A new family of isostructural compounds with formula \([\text{Ln}_7(3,5-\text{DSB})_4(\text{OH})_9(\text{H}_2\text{O})_{15}] \cdot 4\text{H}_2\text{O} \) (RPF-17-Ln, where \( \text{Ln} = \text{Y}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er} \) and \( \text{Yb} \)) is presented. By combining the lanthanide cations with the \( 3,5 \)-DSB ligand the formation of singular hepta-nuclear \([\text{Ln}_7(\text{OH})_9]^{12+}\) metallic core SBU has been promoted. This new core has been defined as a bi-capped dicubane SBU, and acts as a 4-connected node in a bidimensional net with \((4^6 \cdot 6^2)\) topology. The \( 3,5 \)-DSB ligand acts as a di-topic linker in the 2D net, and contributes to the 3D, \( \text{UO}_3 \) type supramolecular network through the non coordinated sulfonate oxygen atoms, via hydrogen bonds. The analysis of the Raman and infrared vibrational modes along the series compared to the DSB-Na salt evidences the stabilization of the aromatic rings in the RPF-17-Ln compounds and a reduced symmetrization of the carboxylic bonds in spite of its bidentate bridging coordination. A competition between a broad emission band related to the ligand and the narrow rare-earth transitions leads to the disappearance of the ligand emission for the most efficient \( f-f \) transitions observed in \( \text{Tb} \) and \( \text{Eu} \) compounds (green and red emissions, respectively)[1,2].

Keywords: metal-organic framework; topological aspects of structure; spectra-structure correlations.


It is significant for constructing gapless dispersion surfaces (GDS) that the diagonal elements in the secular equations in the diffraction physics of the two wave approximation could be formulated from the quadratic forms of wave numbers by the central proper simultaneous linear equations with two unknowns in the following form, by using \( h^2/8m^2 = 1 \) by atomic units:

\[
\begin{pmatrix}
S_{11} & S_{12}
\end{pmatrix}
\begin{pmatrix}
k_1
S_{21}
\end{pmatrix}
= \left( k_1^2 - k_0^2 \right) k_0^2 + \left( k_0^2 - k_1^2 \right) S_{21} - S_{22} = 0,
\]

where \( k_0 \) is the refracted \( O \)-wave and \( k_1 \) the reflected \( G \)-wave, which satisfy the Bragg condition \( k_0 + k_1 = k_g \), where \( k_g \| \| k_0 \) only in an \( \epsilon \)-neighborhood of the Brillouin zone boundary (BZB). Then, two roots of \( X(x^2) \) in eq. (1) could be given by:

\[
X = \left( 1/2 \right) \left( \kappa_0 + k_0 \right) \pm \left( \kappa_0^2 - k_0^2 \right) + 4[S_{12} \cdot S_{21}]/\left( 16 \right),
\]

where omitted \( U_0 \), since the average value of \( U(r) \), which only translates the origin of \( X \). The indefinite refracted states \( k_0 \) are known as characterized by lifting both degenerated states \( k_0 \) and \( k_6 \) due to the perturbations of off-diagonals \( S_{12} \) and \( S_{21} \) and contributing to the momentum GDS. Both of \( S_{12} \) and \( S_{21} \) in eq. (1) are given by the \( g \)-th Fourier components of the periodic potential energy \( U(r) \) in the crystal in electron and neutron diffractions and similarly by \( g \)-th Fourier components of the electric susceptibility \( \chi(r) \) in X-ray diffraction. (Here, when absorption can be neglected, \( 4[S_{12} \cdot S_{21}] \) should be \( S_{12}^2 \) since \( S_{21} \cdot S_{21} \) could be real.) It can be considered that the magnitudes of \( k_0 \) and \( k_6 \) are so different that the term \( 4[S_{12} \cdot S_{21}] \) under the radial sign in eq. (2) can be neglected compared with the first term. Then, \( X \) takes the value \( k_0^2 \) or \( k_6^2 \) and either the amplitudes of \( x_0 \) or \( d_0 \) of \( O \)-wave or those of \( x_g \) or \( d_g \) of \( G \)-wave, which could be determined from the ratio of the elements in a row of eq. (1), becomes zero. Consequently, the solution is a plain wave of \( k_0 \) or \( k_g \). If the magnitudes of \( k_0 \) and \( k_g \) are close each other, then \( 4[S_{12} \cdot S_{21}] \) cannot be neglected. Thus the amplitude of neither plane wave is negligible. When \( \left| k_0 \right| = \left| k_g \right| \), we have \( k^2 = 1/2 \left( k_0^2 + k_6^2 \right) \pm \left| S_{21} \right| \) and hence the ratio of \( \left| x_0 \right|/x_0 \) and \( d_0/d_g \) determined from eq. (1) is \( S_{21} \pm \left| S_{12} \right| \). Therefore, \( \left| x_0 \right|/x_0 \) and \( d_0/d_g \) are 1:1. In case of \( \left| k_0 \right| \| \| k_g \), assuming that \( 4[S_{12} \cdot S_{21}] \) is larger compared with the first term under the radical sign in eq. (2), the roots \( X \) can be expanded in the following series:

\[
X = \left( 1/2 \right) \left( \kappa_0 + k \right) \pm \left( \kappa_0^2 - k^2 \right) \pm [S_{12} \cdot S_{21}] \pm \cdots \quad (3)
\]

If we translate the origin of \( k_0 \) by \( -k_g/2 \) and consider the vector \( k_0 + K_g/2 \), and if we denote by \( x \) the component of \( k_0 + K_g/2 \) parallel to \( K_g \) and by \( z \) the normal component, then eq. (3) can be written as \( x^2 = 2x \times K_g/4 \pm \left| S_{12} \right| \pm x^2/(2[S_{12}] + K_g^2) \pm \cdots \) by using the following relations:

\[
k_g = k_0 + 2k_0K_g + K_g^2 = k_0 + 2zK_g + [S_{12}] + K_g^2 = x^2 + x^2 + [S_{12}] + \left| K_g \right|^2/4.
\]

The result of the solutions of the coupled ellipse and hyperbola as a new universal GDS from the 4th and 5th terms in eq.(3) in an \( \epsilon \)-neighborhood of BZD could be represented as:

\[
\begin{align*}
\chi(X \times x) &= k^2(L \times x + z) = x^2 \pm \left| S_{12} \right| \pm \left| K_g \right|^2/4 \pm \left| K_g \right|^2/4, \\
\chi(x^2) &= \left( \sqrt{2}[S_{12}] + K_g \right)^2 + b^2 = \left| S_{12} \right|, (b \gg a) < \text{from which reason}\end{align*}
\]

able GDS from eq. (4) could be determined. Detailed discussion on the new universal GDS will be given.