

## HIGHLY EFFICIENT INTRINSIC PHOSPHORESCENCE FROM A $\sigma$ -CONJUGATED POLYSILANE POLYMER

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The interest to phosphorescence (Ph) phenomena in organic semiconducting materials has greatly increased in last decade due to creation of highly efficient phosphorescent OLEDs with internal quantum efficiency close to 100% which was achieved by using organometallic complexes as dopants in organic host. In conventional conjugated polymers the reported intrinsic Ph quantum yield is usually very small ( $\sim 10^{-5}$ ) or not detectable at all. The combination of a low intersystem crossing (ISC) rate implying a low population of the triplet state, a low radiative rate and a high non-radiative decay results in an extremely low Ph yield for conjugated polymers devoid of heavy atoms.

In this study we report on a surprisingly highly efficient intrinsic Ph we found in a neat poly[biphenyl(methyl)silylene] (PBMSi)  $\sigma$ -conjugated polymer featuring quantum yield as large as  $\sim 10\%$  in solid films and 20% in a diluted frozen solution, that is unusually large as for conjugated polymers devoid of heavy atoms and is comparable to that of organometallic polymers. The Ph and delayed fluorescence (DF) in this polymer were studied by time-resolved PL techniques and it was shown that Ph is due to the radiative decay of triplets on biphenyl side group under excitation of the  $\sigma$ -conjugated polymer backbone, i. e. with energy well below the lowest singlet state of the biphenyl group, and the DF comes from polymer backbone as a result of triplet-triplet annihilation. Efficient triplet energy transfer in the polymer films has been revealed by PL quenching method using the polymer films doped with different triplet acceptors and organometallic complexes. We argue that the exceptionally strong Ph in this polymer results mostly from a greatly increased ISC rate in this polymer between  $S_1$  and  $T_1$  states of different parts of the macromolecule.

To clarify the nature of the excited states in PBMSi, we calculated the structure and electronic spectra of this polymer using *Gaussian09* package, choosing DFT/ TDDFT with B3LYP functional and 6-31G(d,p) Pople basis set. Transition moment calculations (including spin-orbit coupling) were carried out using *GAMESS-US* program, at the level of GMC-QDPT theory. The calculations yield qualitatively well the energy level positions and wave-function character of electronic excited states in PBMSi. It was found that: (i) the lowest singlet excited state is of a charge-transfer (CT) character due to ( $\nabla$ - $\blacktriangle$ ) transition between Si-chain and biphenyl group and responsible for the fluorescence of this polymer; (ii) it is located well below the  $\nabla$ - $\nabla \rightarrow$  transition of the polymer Si-backbone; (iii) the  $\nabla$ - $\nabla \rightarrow$  transition has the largest oscillator strength and thus dominates the first absorption band of this polymer; (iv) the lowest triplet state  $T_1$  responsible for the phosphorescence of PBMSi was confirmed to be due to  $\blacktriangle$ - $\blacktriangle$  transition in biphenyl group and it is populated via ISC transition mainly from the singlet CT state. Finally, we discuss the reason of the greatly increased ISC rate in PBMSi and demonstrate that this polymer could be promising for application as host material in white-light emitting OLEDs due to rather high intrinsic triplet level.

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