Highly efficient intrinsic phosphorescence from a σ-conjugated poly(silylene) polymer

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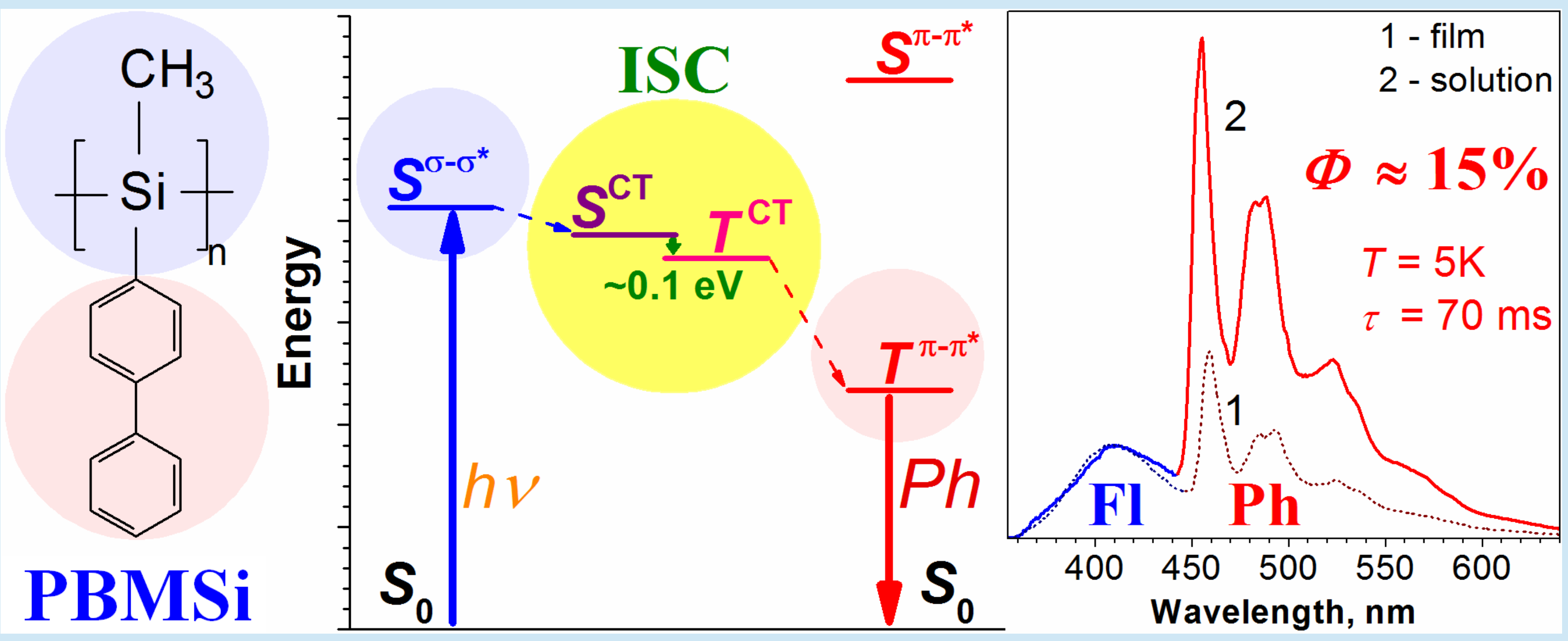
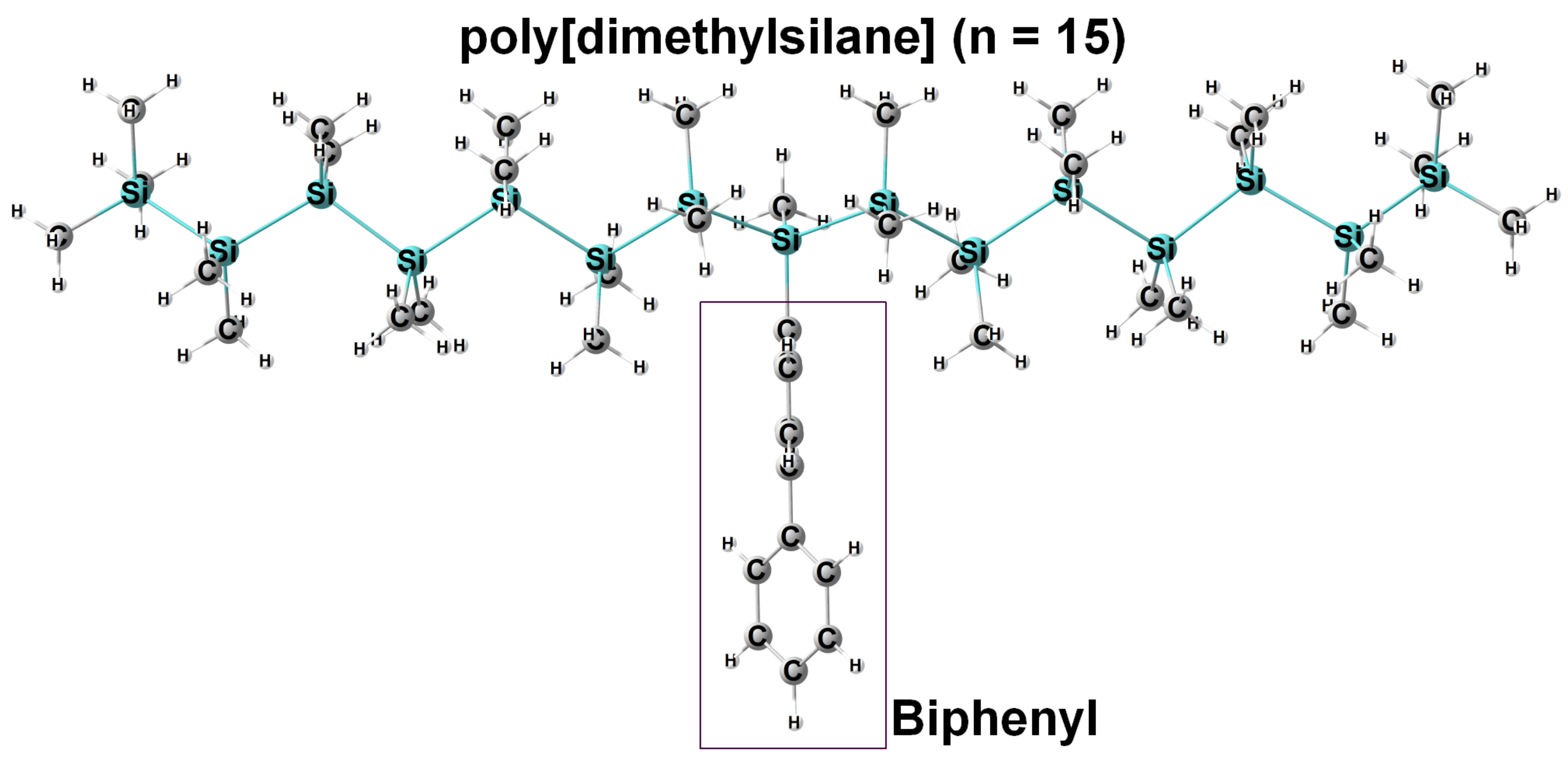
Overview

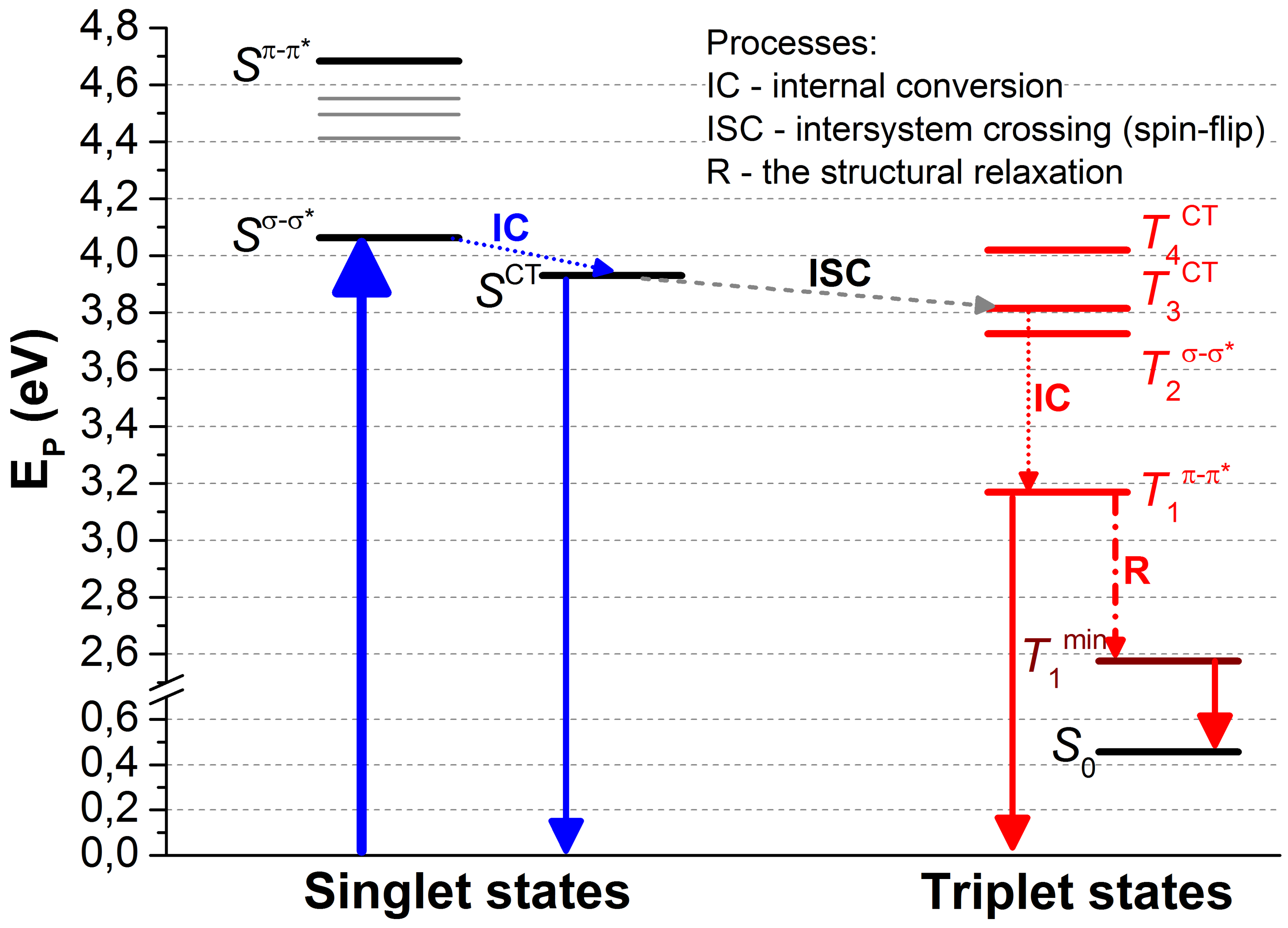


We have observed highly efficient intrinsic phosphorescence of a neat σ-conjugated polymer, **poly[biphenyl(methyl)silylene] (PBMSi)**. At low temperatures, PBMSi solid films feature **~15% phosphorescence** quantum yield, which is unusually high for purely organic conjugated polymers and is comparable to that of organometallic compounds.

Calculations

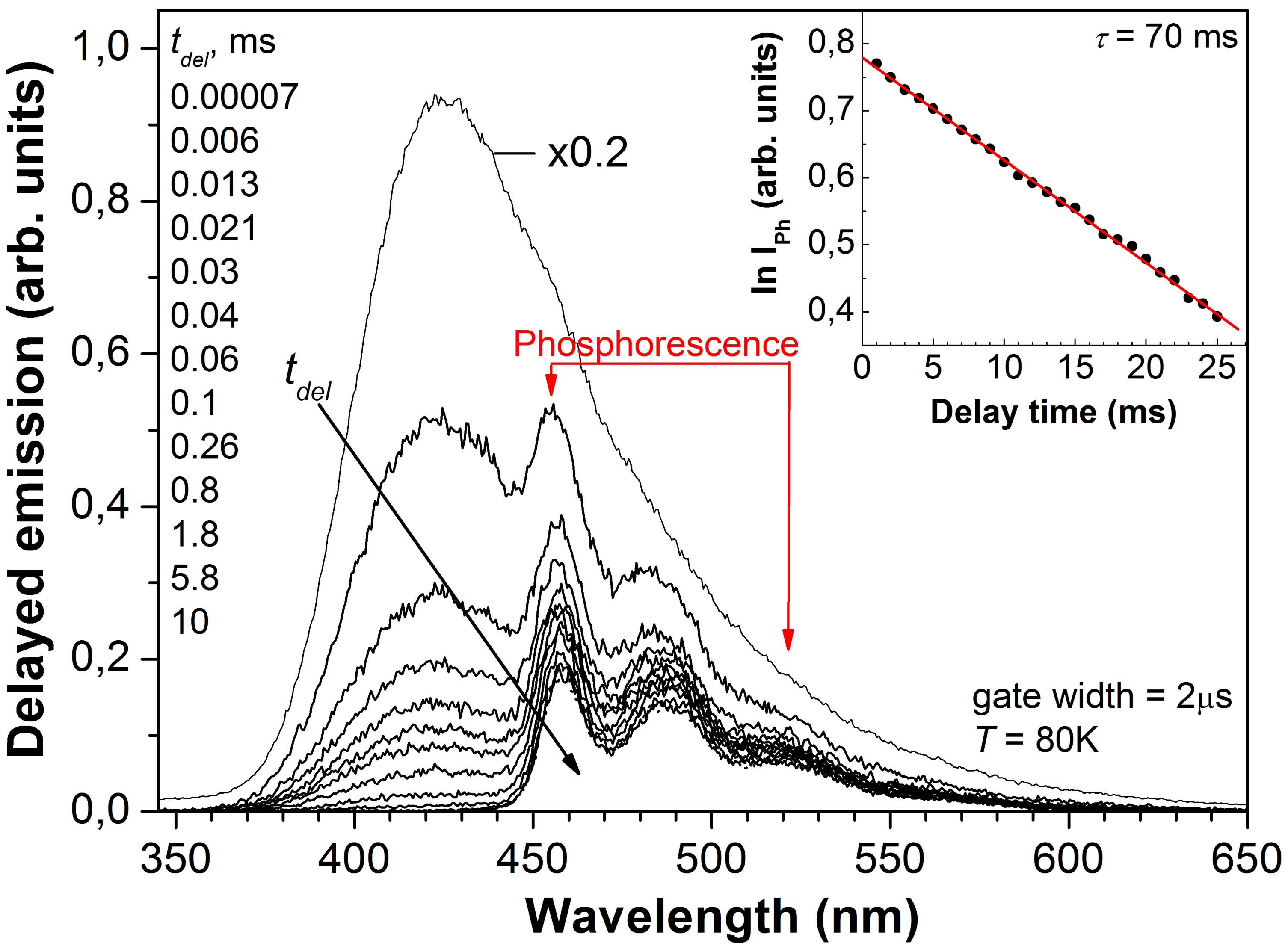


The properties of the **oligomer model** of the compound (**above**) were computed using *Gaussian09* package. DFT theory with B3LYP functional and 6-31G(d,p) basis set was used. The proposed energy conversion path is shown in an energy diagram **below**. The TD-DFT calculations yield the triplet state of the CT character, T_3^{CT}, to be located just below the S^{CT}, implying a very **small singlet-triplet splitting** for the intramolecular charge transfer excitations in this material. The proximity of CT states is very favorable for **enhanced intersystem crossing rate**.

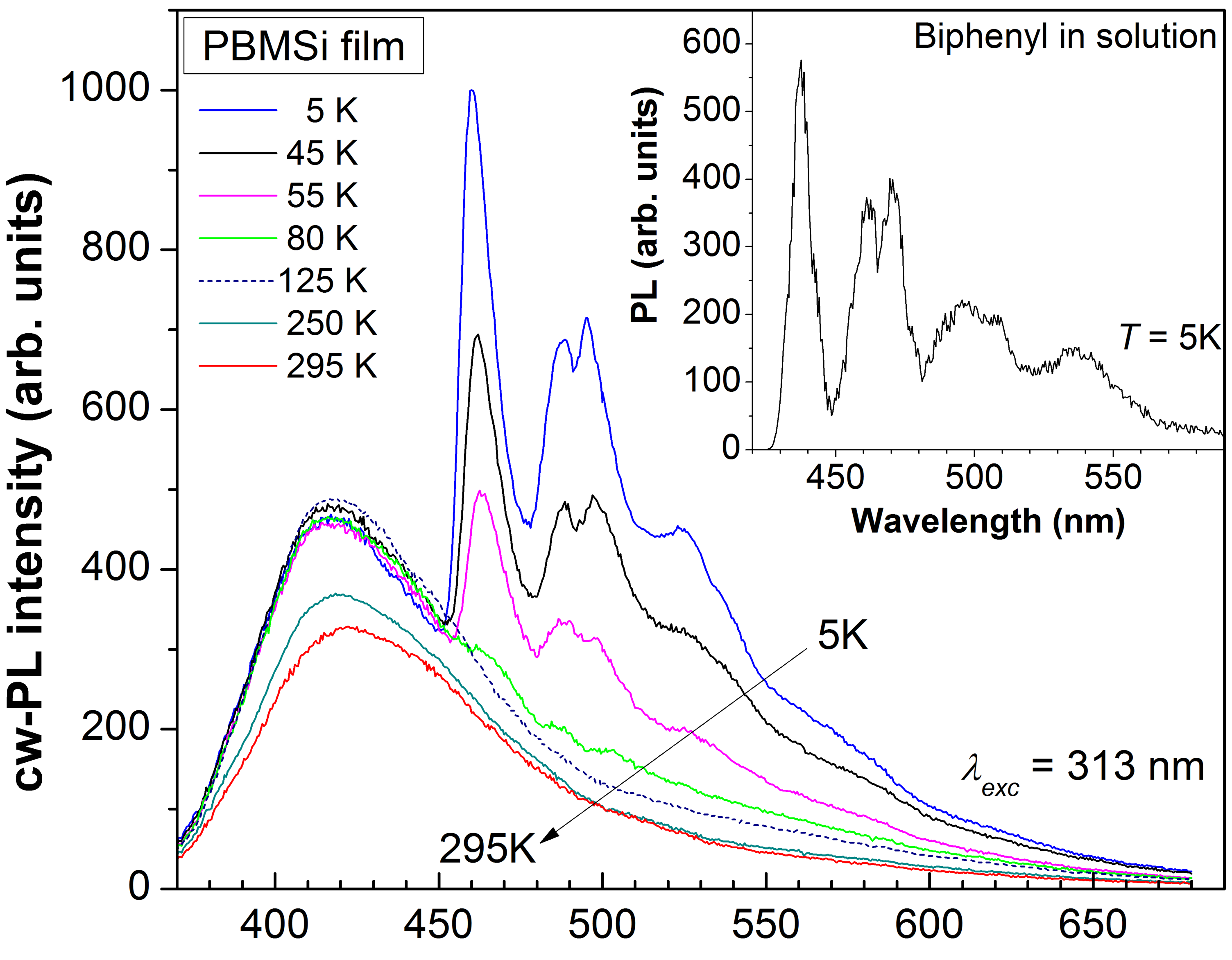


Experiments

The data presented in figure **below** prove unambiguously the existence of two different spectral components in delayed emission spectra of PBMSi, namely the broad structureless band and the red-shifted well-structured narrow spectral component with the main peak at 460 nm. These spectral components feature very different decay times and are identified as **delayed fluorescence** and **intrinsic phosphorescence** of PBMSi.



In contrast to the other conjugated polymers, the observed phosphorescence in PBMSi is **so strong** that it can be readily observable even in cw-PL spectra of the solid films (**below**) for which Ph quenching is expected to be severe because of triplet migration.



Summary and perspective

The results presented here demonstrate the ISC enhancement mechanism realized *intramolecularly* within a neat conjugated polymer comprising suitable donor (σ-conjugated backbone) and acceptor (π-conjugated side group) moieties. Therefore this study can contribute to a new molecular-level engineering approach for strong enhancement of ISC for efficient conversion of primary excited singlets into triplets in conjugated polymers not requiring the heavy atom effect.