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CLUSTEROLUMINOGENIC: Properties, Chirality and Applications

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The current state of the art in the field of luminescent materials is related to a new phenomenon—clusteroluminescence. This phenomenon is due to the occurrence of end-to-end spatial conjugation, which is explained by the overlap of electronic orbitals of atoms in aggregates formed at high concentrations of substances in solutions or in the solid state. Clusteroluminescence is characteristic of a wide range of substances, including low molecular weight organic compounds of various classes, inorganic substances [1], polymers with heteroatoms [2], and some hybrid materials [3].

Clusteroluminescence, the phenomenon of light emission of solid-state materials induced by mechanical stress, has attracted considerable attention due to its potential applications in optoelectronic devices and sensors. Although the clusteroluminescence properties of conjugated polymers have been extensively studied, recent studies have shown that unconjugated polymers can also exhibit such intriguing behavior.

Clusteroluminogenic polymers with their unique luminescent properties have a wide range of applications in the delivery of bioactive substances (Fig.1). One example of non-conventional luminescence is the phenomenon of AIE, where certain non-emissive molecules become highly luminescent when they aggregate or undergo specific molecular transformations. This behavior is often attributed to the restriction of intramolecular motion in the aggregated state, preventing non-radiative processes and leading to enhanced emission.

The practical applications of cluster luminogens are vast, including environmental protection, information security, optoelectronics in devices such as LEDs and displays, and medical applications for diagnosis and treatment as image markers [4]. Their unique optical properties make them valuable across these diverse fields. The chirality of amino acid residues plays a crucial role in the cluster luminescence of polypeptides [5].

Clusteroluminogens

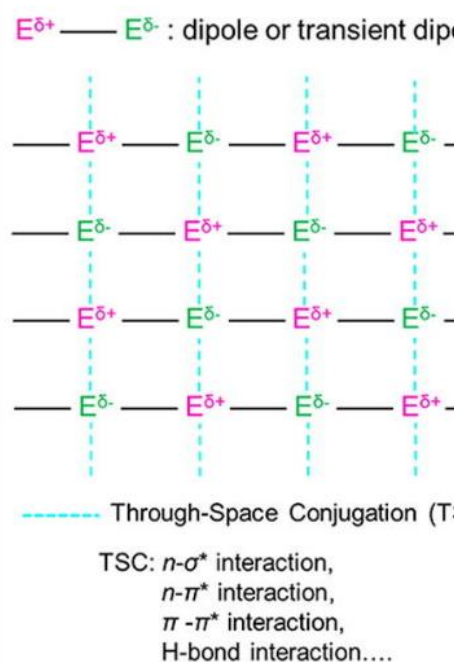
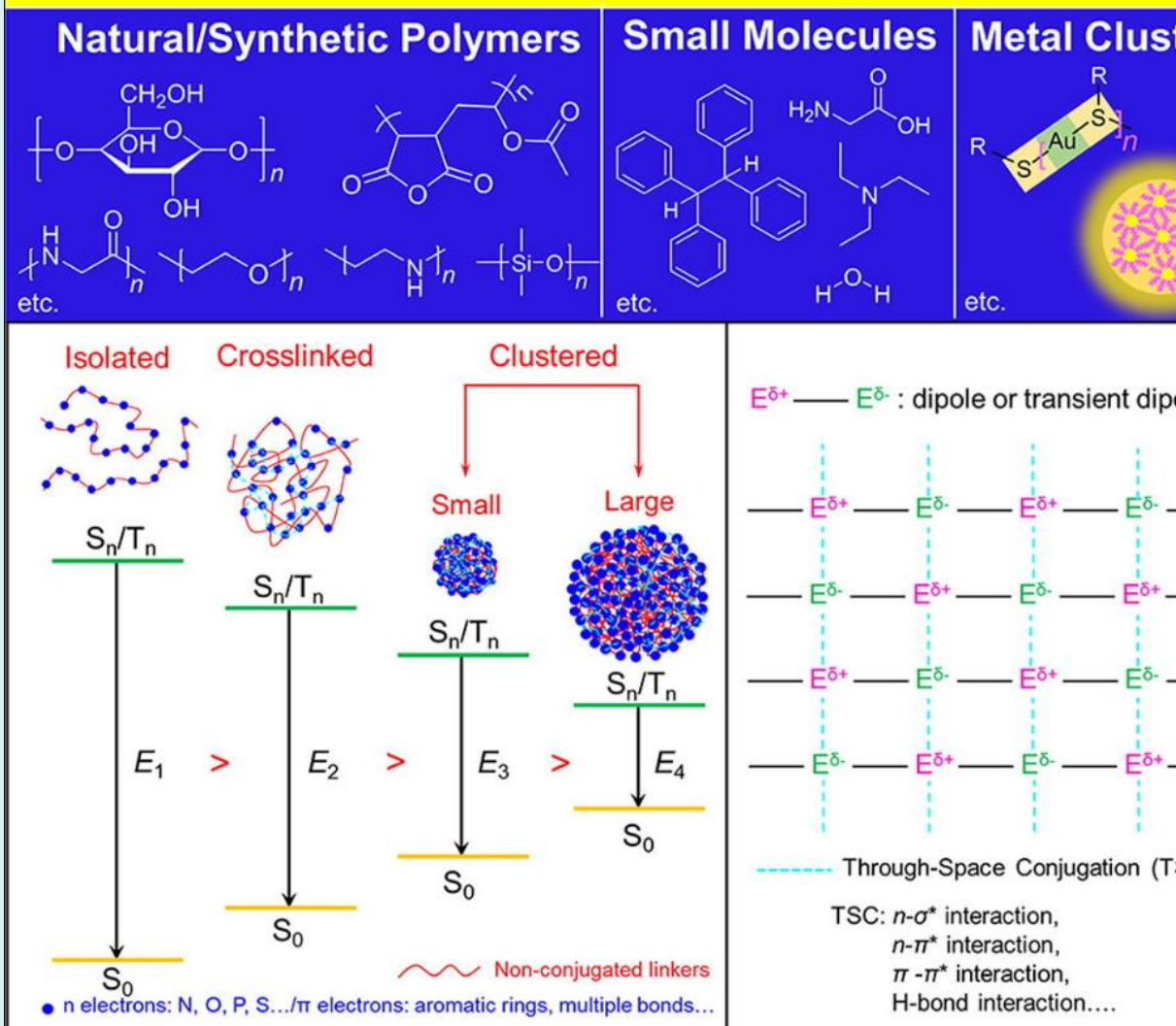


Fig.1 (a) Schematic illustration of the process of clusters formation accompanied with the clusterization-triggered emission properties. (b) Proposed mechanistic picture for clusteroluminescence.

Haoke Zhang, Zheng Zhao, Paul R. McGonigal et al. Clusterization-triggered emission: Uncommon luminescence from common materials *Materials Today* 2020 Volume 32. 275-292

Racemic polypeptides show significantly higher fluorescence intensity than enantiopure polypeptides both in bulk and in solution.

Strong fluorescence intensity originates from the $n-\pi^*$ interaction in the space between the carbonyl groups of polypeptides. The insertion of amino acids with the opposite chirality disrupts the secondary structure of the α -helix of homochiral polypeptides, leading to the formation of a random helical structure. The flexibility of the random coils provides structural mobility for chain entanglement and cluster formation, indicating a stronger interaction between the carbonyl groups of the polypeptide chains. Such chirality-regulated cluster luminescence has been observed in various types of polypeptides, such as polylysine.

The relationship between chirality and structure-property in cluster luminescent polymers can be widely used in many fields. The inclusion of amino acid residues with opposite chirality can be used to create proteins or peptides with strong fluorescence.

Fluorescence spectroscopy provides detailed information about the relaxation, charge transfer, and energy transfer processes that occur

after light absorption. If energy transduction is affected by spin selectivity in the chiral system, then the photoluminescence of the chromophore reflects the spin dependence of the transduction. It is known that the photoluminescence of nanoparticles attached to magnetized ferromagnetic substrates through chiral oligopeptides varies depending on the orientation of the external magnetic field. This is due to chirally induced spin selectivity [6].

Fluorescence spectroscopy can provide detailed insights into relaxation, charge transfer, and energy transfer processes that occur after light absorption. When energy transduction in a chiral system is influenced by spin selectivity, the photoluminescence of a chromophore can reveal spin-dependent effects. For example, researchers demonstrated that the photoluminescence of nanoparticles attached to magnetized ferromagnetic substrates via chiral oligopeptides varies with the orientation of an external magnetic field [7]. In this case, hole transfer—and consequently photoluminescence

quenching—from the nanoparticle to the substrate was highly sensitive to the alignment between the spin selectivity of the oligopeptide and the magnetization orientation of the substrate.

Similar studies have shown that spin-dependent electron transfer [8] and energy transfer [9] processes also regulate the photoluminescence intensity of chromophores based on the substrate's magnetization. Beyond steady-state fluorescence, time-resolved fluorescence measurements offer further insights into the influence of spin on charge transfer kinetics. For instance, in donor-bridge-acceptor nanoparticle systems where the acceptor is chiral, excitation of the donor nanoparticle with circularly polarized light (either clockwise or counterclockwise) produced spin-polarized excitations, leading to significant differences in charge transfer rates to the acceptor due to the chiral-induced spin selectivity (CISS) effect [10].

However, the success of these measurements relies on several key

factors: (i) the system must have a principal excitation axis to define electron spin orientation relative to the transport trajectory, and (ii) the electron transfer time scale must be shorter than the spin decoherence time.

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