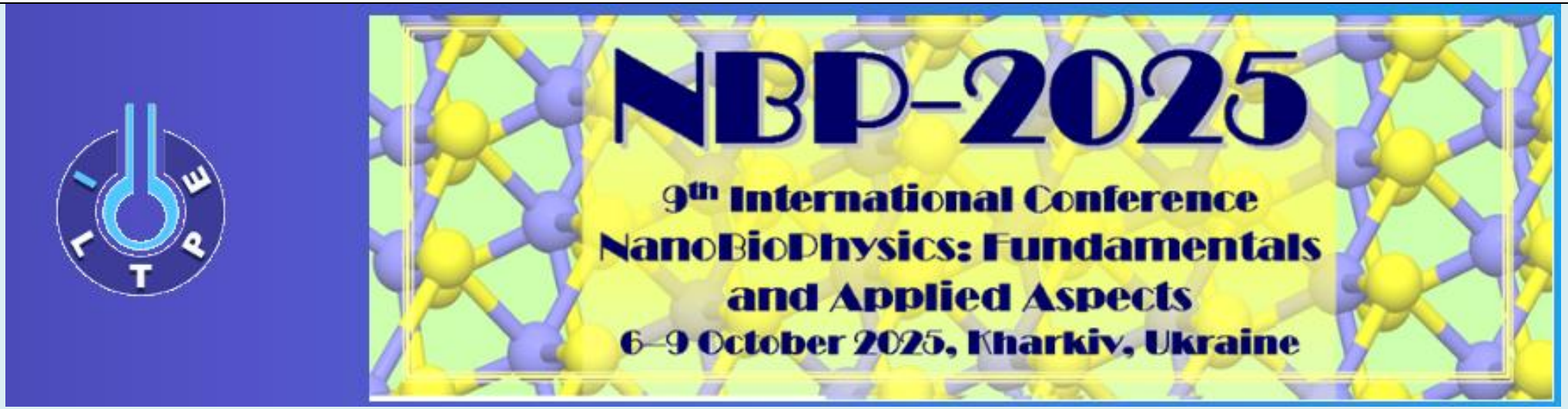

PHYSICOCHEMICAL PROPERTIES OF CHIRAL BIOMOLECULAR NANOSYSTEMS: CLUSTEROLUMINESCENCE, AIE, AND CISS

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Chirality is a fundamental property of molecules that governs their ability to engage in asymmetric interactions, particularly in biological, catalytic, and optical processes. In pharmaceutical chemistry, the enantiomer that provides the primary biological activity is defined as the *eutomer*, whereas the less active or undesirable enantiomer is referred to as the *distomer*. The use of enantiomerically pure compounds allows for improved selectivity and safety of drugs, reduction of side effects, and optimization of their pharmacological profile (Fig.1) [1].. Chirality plays a key role in physicochemical phenomena such as clusteroluminescence (CL), aggregation-induced emission (AIE), and chirality-induced spin selectivity (CISS). This work investigates the interplay between chirality and optical effects, including aggregation-induced circular dichroism (AICD) and aggregation-annihilated circular dichroism (AACD), which arise from the aggregation of chiral or achiral molecules [2–4].

Studies demonstrate that clusteroluminescence in non-conjugated systems may arise from dense molecular packing and n–π* orbital

overlap, especially in polypeptides and amino acids [3,4]. Racemic polypeptides exhibit stronger luminescence than their homochiral counterparts due to conformational changes [1]. Meanwhile, AICD and AACD effects show that aggregation can enhance or suppress chiral optical activity depending on system geometry [2,5,6].

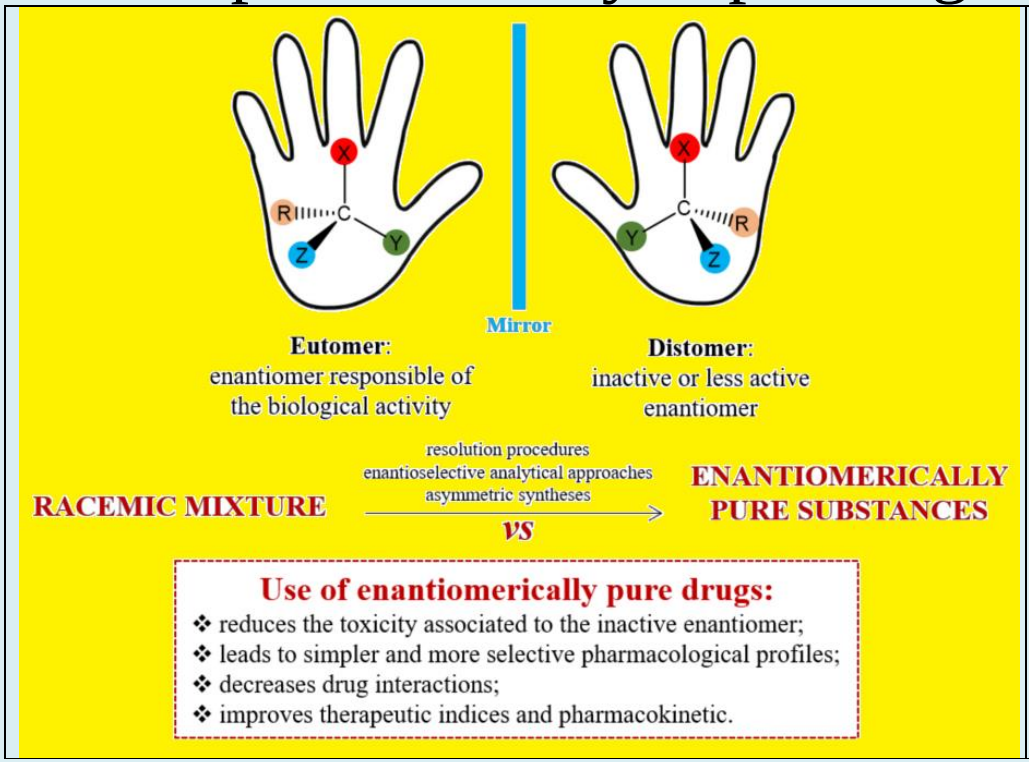

Fig.1. Advantages in the use of single enantiomer drugs

Chirality is a fundamental feature that defines the structure and function of natural and synthetic polymers, strongly influencing their mechanical, optical, and electronic properties.

However, the hierarchical emergence of chirality—from monomers to polymer backbones and supramolecular assemblies—remains

poorly understood due to limitations in nanoscale structural characterization. In this study [7], the authors investigate polymers synthesized via click chemistry and demonstrate how chirality emerges from molecular to supramolecular levels. By combining bulk spectroscopies (CD, FTIR, UV–Vis) with advanced AFM-based imaging and acoustical-mechanical suppressed AFM-IR, they resolve chiral features down to single polymer chains. As illustrated in **Fig.2**, CH groups were identified as markers of central chirality in small molecules, while C=O groups reflected backbone and supramolecular chirality in heterogeneous polymers.

The results highlight that AFM-IR enables direct probing of heterogeneous chiral signatures at the single-chain level, revealing the transition from central chirality to helical conformations and supramolecular order. This framework (**Fig.2**) demonstrates how the integration of spectroscopic and nanoscale imaging techniques opens new avenues for designing polymers and biomacromolecules with

tailored chiral properties for materials science, biotechnology, and medicine.

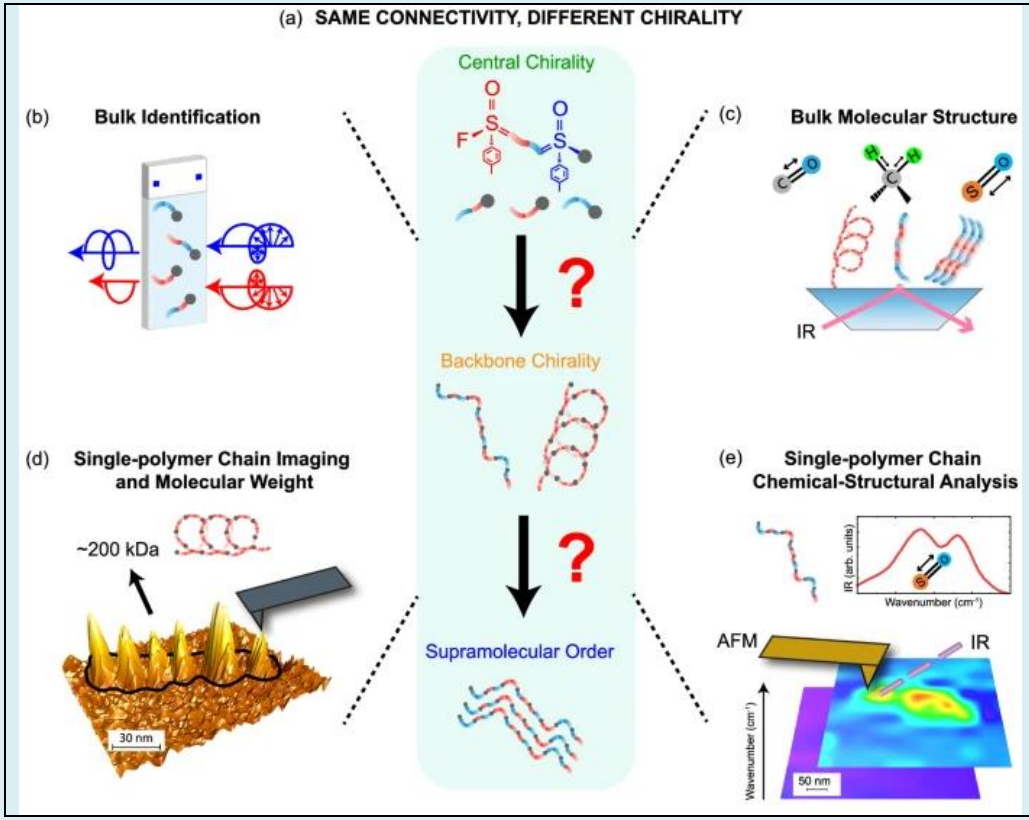

Fig. 2. Framework for multiscale analysis of chirality in SuFEx click polymers: (a) model system with identical connectivity but different stereogenic configurations; (b–c) bulk analyses by CD and FTIR; (d) AFM imaging visualizing backbone helicity at the single-chain level; (e) AFM-IR providing chemical-structural fingerprints of supramolecular assemblies.

Clusteroluminogenic polymers, particularly those incorporating amino acid residues or chiral structural motifs, demonstrate how supramolecular chirality can modulate their luminescence behavior, enabling targeted applications in chiral sensing, bioimaging, and theranostics [5].

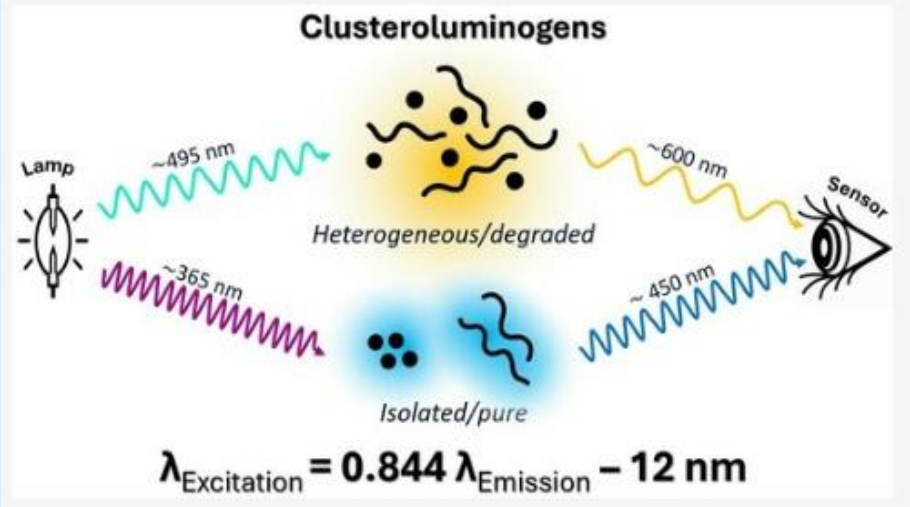

Fig. 3. A Wavelength Rule for the Analysis of Clusteroluminescence

This study [8] establishes a wavelength rule for analyzing clusteroluminescence (**Fig. 3**), based on a strong correlation (r = 0.96) between excitation and emission maxima across chemically diverse clusteroluminogens. All 157 evaluated peaks align along a single regression line ($\lambda_{Ex} = 0.844\,\lambda_{Em} - 12$ nm), distinguishing clusteroluminescence from conventional fluorescence. The spectral positions reflect the degree of molecular interactions: isolated lignin and cellulose show shorter wavelengths, whereas natural wood and degraded samples exhibit red-shifted peaks due to increased molecular heterogeneity. These findings provide a universal principle for clusteroluminescence and a new analytical parameter for assessing polymer purity, aging, and structural modifications.

Of particular interest is the CISS effect, observed in systems with fluorescent probes bound to magnetic surfaces or in chiral sensors, where spin transport depends on molecular chirality (Fig. 4) [9]. The CISS phenomenon arises from spin-selective interactions between chiral molecules and electrons, leading to asymmetric charge transport depending on the relative alignment of electron spin and molecular geometry.

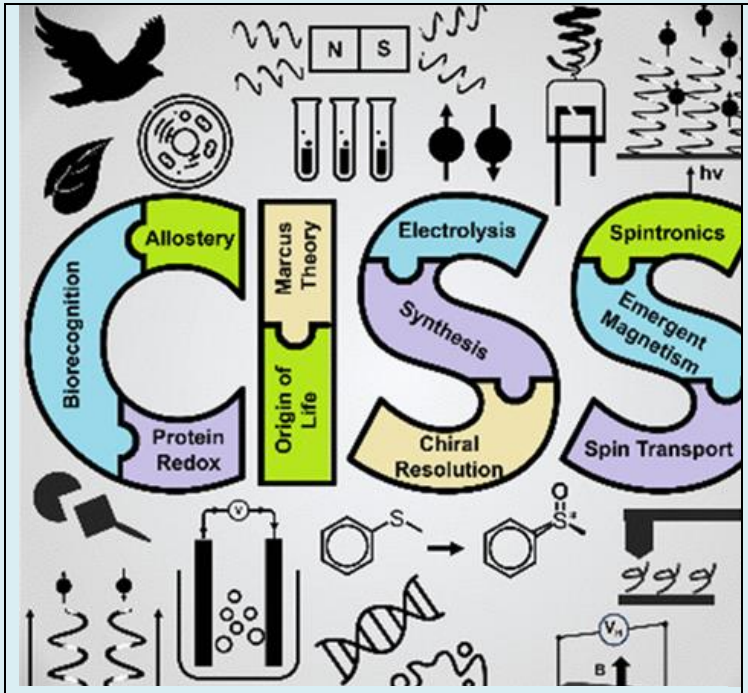

Fig. 4. Chiral Induced Spin Selectivity

This effect is also sensitive to external magnetic fields, which modulate electron spin orientation and thus affect electron transfer efficiency. Chiral molecules provide a structural framework for the spin-dependent transmission of electrons, and

theoretical models incorporate spin-orbit interactions and quantum interference to explain these effects. The CISS mechanism has practical implications for DNA-based sensors, catalysis, and the development of spintronic devices [9].An example of the interrelation between AIE and chirality can be found in nanoparticles-based photosensitizers that exhibit enhanced luminescence upon aggregation [10]. When such nanoparticles are functionalized with chiral molecules or assembled in chiral configurations, their emission properties become sensitive to the supramolecular chirality of the system. This allows for the design of photoactive nanomaterials that combine efficient AIE behavior with selective chiral recognition, enabling their use in enantioselective sensing and light-activated therapy. Overall, these results highlight the critical role of chirality in tuning photophysical properties, paving the way for CPL-active, AIE-efficient, and CISS-sensitive systems based on controlled self-assembly.

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