range of spectroscopic methods with the results of carefully calibrated theoretical spectroscopy has been widely used on the fields of (bio)inorganic chemistry and catalysis. It has been indeed shown that this approach has been proven instrumental to characterize exotic reactive species in model systems (e.g., the genuine Fe(V) centers in coordinate complexes), clarifying the structure and oxidation states in enzymes, for example, the identification of a unique carbide center in the active site of the dinitrogen-activating enzyme nitrogenase or the characterization of the structure and oxidation states of the oxygen-evolving complex in photosynthesis. Moreover, this approach has shown great potential in bridging the worlds of homogeneous and heterogeneous catalysis by interpreting simultaneously the spectroscopic response of vanadium-based oxidation catalysts. It should be emphasized that in order to successfully apply the theoretical methodologies to interpret the spectroscopic response of real-life chemical problems, it is of paramount importance that the theoretical methods are properly calibrated, implying that the error bars of the theoretical predictions must be known from studying a series of known and understood systems. Hence, in all the above-described cases, all predictions of the theoretical methods are only valid within the confidence intervals defined by the calibration procedure.

In this work, we will use high-level wavefunction-based and empirical quantum chemistry in conjunction with time-dependent density functional theory (TD-DFT) and an excited-state dynamics (ESD) approach to show that a carefully calibrated multimethod protocol can be developed that is able to quantitatively predict the spectroscopic properties of pc-LED phosphors in terms of energy position and the bandwidth of the targeted emission spectrum. However, in addition to producing predictions of near quantitative accuracy, it is possible to extract more qualitative data from the calculations that can serve to guide chemical intuition in the design of new and improved systems based on geometric and electronic structure properties such as the crystal field strength, the band gap, and the Stokes shift of the investigated phosphor. For this purpose, a selection of Eu2+-doped phosphors in nitride/oxo-nitride/oxide inorganic hosts is chosen. These phosphors adopt a UCr4C4-type or related crystal structure and exhibit promising luminescence spectral features, such as narrow-band emission, with a high degree of tunability that is offered by the host structure. In a first step, a multimethod theoretical protocol will be developed that is able to predict the bandwidth and the energy position of the absorption and fluorescence spectra of four nitride phosphors Sr[LiAl3N4]:Eu2+ (SLA), Ba[LiAl3N4]:Eu2+ (BMS), Sr[LiAl3N4]:Eu2+ (CLA), and Sr[LiAl3N4]:Eu2+ (SLA). In a second step the above protocol will be employed to study the electronic structure and the spectroscopic response of narrow-band oxo-nitride red phosphor Sr[LiAl3N4]:Eu2+ (SLA) and the ultranarrow-band blue oxide phosphor Sr[LiAl3N4]:Eu2+ (SLBO). In a final step, a homogeneous set of descriptors will be extracted from the developed computational protocol that is able to predict the emission
Energy position and the bandwidth of $\text{Eu}^{2+}$ phosphors in an attempt to aid the synthetic efforts toward new phosphors with desired photoluminescence properties.

**EXPERIMENTAL/METHODS**

**Study Set: Geometric Structure.** The chosen study set of phosphors is presented in Figure 1 together with the major structural characteristics of the different coordination environments around the doped Eu$^{2+}$ centers. As seen in Figure 1, the selected nitride phosphors contain an ordered distribution of edge- and corner-sharing (Si,Mg)N$_4$ or (Al, Li)N$_4$ tetrahedral building units, which form vierer ring channels. The host M$^{2+}$ ions (M = Ba, Sr, Ca) as well as the doped Eu$^{2+}$ ions are placed at the center of those vierer ring channels, and they are 8-fold coordinated by nitride N$^{3-}$ ions. In all the cases, the symmetry is lower than cubic; as a result, cuboid-like polyhedra Eu/ML$_8$ are formed (for simplicity, these polyhedra will be referred to as cuboids).

In particular, the nitridomagnesosilicate phosphors M[LiMg$_3$Si$_3$N$_8$]:Eu$^{2+}$ (M = Sr (SMS), Ba (BMS)) crystallize in an ordered variant of the UCr$_4$C$_4$ structure type that crystallizes in the tetragonal space group $P4/m$ (for simplicity, these polyhedra will be referred to as cuboids). The channel hosting the Sr$^{2+}$ or the doped Eu$^{2+}$ cations forms Eu/SrN$_4$O$_4$C$_{16}$ symmetric cuboids with Sr−N of 2.76 Å, Sr−O of 2.66 Å, and Eu−Sr of 3.21 Å bond lengths. These structural characteristics are very similar to the CLA nitride phosphors as will be discussed below. Finally, the oxoberyllate phosphor SrLi$_2$[Be$_4$O$_6$]:Eu$^{2+}$ (SLBO) crystallizes in the space group $P4/ncc$ and contains edge- and corner-sharing BeO$_4$ tetrahedra, which are forming two kinds of vierer ring channels along the [001] direction. The channel hosting the Sr$^{2+}$ or the doped Eu$^{2+}$ ions forms Eu/SrO$_8$C$_8$ sequences of truncated bipyramidal cuboids in which the individual Eu/SrO$_8$ cuboids are rotated by 45° with respect to each other. The Eu−O bond lengths range between 2.6 and 2.8 Å while the Eu−Sr bond lengths are quite elongated (4.5 Å). This is due to the fact that the rotated pairs of Eu/SrO$_8$ cuboids do not share common faces, as in all the other selected phosphors. To show that our new method can be applied on phosphors comprising the entire visible spectrum, and having a structure that is not related to the UCr$_4$C$_4$ type, a blue phosphor was additionally selected with SLBO, in contrast to all the above-presented nitride and oxo-nitride red phosphors. All these structural characteristics and their influence on the emission properties of the study set of chosen phosphors will be thoroughly investigated below.

**Experimental Spectra.** The experimental absorption and emission spectra of the chosen study set of Eu$^{2+}$−doped phosphors are presented in Figure 2. As seen, all the absorption spectra are quite broad in the visible energy region 15,000−25,000 cm$^{-1}$. The nitride phosphors CLA, SLA, and SMS show a broad absorption band with increasing band maximum positions observed at 21,280, 21,460, and 22,730 cm$^{-1}$, respectively. In accordance, the oxo-nitride SALON and oxide SLBO phosphors show absorption spectra with band maxima at 22,220 and 23,100 cm$^{-1}$, respectively. Interestingly, the band maxima increase in the sequence CLA, SLA, SALON, and SMS, which are now forming a condensed network of tetrahedra leading to three different types of channels along the [001] direction. The channel hosting the Sr$^{2+}$ or the doped Eu$^{2+}$ ions forms Eu/SrO$_8$C$_8$ sequences of truncated bipyramidal cuboids in which the individual Eu/SrO$_8$ cuboids are rotated by 45° with respect to each other. The Eu−O bond lengths range between 2.6 and 2.8 Å while the Eu−Sr bond lengths are quite elongated (4.5 Å). This is due to the fact that the rotated pairs of Eu/SrO$_8$ cuboids do not share common faces, as in all the other selected phosphors. To show that our new method can be applied on phosphors comprising the entire visible spectrum, and having a structure that is not related to the UCr$_4$C$_4$ type, a blue phosphor was additionally selected with SLBO, in contrast to all the above-presented nitride and oxo-nitride red phosphors. All these structural characteristics and their influence on the emission properties of the study set of chosen phosphors will be thoroughly investigated below. Finally, the oxoberyllate phosphor SrLi$_2$[Be$_4$O$_6$]:Eu$^{2+}$ (SLBO) crystallizes in the space group $P4/ncc$ and contains edge- and corner-sharing BeO$_4$ tetrahedra, which are forming two kinds of vierer ring channels along the [001] direction. The channel hosting the Sr$^{2+}$ or the doped Eu$^{2+}$ ions forms Eu/SrO$_8$C$_8$ sequences of truncated bipyramidal cuboids in which the individual Eu/SrO$_8$ cuboids are rotated by 45° with respect to each other. The Eu−O bond lengths range between 2.6 and 2.8 Å while the Eu−Sr bond lengths are quite elongated (4.5 Å). This is due to the fact that the rotated pairs of Eu/SrO$_8$ cuboids do not share common faces, as in all the other selected phosphors. To show that our new method can be applied on phosphors comprising the entire visible spectrum, and having a structure that is not related to the UCr$_4$C$_4$ type, a blue phosphor was additionally selected with SLBO, in contrast to all the above-presented nitride and oxo-nitride red phosphors. All these structural characteristics and their influence on the emission properties of the study set of chosen phosphors will be thoroughly investigated below.

**Figure 2.** Experimental absorption (right) and emission (left) spectra of the selected phosphors (CLA: green; SALON: pink; SMS: blue; SLBO: dark blue).
Kroll calculations were performed using the second-order Douglas–Hess correction (DKH2) \(^{70,71}\) to account for the scalar relativistic effects, employing the finite nucleus model. \(^{70,72}\) The Hartree–Fock (HF) layers used in the embedding cluster calculations were equipped with a minimal LANL2DZ basis set with the respective correlation auxiliary basis sets, respectively. All the calculations were performed with the ORCA 5.0 suite of programs. \(^{43}\) Single-point energies and properties, employing the \(\text{CCSD}(T)\) \(^{55,56}\) approximation, were computed at the TD-DFT(PBE0)/DFT level of theory by employing the excited state dynamics (ESD) path integral protocol \(^{70-72}\) in which vibronic coupling is included within the Franck–Condon and Herzberg–Teller coupling schemes. A constant Gaussian broadening was used for all presented absorption and emission spectra, which amounts to a FWHM of 1500 and 500 cm\(^{-1}\), respectively. For better visual agreement with the experimental absorption spectra, a second Gaussian broadening with FWHM of 3000 cm\(^{-1}\) was used in some of the computed absorption spectra. For clarity, natural transition orbital (NTO) analysis is performed on dimer structures.

**Embedding Cluster Approach. Construction of the Cluster Models.** Representative model structures for the calculations of the spectroscopic properties of the host and Eu\(^{2+}\)-doped phosphors were constructed in the framework of the embedded cluster approach. In a first step, various quantum clusters (QCs) were constructed from the crystallographic data by preserving the 8-fold cubic coordination environment around the central alkaline earth metal ions (\(\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}\)). Structure expansions containing one, two, three, or four central cations of the host phosphors were considered, abbreviated as monomers, dimers, trimers, or tetramers. The respective quantum clusters of the host structures of SMS, BMS, CLA, SALON, and SLBO phosphors are visualized in Figure 3.

Formation of Eu\(^{2+}\)-doped phosphors involves the substitution of the Sr\(^{2+}\), Ca\(^{2+}\), or Ba\(^{2+}\) cations with Eu\(^{2+}\) due to the similarity of their ionic radii \([\text{Eu}^{2+}: 1.25, \text{Ca}^{2+}: 1.06, \text{Sr}^{2+}: 1.26, \text{Ba}^{2+}: 1.35 \text{ Å}]\) \(^{73}\). It should be noted that in this study set of phosphors, no other cation substitutions (e.g., Li\(^{+}\), Mg\(^{2+}\), Al\(^{3+}\), or Si\(^{4+}\)) with Eu\(^{2+}\) are possible while occupation of interstitial sites on the unsaturated channels is not possible due to steric reasons. \(^{45}\) For example, in the case of SMS, the Eu\(_N\) host cuboid has a volume of 37 Å\(^3\) while the nearby unsaturated channels would form Eu\(_N\) octahedra with a 20 Å\(^3\) volume. Preliminary DLPNO-CCSD(T) calculations indicate that such Eu–polyhedra formations do not lead to more stable structures with respect to the Eu\(^{2+}\)-doped cuboids as they require significant structural relaxation. As shown in Table S2, similar observations are found for all the phosphors of the study set. Hence, the corresponding candidate structures for the respective Eu\(^{2+}\)-doped phosphors are straightforwardly constructed from the host model structures of Figure 3 by replacing one Sr\(^{2+}\), Ca\(^{2+}\), or Ba\(^{2+}\) cation with Eu\(^{2+}\). As

![Figure 3. Graphical representation of (monomer, dimer, trimer, or tetramer) undoped clusters of SMS, BMS, CLA, SALON, and SLBO used for BG calculations. The respective doped clusters were constructed by replacing one of the central cations (M = Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\)), with Eu\(^{2+}\). Atom color coding: Ca (light green), Sr (green), Ba (deep green), Si (gray), Mg (orange), Al (yellowish pink), Li (pink), N (blue), O (red).](Image)
shown in Table S1, all these clusters are highly negatively charged; hence, in the next step, one layer equipped with the surrounding cations is added. As described in the Computational Details, this layer, also called a Hartree–Fock layer (HF layer), is treated at the HF level during the calculation together with a minimal basis set. In following, the QC + HF clusters are embedded in an external point charge (PC) field, consisting of about 35,000 to 45,000 charges, to account for the long-range Coulombic forces. In order to avoid electron flow and overdelocalization from the QC to the PC region, a boundary region (BR), 2 or 3 layers, of repulsive capped effective core potentials (c-ECPs) is introduced between the QC and PC regions. This region is also called an ECP region. In particular, an up to triple layer of cECPs:ECP2SDF (Li, Be, N),\(^{74}\) ECP10SDF (Sr, Mg, Ca, Si, Al)\(^{75}\) (included in the SDD framework) was used to replace the corresponding atoms. For the cECPs and PCs, the charges are chosen imposing cluster neutrality conditions (i.e., \(q(QC + HF) = -q(BR + PC)\))\(^{76}\) and by ensuring uniform charge distribution in the QC, BR, and PC regions. For this purpose, the charge values of the ECP and PC regions were matched with the computed electrostatic potential charges (CHELPG)\(^{77,78}\) of the QC iteratively. Further details regarding the employed embedding scheme have been described elsewhere.\(^{79}\) It should be noted that within the employed embedding scheme, the positions and magnitudes of the point charges are kept fixed while no additional corrections for the long-range electrostatics are taken into account.\(^{80}\) An example is provided in Figure 4 for the monomeric SMS \([\text{EuMg}_9\text{Si}_3\text{N}_{24}]^{40-}\).
Most Important Energy Quantities That Dominate the Energy Position and the Bandwidth of the Spectral Features of Eu2+-doped phosphors. In the case of SLA, tetramer clusters presented in Figure 3.

Cluster Size Convergence. In a next step, we perform cluster size convergence of the candidate clusters presented in Figure 3 and Table S1 with respect to the optical band gap (BG) energies of the host phosphor structures and the absorption and emission spectral shapes of the Eu2+-doped phosphors. For these purposes, we choose to present the cases of SMS and CLA. As seen in Figure 5a,c, the computed optical band gap energies at the PBE0 TD-DFT and STEOM-DLPNO-CCSD levels of theory in both cases are converged for the trimeric structures ((Sr2Mg2Si3)68+ and (Sr2Mg2Si3)68+) and ((EuCa2Li7Al21N48)68+). However, only when the STEOM-DLPNO-CCSD method is employed, the computed BG energies of the SMS and CLA host trimer structures are matching the experimental values with errors that are below 0.05 eV, while the respective PBE0 TD-DFT results deviate more than 0.5 eV from the experimental values. Nevertheless, this is still an acceptable deviation showing that PBE0 TD-DFT is a valid method to describe the absorption and emission spectra of these systems. In fact, as shown in Figure 5b,d, the shape of the PBE0 TD-DFT computed absorption and emission spectra of the Eu2+-doped trimer structures has converged while both types of spectra show nice agreement with the experiment. It should be emphasized that at the converged cluster sizes (e.g., trimer structures), placing Eu2+ at the center or the edge cuboids does not alter the computed quantities. Hence, based on the above results, in the case of SMS, BMS, CLA, SALON, and SLBO, the trimer Eu2+-doped structures have been chosen to study the absorption and fluorescence spectra of the study set of Eu2+-doped phosphors. In the case of SLA, tetramer clusters were used due to the two possible doping sites.

Absorption and Emission Processes: A Qualitative Electronic Structure Analysis. Let us now discuss the most important factors that influence the absorption and emission processes in Eu2+-doped phosphors in which Eu2+ is doped in 8-fold coordinated host environments. For this purpose, we will undertake an electronic structure analysis based on the monomer (dimer, trimer, etc.) structures presented in Figure 3.

The divalent europium ion (Eu2+) has a [Xe]4f7 electronic configuration with a half-filled f electronic shell. The f shell is highly shielded due to the closed shell Sx2 and Sp6 outer shells. The seven electrons in the f shell can be arranged in many different ways leading to 3432 degenerate atomic microstates (2 octet (S = 7/2), 98 sextet (S = 5/2), 882 quartet (S = 3/2), and 2450 doublet (S = 1/2)). This degeneracy can be partly or totally lifted due to several perturbations like interelectronic repulsion, ligand field splitting, spin orbit coupling, or even the Zeeman effect. In the ion, the half-filled f shell leads to a very stable octet ground state (S = 7/2) multiplet with a 4f5d0 electron configuration of multiplicity 2S + 1 = 8 (where S is the total spin). The lowest excited state of an atom is 4f5d1 electron configuration arising from a spin flip type of excitations of the same 4f5d0 electron configuration with multiplicity 2S + 1 = 6 (S = 3/2), which is difficult to reach as it is separated by >4.5 eV from S = 7/2. The other and more interesting excitation pathway is to excite electron(s) to the empty 5d orbitals via spin-conserving 4f → 5d single electron excitations involving the 4f5d0 electron configuration with multiplicity 2S + 1 = 8 (F ⊗ D). In the ion, this excited shell remains still high in energy. As shown in Scheme 1, when Eu2+ is doped in 8-fold coordinated host environments, under the 1-electron picture, the action of interelectronic repulsion will stabilize the 2S + 1 = 8 excited state multiplets of the 4f5d0 shell above the 2S + 1 = 8 4f5d0 ground state multiplets. It follows that the cubic ligand field splitting will lift the degeneracy of the 4f and 5d orbitals in an inverted octahedral order (ΔEexc = −8/9ΔEdn) leading to a ground state electron configuration t1u a2u a2u a1g a1g a1g leading to further distortions toward tetragonal/trigonal ligand fields will further lift the remaining orbital degeneracies and consequently the ground- and excited-state degeneracy. It follows that quantities like ligand field splittings (ΔEdn, ΔEexc) band gap energies, Eabs, and Stokes shifts are important quantities of the absorption and emission processes, which determine the energy position and the bandwidth of the different spectral features. In addition, as will be explicitly discussed, the energy difference between the valence Eu 4f → Eu 5d2/3 multiplets (MMCT) excitations or the metal to ligand charge transfer Eu 4f → Eu 5d2/3 multiplets (MMCT) excitations are of a measure of the Eu2+-doped phosphors’ thermal stability. It has been shown that synchrotron-based X-ray reflectivity techniques like nitrogen 1s2p resonance X-ray emission (RXES) spectroscopy provide a direct measurement of this energy separation in nitride phosphors, making it a key indicator of quantum efficiency.

Focusing now on the Eu2+-doped nitride phosphors (SMS, BMS, SLA, and CLA), while in BMS, Eu2+ is coordinated in an 8-fold N8 cluster building block of cubic (inverted Oh) to D4h. In reality, due to additional distortions in the host frame, the center of inversion is lost reducing further the symmetry of EuN8 to D3h. This scheme has been proven successful in treating a variety of chemical problems in the field of semiconductors and insulators as well as molecular crystals. Note that while this scheme can be applied to a broad range of systems, metallic systems or materials for which the electronic structure is strongly delocalized cannot be treated.
4. The molecular orbital (MO) energy splitting of the ground-state configurations of BMS, SMS, SLA, and CLA, in cubic and $S_4$ symmetries, together with the most important single electron excitations arising from these ground state electron configurations within the 1-electron picture is visualized in Figure 6. In SMS, SLA, and CLA, the $S_4$ symmetric 8A ground state obtains the $1t_{2u}^1\ 1t_{1u}^1\ 1a_2^1\ 2a_2^0\ 1e_0^1\ 1t_{2g}^0$ electron configuration. It follows that valence Eu 4f $\rightarrow$ Eu 5d $z^2/x^2−y^2$ single electron excitations or electron decays Eu 5d $z^2/x^2−y^2$ $\rightarrow$ Eu 4f will give rise to $2S + 1 = 8$ and $2S + 1 = 6$ multiplets of A and E symmetries along the absorption and emission processes, respectively. BMS on the contrary obtains an 8A$_1$ ground state. As illustrated in Figure 6 under cubic symmetry, the Si-2s and N-2p orbitals in the SiN$_4$ cuboid are correctly oriented to allow maximum overlap. As a result, the ligand-based antibonding $\sigma^*(Si-2s, N-2p)$ MO is stabilized below the Eu-5d MOs leading to the ground-state $1t_{1u}^1\ 1t_{2u}^1\ 1a_2^1\ 2a_2^0\ 1e_0^1\ 1t_{2g}^0$ electron configuration. Hence, the lowest multiplets in the absorption and emission processes will be dominated by Eu 4f $\rightarrow$ L $\sigma^*(Si-2s, N-2p)$ and L $\sigma^*(Si-2s, N-2p)$ $\rightarrow$ Eu 4f$_{syn}$ electron excitations and electron decays, respectively.

Similar to Eu$^{2+}$-doped nitrile phosphors SMS and SLA, oxo-nitride SALON and oxide SLBO phosphors show distorted cubic geometries in which the EuO$_4$N$_4$ and EuO$_8$ building units show $C_2h$ and $C_4$ symmetries around the Eu$^{2+}$ centers (Figure 7). Under these symmetry assumptions, SALON has an 8A$_1$ ground state with a $1a_2^1\ 1a_2^1\ 2a_2^0\ 1e_0^1\ 1t_{2g}^0$ electron configuration. Hence, the lowest multiplets in the absorption and emission processes will be dominated by Eu 4f $\rightarrow$ L $\sigma^*(Si-2s, N-2p)$ and L $\sigma^*(Si-2s, N-2p)$ $\rightarrow$ Eu 4f$_{syn}$ electron excitations and electron decays, respectively.

Figure 6. Qualitative molecular orbital diagram of the monomeric of nitrile doped Eu$^{2+}$ phosphors adopted for cubic (reversed $O_h$) EuN$_8$ centers (BMS) and for EuN$_8$ centers (SMS, SLA and CLA) of in $S_4$ symmetry. Black arrows indicate absorption processes. Red arrows indicate emission processes and red crosses indicate dipole forbidden transitions.

Figure 7. Qualitative molecular orbital diagram of the monomeric oxo-nitride and oxide-doped Eu$^{2+}$ phosphors adopted for cubic (reversed $O_h$) EuO$_4$N$_4$ centers (SALON) and for tetragonally distorted ($C_i$) EuO$_8$ centers (SLBO). Black arrows indicate absorption processes. Red arrows indicate emission processes and red crosses indicate dipole forbidden transitions.

S$_4$ The molecular orbital (MO) energy splitting of the ground-state configurations of BMS, SMS, SLA, and CLA, and CLA, in cubic and $S_4$ symmetries, together with the most important single electron excitations arising from these ground state electron configurations within the 1-electron picture is visualized in Figure 6. In SMS, SLA, and CLA, the $S_4$ symmetric 8A ground state obtains the $1e_1a_1^1b_2^1e_2^12a_2^2b_2^3a_3^34b_3^3$ electron configuration. It follows that valence Eu 4f $\rightarrow$ Eu 5d $z^2/x^2−y^2$ single electron excitations or electron decays Eu 5d $z^2/x^2−y^2$ $\rightarrow$ Eu 4f will give rise to $2S + 1 = 8$ and $2S + 1 = 6$ multiplets of A and E symmetries along the absorption and emission processes, respectively. BMS on the contrary obtains an 8A$_1$ ground state. As illustrated in Figure 6 under cubic symmetry, the Si-2s and N-2p orbitals in the SiN$_4$ cuboid are correctly oriented to allow maximum overlap. As a result, the ligand-based antibonding $\sigma^*(Si-2s, N-2p)$ MO is stabilized below the Eu-5d MOs leading to the ground-state 1t$_{1u}^1\ 1t_{2u}^1\ 1a_2^1\ 2a_2^0\ 1e_0^1\ 1t_{2g}^0$ electron configuration. Hence, the lowest multiplets in the absorption and emission processes will be dominated by Eu 4f $\rightarrow$ L $\sigma^*(Si-2s, N-2p)$ and L $\sigma^*(Si-2s, N-2p)$ $\rightarrow$ Eu 4f$_{syn}$ electron excitations and electron decays, respectively.
6 multiplets of A and B symmetries along the absorption and emission processes.

**RESULTS AND DISCUSSION**

**Theoretical Protocol for Understanding the Absorption and Fluorescence Spectra as well as the Thermal Stability of Narrow Band Phosphors. Nitride Phosphors.** All the above qualitative observations will be used in this section in order to develop a theoretical protocol that is able to (1) predict the absorption and fluorescence spectra band shapes, (2) provide insight on the nature of the dominating spectral features, and (3) predict the thermal stability of the different phosphors. For this purpose, we first focus on the nitride Eu$^{3+}$-doped phosphors SMS, BMS, SLA, and CLA. As discussed in the computational section in more detail, the absorption and fluorescence spectra are computed at the PBE0 TD-DFT level of theory in the framework of the ESD approach. Analysis of the spectral features is performed on the basis of natural transition orbitals (NTOs).

Starting with SMS, the computed versus experimental absorption and fluorescence spectra are visualized in Figure 8. As seen, the agreement between theory and experiment is very good, allowing a quantitative analysis of the spectral features. In fact, four bands dominate the absorption spectrum. The first two bands (1 and 2) according to the NTO analysis involve Eu 4f$_{xyz}$ → Eu 5d$_{z^2}$ Eu 4f$_{xyz}$ → Eu 5d$_{x^2}$−y$_2$ and Eu 4f$_{xz^2/yz^2}$ → Eu 5d$_{z^2}$ single electron excitations while the shoulder (band 3) and the other two bands (4 and 5) are dominated by an MLCT type of excitation. Band 1 shows that the emission process involves electron decay from a non-bonding Eu 5d$_{z^2}$ orbital to an isolated Eu 4f$_{xyz}$ orbital. Since there is no significant distortion in the excited state relative to the electronic ground state, there can also not be any vibronic progression, thus leading to narrow band emission. Consequently, the rigid nature of this transition causes narrow band emission. The energy separation between the valence bands (1 and 2) and the MLCT bands (3−5) is ∼1150 cm$^{-1}$ (0.14 eV). Such a small energy separation indicates that thermal quenching of the emission through non-radiative...
relaxation processes is possible explaining the poor thermal stability of SMS. In fact, the computed emission spectra from bands 3 and 4 lead to negligible intensity emission lines.

Let us now discuss the case of the narrow band phosphors SLA and CLA. These phosphors have shown somewhat larger emission bandwidths ($\text{SLA}_{\text{FWHM}} = 50 \text{ nm}/1190 \text{ cm}^{-1}$, $\text{CLA}_{\text{FWHM}} = 60 \text{ nm}/1330 \text{ cm}^{-1}$) with respect to that of SMS ($\text{SMS}_{\text{FWHM}} = 43 \text{ nm}/1170 \text{ cm}^{-1}$). The computed versus experimental absorption and fluorescence spectra are visualized in Figure 9 and Figure S1. Once again, the agreement between theory and experiment is satisfactory, allowing a quantitative analysis of the experimentally observed spectral features. In the case of SLA presented in Figure 9, there are two different Eu doping candidate sites, with similar local geometric and electronic structure. This also leads to similar absorption spectra and hence to similar emission spectra maintaining the narrow bandwidth. The computed absorption spectrum is dominated by three bands, which according to the NTO analysis are characterized by $\text{Eu} 4f_{\text{xyz}} \rightarrow \text{Eu} 5d_{x^2-y^2} - \text{N} 2p$ (band 1) $\text{Eu} 4f_{\text{xyz}} \rightarrow \text{Eu} 5d_{x^2-y^2} - \text{N} 2p$ and metal to ligand charge transfer (MLCT, band 3) single electron excitation contributions. As band 1 indicates, the emission process involves an electron decay from a practically antibonding $\text{Eu} 5d_{x^2-y^2} - \text{N} 2p$ molecular orbital to an isolated $\text{Eu} 4f_{\text{xyz}}$ orbital, which again introduces little vibronic interaction with the environment.

In comparison to SLA, the $\text{N} 2p$ contribution to the NTO donor orbital dominating band 1 increases from 2 to 4%. Such an increase in the NTO orbital antibonding character is associated with the higher degree of compression of the EuN$_8$ cuboid and consequently the further increase of the crystal field strength in CLA in comparison to SLA. As a result, a narrow band emission is observed with a larger bandwidth with respect to both SLA and SMS. The energy separation between the valence band (3) and MLCT (5) band is $\approx 2500 \text{ cm}^{-1}$, indicating an intermediate thermal stability between SLA and SMS.

In the case of BMS, the situation changes rapidly. As discussed in Figure 6, the ligand-based antibonding $\sigma^*(\text{Si-2 s, N-2p})$ MO is stabilized below the $\text{Eu} 5d$ MOs. This situation is reflected by both the absorption and emission spectra. The computed absorption spectrum presented in Figure 10 indicates that five bands dominate the broad unresolved experimental spectral feature in the energy range 18,000 and 26,000 cm$^{-1}$. According to the NTO analysis, all these bands have a significant metal to ligand charge transfer character (MLCT). In particular, bands 1 and 2 in contrast to all other nitride phosphors have a pure MLCT character dominated by $\text{Eu} 4f_{\text{xyz}} \rightarrow \sigma^*(\text{N} 2p - \text{Si 2 s})$ single electron excitation. Band 3 has mixed valence $\text{Eu} 4f_{\text{yz}} \rightarrow \text{Eu} 5d_{x^2-y^2} - \text{N} 2p$ and MLCT characters while bands 4 and 5 have solely MLCT single electron excitation characters. Hence, the emission process from band 1 results in a red-shifted emission spectrum in contrast to what is expected by the crystal field strength (Figures 1 and 2). This is also reflected by the experimental and computed Stokes shifts presented in Table 1. As seen, while the Stokes shifts in the case of SMS, SLA, and CLS range between 500 and 1000 cm$^{-1}$ in the case of BMS, they are larger than 2500 cm$^{-1}$. The bandwidth of the computed absorption spectrum presented in Figure S1 shows five bands, which according to the NTO analysis are characterized by $\text{Eu} 4f_{\text{xyz}} \rightarrow \text{Eu} 5d_{x^2-y^2} - \text{N} 2p$ (band 1) $\text{Eu} 4f_{\text{xyz}} \rightarrow \text{Eu} 5d_{x^2-y^2} - \text{N} 2p$ (band 2), $\text{Eu} 4f_{\text{xyz}} \rightarrow \text{Eu} 5d_{x^2-y^2}$ and metal to ligand charge transfer (MLCT, shoulder band 4 and bands 5 and 6) single electron excitation contributions. As in the case of SLA, band 1 indicates that the emission process involves an electron decay from a practically antibonding $\text{Eu} 5d_{x^2-y^2} - \text{N} 2p$ molecular orbital to an isolated $\text{Eu} 4f_{\text{xyz}}$ orbital, which again introduces little vibronic interaction with the environment.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10}
\caption{(a) BMS experimental (black), calculated TD-DFT/PBE0 absorption (blue, light blue) spectra and experimental (brown), and TD-DFT/PBE0/ESD-calculated (red) emission spectra. (b) NTO analysis of the relevant bands in absorption spectra and (c) the 1st transition responsible for emission upon relaxation.}
\end{figure}

\begin{table}
\centering
\begin{tabular}{|c|c|c|}
\hline
Band & NTO Analysis & Energy (eV) \\
\hline
1 & Donor NTO & 0.21 \\
2 & Donor NTO & 0.35 \\
3 & MLCT & 0.78 \\
4 & MLCT & 1.18 \\
5 & MLCT & 1.54 \\
\hline
\end{tabular}
\caption{Comparison of NTO Analysis and Energy Levels for Bands 1-5 in BMS.}
\end{table}
emission spectrum in accordance to the experimental one is also increased (FWHM = 90 nm/1990 cm\(^{-1}\)) in comparison to the observed and computed bandwidths in SMS, SLA, and CLA. This is due to the non-rigid nature of the transition, in which vibrations within the host ligand framework participate and apparently dominate the band broadening mechanism. This is also supported by the computed fluorescence rates and relaxation times presented in Table S4. As seen in the Frank–Condon approximation and upon applying Herzberg–Teller corrections, in the case of BMS, the computed fluorescence rates are >3 orders of magnitude smaller while the respective relaxation times are >5 orders of magnitude larger in comparison to the other phosphors reflecting a different relaxation pathway. Nevertheless, these relaxation times at the fluorescence time frame are very small and cannot be safely used to define rigidity.

It should be noted that one of the most commonly used quantity to define rigidity and thermal quenching is the Debye temperature.\(^92,93\) The Debye temperature although it is a proxy of rigidity is not always predictive of thermal quenching.\(^94,95\) A more valid quantity is the Huang–Rhys factor \(S\), which is a measure of the strength of the electron–phonon coupling in the emission process.\(^96,97\) In fact, along the study set, the computed Huang–Rhys factors presented in Table S3 follow the trend of the energy separation of the MLCT band. In particular, small Huang–Rhys factors that are indicative of structural rigidity are associated with large MLCT band separation, reflecting a higher thermally stable phosphor.

To conclude this part, we have developed in this section a computational protocol that is able to relate the emission bandwidth of the nitride phosphors to the nature of the single electron decay that dominates the emission process from the first excited state that is reached in the absorption spectrum. In the next section, we will apply this protocol to characteristic examples from the oxo-nitride and the oxide families of phosphors, namely, SALON and SLBO.

**Oxo-nitride and Oxide Phosphors.** In the case of SALON, the computed versus experimental absorption and fluorescence spectra are visualized in Figure 11. As seen, the agreement between theory and experiment is once again very good, thus allowing a quantitative analysis of the experimentally observed spectral features. The absorption spectrum consists of five bands, which according to NTO analysis all involve valence Eu 4f \(\rightarrow\) Eu 5d single electron excitations, namely, Eu 4f\(_{xy}\) \(\rightarrow\) Eu 5d\(_{x^2-y^2}\) (band 1), Eu 4f\(_{x^2}\) \(\rightarrow\) Eu 5d\(_{z^2}\) (band 2), Eu 4f\(_{y^2}\)/4f\(_{x^2}\) \(\rightarrow\) Eu 5d\(_{xy}\)-\(\rightarrow\) N/O 2p (band 3, band 4), Eu 4f\(_{x^2}\) \(\rightarrow\) Eu 5d\(_{x^2}\)-\(\rightarrow\) N/O 2p, and Eu 4f\(_{x^2}\) \(\rightarrow\) Eu 5d\(_{z^2}\)-\(\rightarrow\) N/O 2p (band 5) single electron excitation contributions. According to SMS, the emission process involves an electron decay from a non-bonding Eu 5d\(_{x^2}\) orbital to an isolated Eu 4f\(_{xy}\) orbital, with practically negligible vibronic interaction with the lattice environment. Again, the rigid nature of the transition is the reason for the observed narrow bandwidth emission (46 nm/1220 cm\(^{-1}\)). As described above, band 5 has a significant MLCT character. Hence, as in the case of SLA, the energy separation between the valence bands (1–4) and the MLCT band (5) (∼10,000 cm\(^{-1}\), ∼1.0 eV) is associated with an observed high thermal stability.

As a final example, we discuss the case of blue-emitting SLBO. The computed versus experimental absorption and fluorescence spectra are visualized in Figure 12. The good

| phosphor | experimental Stokes shift \(\Delta\lambda\) (cm\(^{-1}\)) | calculated Stokes shift \(\Delta\lambda\) (cm\(^{-1}\)) |
|----------|---------------------------------|---------------------------------|
| Ba[Mg,Sn\(_2\)]\(_3\):Eu\(^{3+}\) | BMS | 3500 | 2810 |
| Sr[Mg,Sn\(_2\)]\(_3\):Eu\(^{3+}\) | SMS | 750 | 950 |
| Ca[LiAl\(_3\)N\(_4\)]:Eu\(^{2+}\) | CLA | 1000 | 847 |
| Sr[LiAl\(_3\)N\(_4\)]:Eu\(^{2+}\) | SLA | 800 | 840 |
| Sr[Li\(_3\)Al\(_2\)O\(_2\)N\(_2\)]:Eu\(^{2+}\) | SALON | 1100 | 1150 |
| SrLi\(_2\)[Be\(_4\)O\(_6\)]:Eu\(^{2+}\) | SLBO | 980 | 750 |

Table 1. Experimentally Observed and Calculated Stokes Shifts for the Study Set of Phosphors

![Figure 11](https://doi.org/10.1021/jacs.2c00218)

Figure 11. (a) SALON experimental (black), calculated TD-DFT/PBE0 absorption (blue, light blue) spectra and experimental (brown), and TD-DFT/PBE0/ESD-calculated (red) emission spectra. (b) NTO analysis of the relevant bands in absorption spectra and (c) the 1st transition responsible for emission upon relaxation.
agreement between theory and experiment allows again for a quantitative analysis of the observed spectral features. According to NTO analysis, the absorption spectral features are dominated by the valence Eu 4f\(_{xyz}\) \(\rightarrow\) Eu 5d\(_{x^2-y^2}\) (band 1) and Eu 4f\(_{eq2/yz2}\) \(\rightarrow\) Eu 5d\(_{x^2-y^2}\) (band 2) single electron excitations. Under a C\(_4\) truncated square bipyramidal coordination environment of the EuO\(_8\) building units, the manifold of the f orbitals remains compact. This results in a blue shift of all the absorption bands in comparison to all other phosphors, which adopt distorted cubic EuN\(_4\) or EuN\(_4\)O\(_4\) building units. In addition, in such a coordination environment around the Eu\(^{2+}\) center, the Eu 5d\(_{x^2-y^2}\) MO remains essentially nonbonded. Once again, the rigid nature of the Eu 5d\(_{x^2-y^2}\) \(\rightarrow\) 4f\(_{xyz}\) transition is the reason for the observed narrow bandwidth emission (25 nm/1220 cm\(^{-1}\)). This also results in the smallest experimental and calculated Stokes shift (Table 1) across the series, validating the blue shift in the results in the smallest experimental and calculated Stokes shift. Hence, typically for a given material, the band gap energies are closely related to the experimental conditions, and the experimental resolution.

DEFINITION OF GEOMETRICAL VERSUS COVALENCY DESCRIPTORS

Up to this point of analysis, we have described a computational protocol that provides actual computation of the absorption and emission spectra of a study set of phosphors accompanied by a thorough electronic structure analysis of all the observed spectral features. The protocol has a high predictive ability and is able to explain the energy position and the bandwidth of all the experimentally observed absorption and emission bands. Hence, it serves as a powerful analytical tool in the design and synthesis of new phosphors for analyzing or even predicting the spectroscopic response of known or newly synthesized candidate phosphors. In the same direction, it is also desirable to define descriptors, which could aid the experimental synthesis of candidate phosphors without the need for employing such elaborate calculations in each and every design idea that arrives on the synthesis table. In this sense, a successful definition of descriptors may play a pre-screening role across a massive selection of candidate phosphors toward only those that fulfill the design criteria.

In the Supporting Information, a number of commonly employed descriptors are discussed. It is demonstrated that the energy distribution as well as the intensity mechanism of the absorption and emission process in phosphors goes beyond the geometrical characteristics of the first and second coordination spheres. In contrast, experimental optical band gaps have been employed in order to find linear relationships between absorption and emission energy maxima defining emission color descriptors in a large set of phosphors.\(^8,29\) However, for a given material, the band gap energies are closely related to the type of employed experimental spectroscopic measurement, the experimental conditions, and the experimental resolution. Hence, typically for a given material, the experimental band gap energy variations range between 0.5 and 1 eV and can reach up to 2–3 eV (e.g., in inorganic semiconductors).\(^79\) These variations might not always be systematic rendering the definition of experimental band gap energies within a narrow energy window for every candidate-studied system a difficult task. In an alternative scenario, the calculated band gap energies can be used, provided that the employed methodology is carefully calibrated.

It was shown above that the computed PBE0/TD-DFT band gap energies of the SMS and CLA host structures are deviating from experiment and reference DLPNO-STEOM-CCSD calculations by about 0.5–0.8 eV while the computed PBE0/TD-DFT absorption spectra are in very good agreement with respect to the experimental absorption spectral for all the studied phosphors. Hence, in a subsequent step, we investigate the relation of the computed PBE0/TD-DFT absorption energy maximum of band 1 (corresponding to the BG energy) with respect to the experimental emission maximum across the study set of the phosphors (Figure 13a). An excellent linear relation is observed, thus defining a direct emission color descriptor across the study set of the phosphors. The advantage of using computed over experimentally determined optical band gaps is the resolution of the computed band 1, which allows the better definition of the linear relation. At the PBE0/def2-TZVP TD-DFT level, the resulting linear relation reads:

\begin{align*}
\text{Energy gap} & = a \cdot \text{Experimental emission maximum} + b
\end{align*}

where a and b are constants that can be determined by a linear regression analysis.
and the computed Eu 5d $a^2$, which at the PBE0/def2-TZVP TD-DFT level reads:

$$\text{experimental emission FWHM} (\text{cm}^{-1}) = -2530.7 \times \text{Eu 5d } a^2 + 3638.4 (\text{cm}^{-1})$$

Hence, according to the discussion above for a candidate Eu$^{2+}$ phosphor, one only needs to perform a conventional TD-DFT calculation in order to estimate the energy position of the 1st absorption band as well as the Eu 5d $a^2$ coefficient from an accompanied NTO analysis on this band. This will provide a robust prediction of the expected color and bandwidth of the emission spectrum of the candidate Eu$^{2+}$ phosphor.

### Conclusions

In this work, a computational protocol was developed for the first time that is able to predict the energy position, the shape, and the bandwidth of the absorption and emission spectra of Eu$^{2+}$-doped phosphors. For this purpose, a study set of well-known Eu$^{2+}$-doped nitride, oxo-nitride, and oxide phosphors was chosen, namely, Sr$[\text{Mg}_3\text{SiN}_4]$:Eu$^{2+}$ (SMS), Ba$[\text{Mg}_3\text{SiN}_4]$:Eu$^{2+}$ (SMS), Ca$[\text{LiAl}_2\text{N}_4]$:Eu$^{2+}$ (CLA), Sr$[\text{LiAl}_2\text{N}_4]$:Eu$^{2+}$ (SLA), Sr$[\text{Al}_2\text{Li}_2\text{O}_5]$:Eu$^{2+}$ (SALON), and Sr$[\text{Li}_2\text{Be}_2\text{O}_4]$:Eu$^{2+}$ (SLBO). This set of phosphors contains a broad variety of energy shifts of the absorption and emission spectral features as well as the emission bandwidths. The construction of cluster models was performed in the framework of the embedded cluster approach. The size of the designed cluster models converged rapidly with respect to the band gap of the host ligand families computed at the STEOM-DLPNO-CCSD and TD-DFT levels of theories as well as the absorption spectra shapes computed at the TD-DFT level of theory.

Prior to the spectra computations, a detailed geometrical and electronic structure analysis was performed, which helped to identify those factors that influence the intensities and the energy distribution of the absorption and emission spectra in terms of (1) crystal field strengths, (2) the coordination environment around the Eu centers, (3) the Stokes shift variations, and (4) the nature of the single electron excitations or electron decays dominating the absorption and emission processes.

In a next step, the shapes of the absorption and the fluorescence spectra of the family of the chosen Eu$^{2+}$-doped phosphors were computed at the TD-DFT level in the framework of the excited state dynamics (ESD) approach. The excellent agreement between theory and experiment allowed a quantitative electronic structure analysis in the framework of natural transition orbitals analysis. It was shown that the energy position and the bandwidth of the emission band are influenced by the rigidity of the electron decay processes dominating the emission spectral feature. In particular, the nonbonding character of the acceptor Eu 5d NTO is responsible for the narrow band emission and the small Stokes shift of the emission bands in SMS and SLBO. On the contrary, the antibonding character of the acceptor Eu 5d NTO increases (the cases of SLA, CLA, and SALON), the bandwidth as well as the Stokes shift of the emission band increases. In BMS, the ligand-based antibonding $\sigma^*(\text{Si}_2\text{N}_2\text{P})$ MO is stabilized below the Eu 5d MOs. As a result, the rigidity of the electron decay dominating the emission process is altered, leading to an increase in both the emission bandwidth and the Stokes shift. The effect is strong and is
able to overcome the expectations from the crystal field strength. As a result, a red shift broad emission spectrum is observed. It should be mentioned that such broadening effects owing to the low-lying MLCT transitions are also referred to as “trapped exciton emission” or “anomalous emission” and have been observed in other phosphor materials.\(^\text{101}\) As a measure of the thermal stability of the studied Eu\(^{2+}\)-doped phosphors, the energy separation between the valence and MLCT absorption bands was defined. In principle, an energy separation that is above 0.3 eV points to thermally stable Eu\(^{2+}\)-doped phosphors as in the case of SLA, SALON, and SLBO. The above-presented protocol was found to perform equally well in all the studied phosphors. Hence, in a final step of the analysis, it was employed to identify a uniform set of descriptors that are able to estimate both the energy position and the bandwidth of the emission bands of newly designed Eu\(^{2+}\)-doped candidate materials. It was found that the energy position of the 1st computed band relates linearly with the energy position of the experimental emission band. Meanwhile, analysis of the nature of the one electron excitation dominating this band revealed that the covalency coefficient Eu 5d a\(^*\) relates also linearly with the bandwidth of the emission band. We foresee that it will be possible in the future to employ these descriptors for pre-screening large datasets of Eu\(^{2+}\)-doped phosphor candidates for application in LEDs.

Ongoing research in our laboratories is focusing on further understanding the intensity mechanism as well as the quantum efficiency of narrow band phosphors in terms of multiplet effects and vibronic couplings through extension of the developed computational protocol. In parallel, a real-life application of the identified descriptors is performed in an effort to possibly identify new materials that can serve as narrow band phosphors with tailored properties.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c00218.

Further details regarding the probable Eu\(^{2+}\)-doped centers, rigidity factors, and absorption and emission spectra and relaxation times/rates of the studied phosphors (PDF)

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**Funding**

Open access funded by Max Planck Society.

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

F.N., D.M., and R.S. would like to thank the Max Planck society for financial support. F.N., D.M., and W.S. acknowledge funding support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany’s Excellence Strategy-EXC 2089/1-390776260 (e-conversion). R.S. would like to thank the Egyptian Ministry of Higher Education and Scientific Research for financial support. Faccts is acknowledged for their contribution to the ORCA code. The referees of the manuscript are acknowledged for their constructive comments.

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