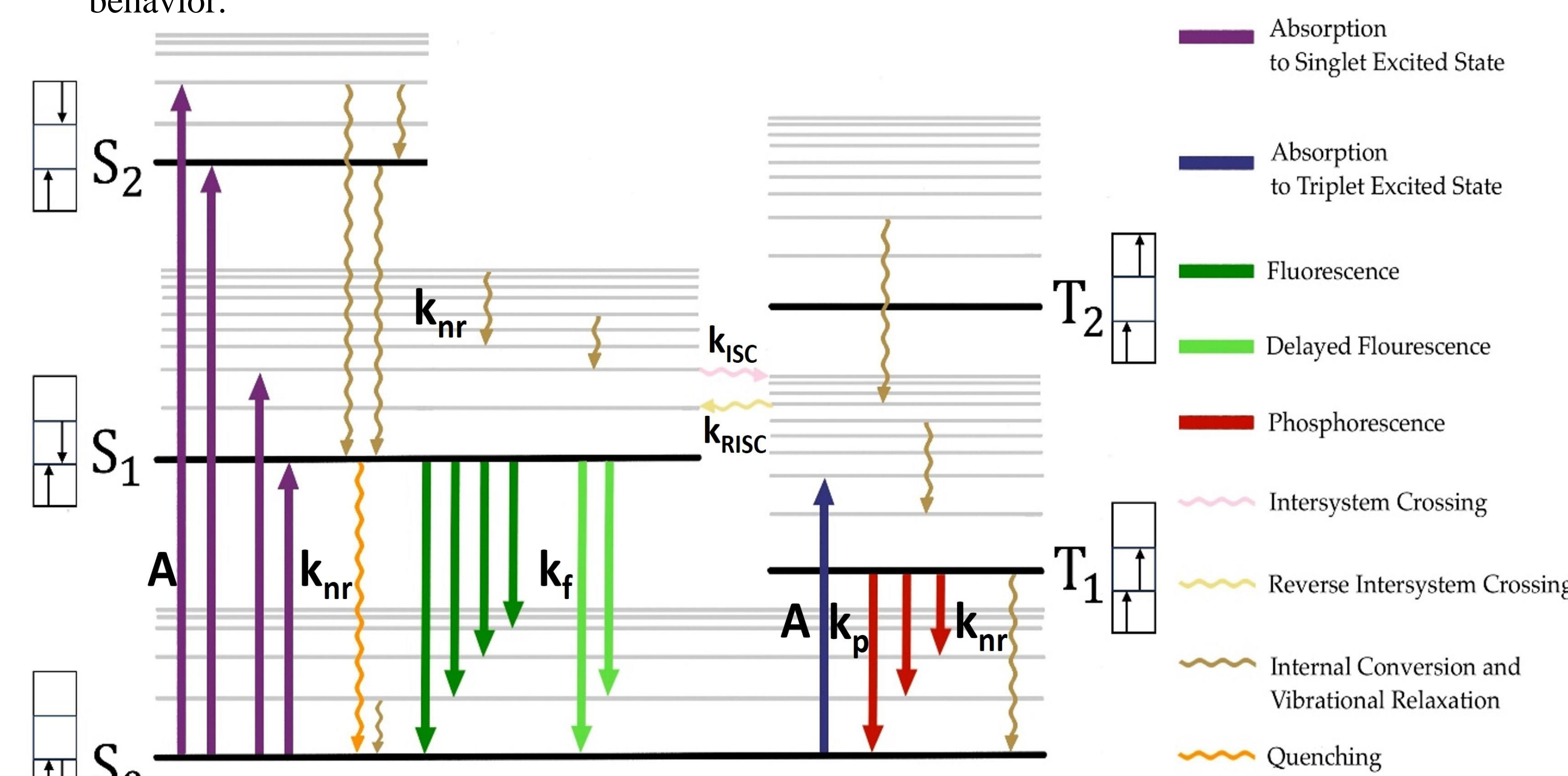


## Abstract

Indole derivatives are known to exhibit diverse luminescent behavior that is strongly affected by molecular structure and the surrounding environment. In this work, we investigate a series of regioisomeric indole-based compounds embedded in poly(vinyl alcohol) (PVA) films. By combining absorption and steady-state fluorescence measurements with room-temperature phosphorescence (RTP), fluorescence and phosphorescence anisotropy, and time-resolved emission decays under UV excitation, we examine how small changes in the substitution pattern determine the luminescent properties of the studied compounds. Although structurally similar, the regioisomers exhibit distinct absorption and emission maxima, visibly different emission colors, and significantly varied excited-state lifetimes. Immobilization in the PVA matrix selectively enhances RTP for certain compounds, while others remain predominantly fluorescent, indicating a substitution-dependent balance between intersystem crossing and nonradiative decay pathways. Overall, the results indicate that even minor structural modifications in indole-based luminophores result in significant changes in their luminescent properties, and that regioisomerism can be used to control luminescent behavior in polymer matrices.

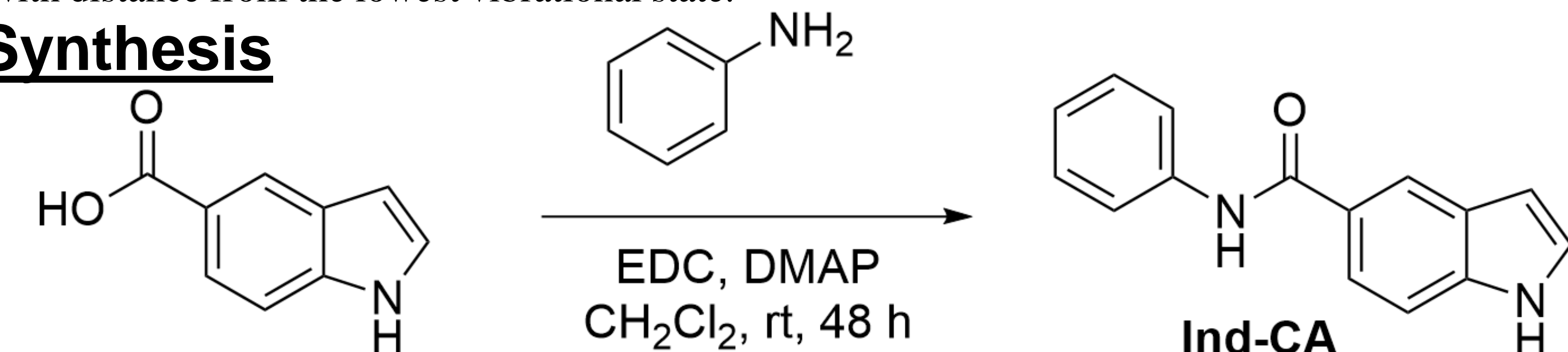
## Background

- Molecular engineering of indole derivatives provides a powerful strategy to control excited-state dynamics. Even minor regioisomeric variations in substituent position or carbonyl orientation lead to pronounced changes in photophysical properties.
- Regioisomer-dependent molecular rigidity and electronic structure modulate the singlet-triplet energy gap ( $\Delta E$ ) and intersystem crossing (ISC) efficiency, thereby determining whether fluorescence or room-temperature phosphorescence (RTP) is the dominant emission pathway.
- Incorporation of indole luminophores into rigid polymer hosts such as poly(vinyl alcohol) (PVA) suppresses non-radiative decay and oxygen quenching, enabling stabilization of triplet states and revealing how structural design governs long-lived emissive behavior.

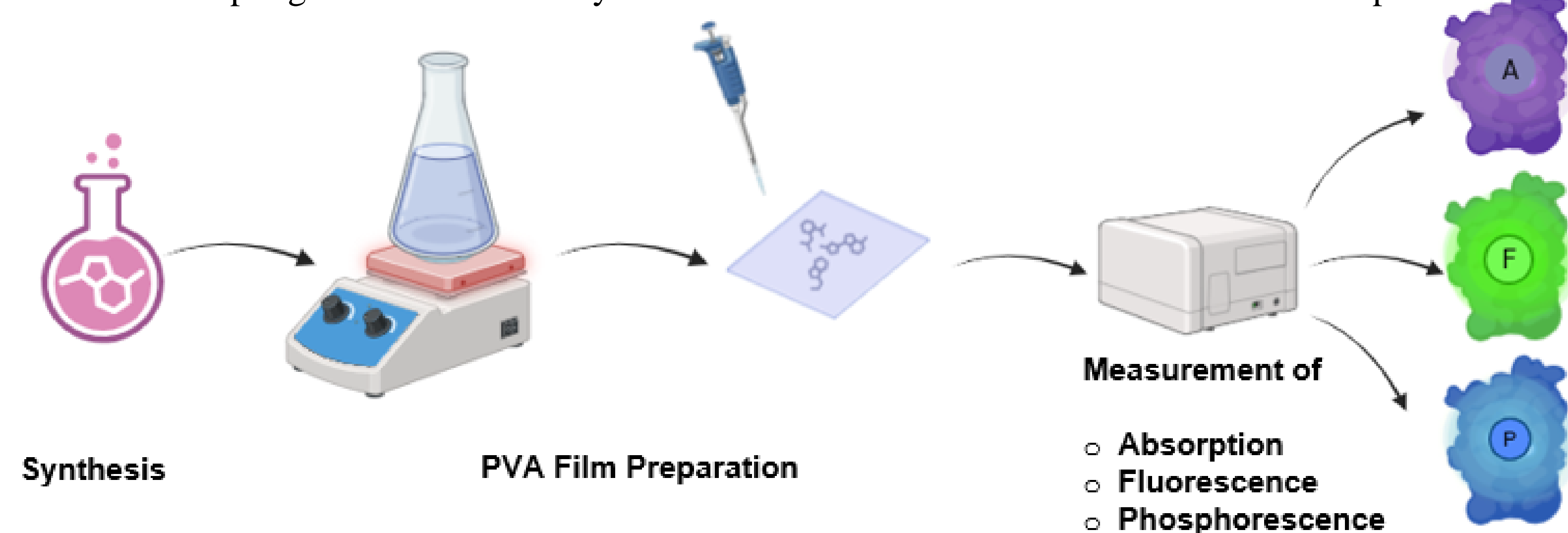


**Figure 1.** Jablonski diagram illustrating electronic states of a molecule and the possible radiative and non-radiative transitions (shown by arrows) between them, where: absorption (A), fluorescence (kf), non-radiative decay (knr), intersystem crossing (kisc, krisc) and phosphorescence (kp). The black horizontal lines at each state represent the lowest vibrational energy level of that state. Higher vibrational energy levels are denoted by light grey lines, where the energy of the state increases with distance from the lowest vibrational state.

## Synthesis



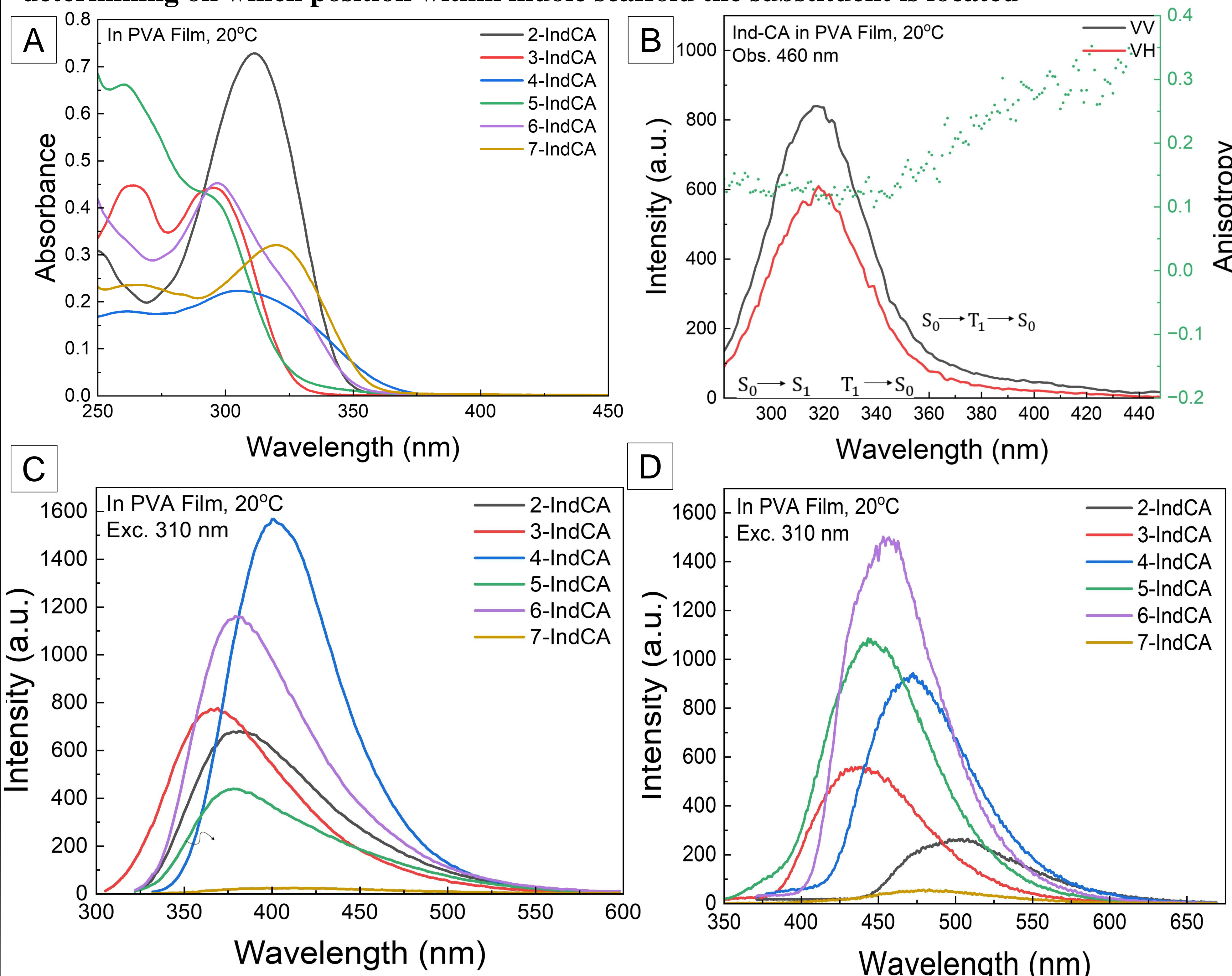
**Figure 2.** Synthetic route to *N*-phenyl-1*H*-indole-5-carboxamide (Ind-CA) using EDC/DMAP-mediated coupling of indole-5-carboxylic acid and aniline in dichloromethane at room temperature.



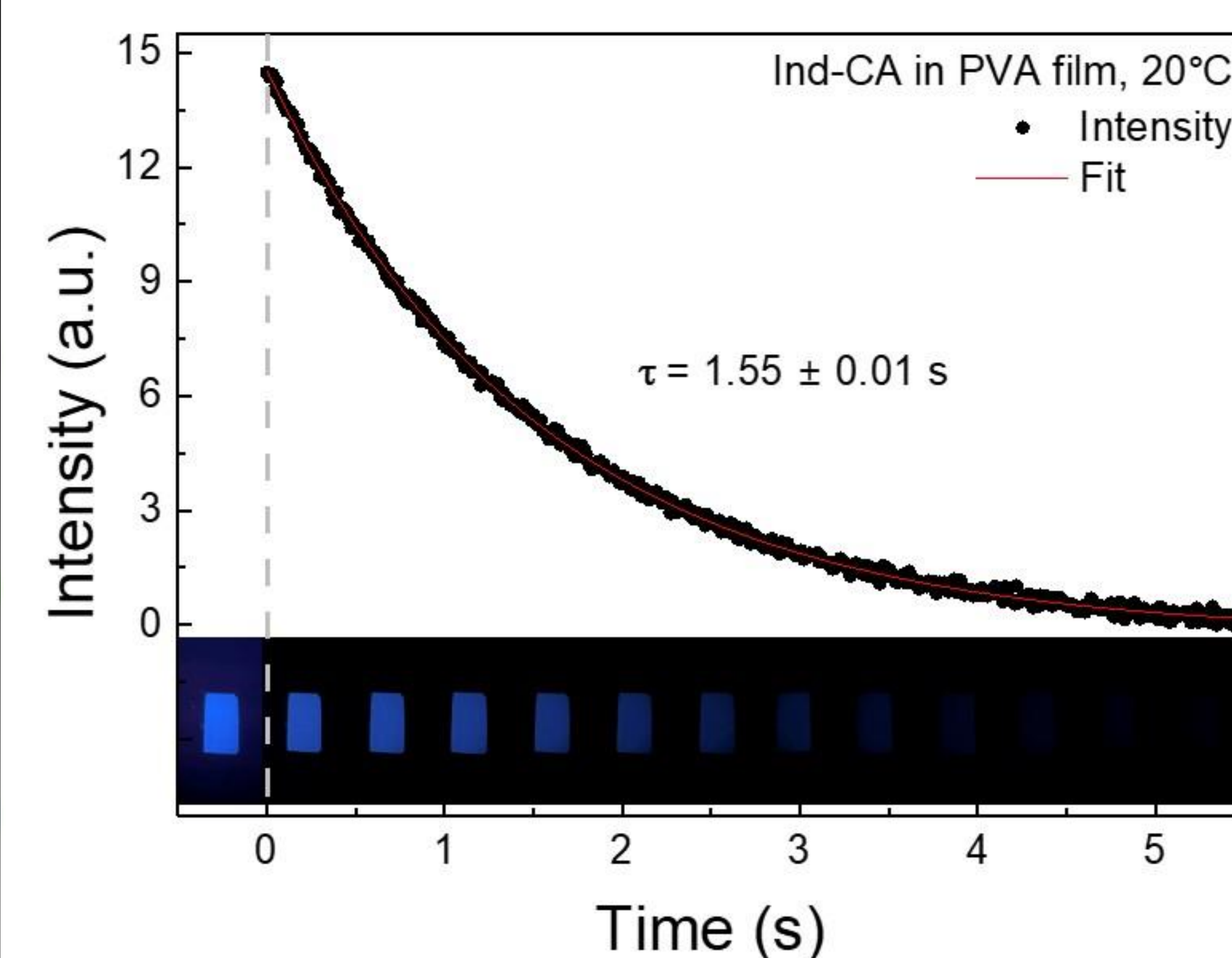
**Figure 3.** Experimental procedure showing synthesis of indole-based luminophores, incorporation into poly(vinyl alcohol) (PVA) films, and spectroscopic characterization including absorption, fluorescence, and phosphorescence measurements.

## Results

### Six different regioisomers of *N*-phenyl-1*H*-Indole-*X*-carboxamide (where *X* varies from 2 to 7) determining on which position within indole scaffold the substituent is located

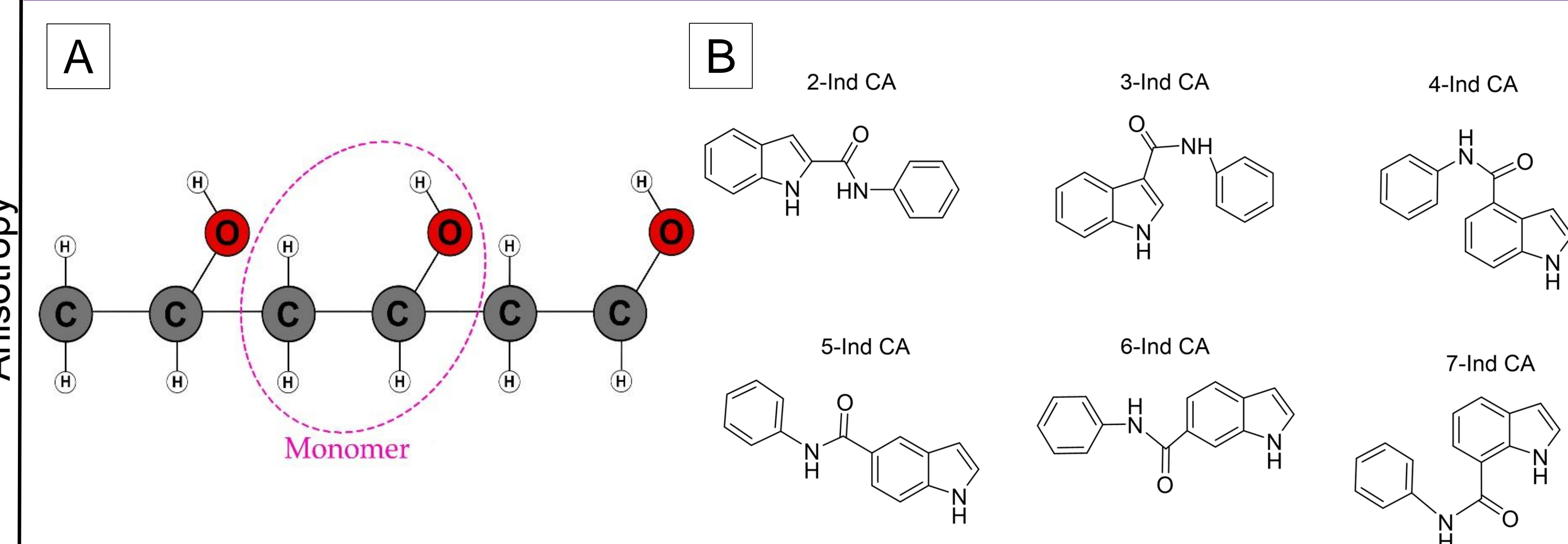


**Figure 4.** (A) Absorption spectra of 6 regioisomers of X-IndCA in PVA film. (B) Phosphorescence excitation anisotropy of 5-IndCA in PVA film. (C) Fluorescence emission spectra of X-IndCA in PVA film. (D) Phosphorescence emission spectra of X-IndCA in PVA film.

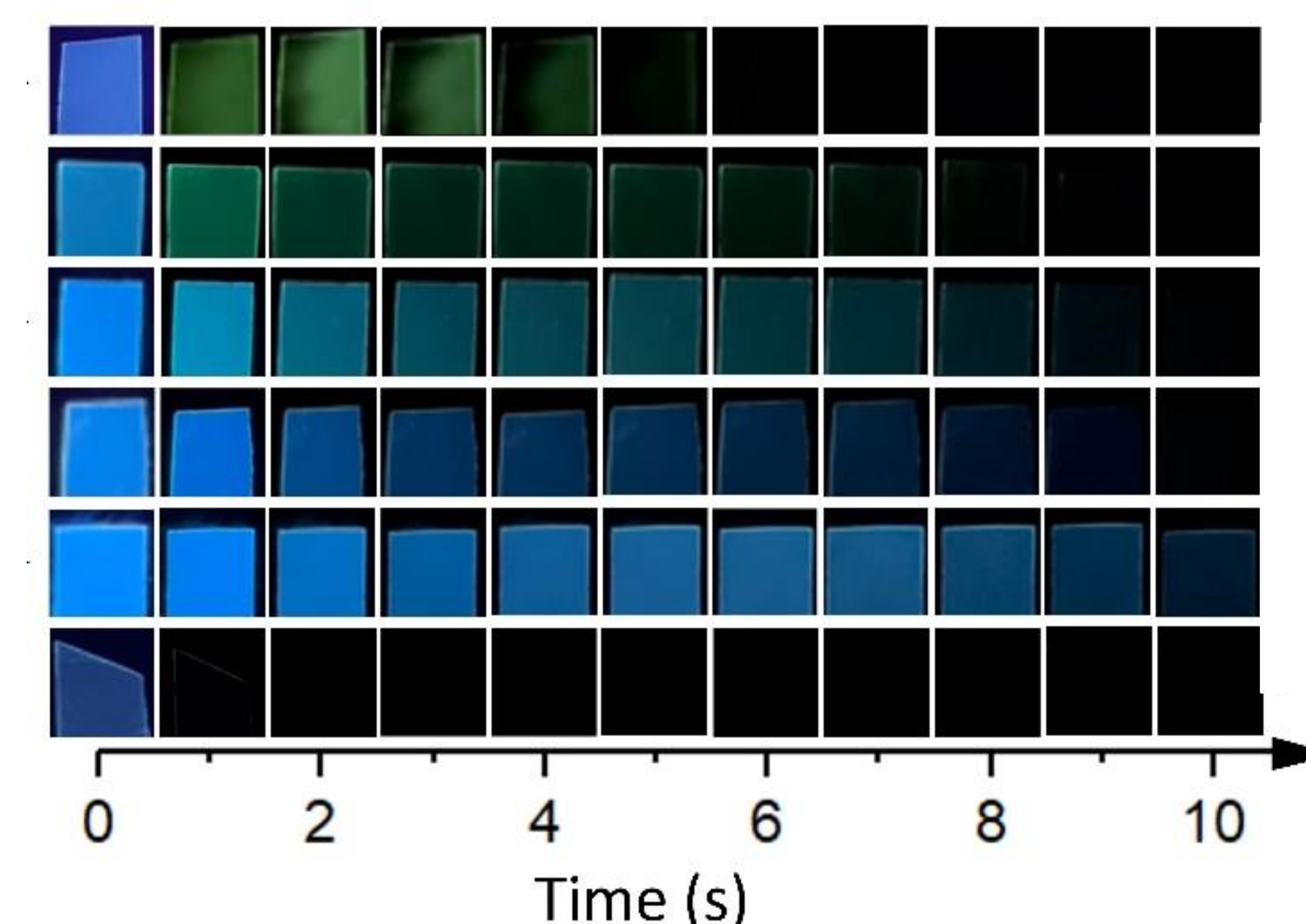


**Figure 5.** Phosphorescence intensity decay of Ind-CA in PVA film.

## Exploring how subtle molecular changes within indole scaffold affect excited-state dynamics and RTP



**Figure 6.** (A) Schematic of PVA polymer chain fragment. (B) Chemical structures of six different regioisomers of *N*-phenyl-1*H*-Indole-*X*-carboxamide (where *X* varies from 2 to 7) determining on which position within indole scaffold the substituent is located.



**Figure 7.** Time-resolved photographs of indole derivatives embedded in PVA films showing afterglow after switching off the UV excitation. These are ordered 2- to 7-IndCA, top to bottom.

- The phosphorescence decay of 5-IndCA in a PVA matrix at 20 °C follows a single-exponential profile with a lifetime of  $\tau = 1.55 \pm 0.01$  s, indicative of long-lived triplet emission.
- The rigid polymer environment suppresses non-radiative relaxation and oxygen quenching, thereby facilitating efficient room-temperature phosphorescence (RTP).
- Phosphorescence excitation anisotropy spectra of 5-IndCA show clear wavelength dependence. At shorter excitation wavelengths, anisotropy remains low ( $\sim 0.1$ ), indicating triplet population via intersystem crossing where absorption and phosphorescence transition moments are misaligned. At longer wavelengths ( $>340$  nm), anisotropy increases to  $\sim 0.3$ -comparable to fluorescence-suggesting partial direct triplet excitation alongside the conventional ISC pathway.

## References

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