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 polymers.

It is shown experimentally that the phosphorescence of PBMSi originates from the radiative decay of triplets on the π-conjugated biphenyl group constituting the lowest triplet state, \( T_1 \). This state is populated under the excitation of the σ-conjugated polymer backbone, i.e., with energy well below the lowest singlet excited state of the biphenyl group itself. The nature of the excited states in PBMSi is further investigated by performing quantum chemical calculations of the model compound. The calculations show that the lowest singlet excited state has charge-transfer (CT) character involving different parts of the same macromolecule. Energetically this state lies very close to the CT triplet excited state. We argue that the intramolecular CT state is responsible for the strongly enhanced intersystem crossing (ISC) in PBMSi due to the small positive CT singlet-triplet energy splitting (Fig. 1).

This study suggests a new molecular-level engineering approach for the enhancement of the ISC, enabling efficient conversion of primary excited singlets into triplets in conjugated polymers without involving heavy atom effect, while leaving the rate of radiative \( T_1 \rightarrow S_0 \) transition virtually unaffected.