Photoluminescence Anisotropy in Organic Semiconducting Single Crystals

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Time-resolved photoluminescence (PL) anisotropy is studied in novel thiophene-phenylene co-oligomers single crystals. PL is mainly polarized along the molecular backbones regardless of the excitation polarization. PL induced by orthogonal polarizations, has very different time signatures. The origin of such PL behavior is discussed in relation to the molecular packing.

Single crystals of thiophene-phenylene co-oligomers (TPCO) have demonstrated high potential for organic optoelectronics as they combine high charge carriers mobility and excellent photoluminescence (PL) efficiency [1, 2]. In TPCO single crystals a strong PL anisotropy has been observed due to their long-range structural ordering of the luminophore molecules. Despite a considerable amount of theoretical work, the detailed understanding of photophysical properties of such crystals is still lacking. Time-resolved PL provides important insights for establishing the relationship between the molecular structure and optical properties.

In this contribution, we analyze time-resolved PL anisotropy in a novel TPCO single crystal based on the 1,4-bis{5-[4-(trimethylsilyl)phenyl]thiophen-2-yl}benzene (AC5-TMS) molecule (Fig.1a). PL spectra of the crystal are clearly different for X- and Y-polarized excitation (Fig.1b), with the 450-nm band absent for the Y-polarized excitation. Anisotropy shows that PL is mainly X-polarized regardless of the excitation polarization. Moreover, the time-resolved PL exhibits two characteristic decays at ~50 ps (share of 0.8) and ~250 ps (0.2) for the X-polarized excitation, and decays at ~200 ps (0.7) and ~550 ps (0.3) for the Y-polarized excitation. In other words, PL kinetics with the X-polarized excitation decay much faster than with the Y-polarized one (Fig.1c). The relation between the molecular packing in the crystal and their PL properties will be discussed further

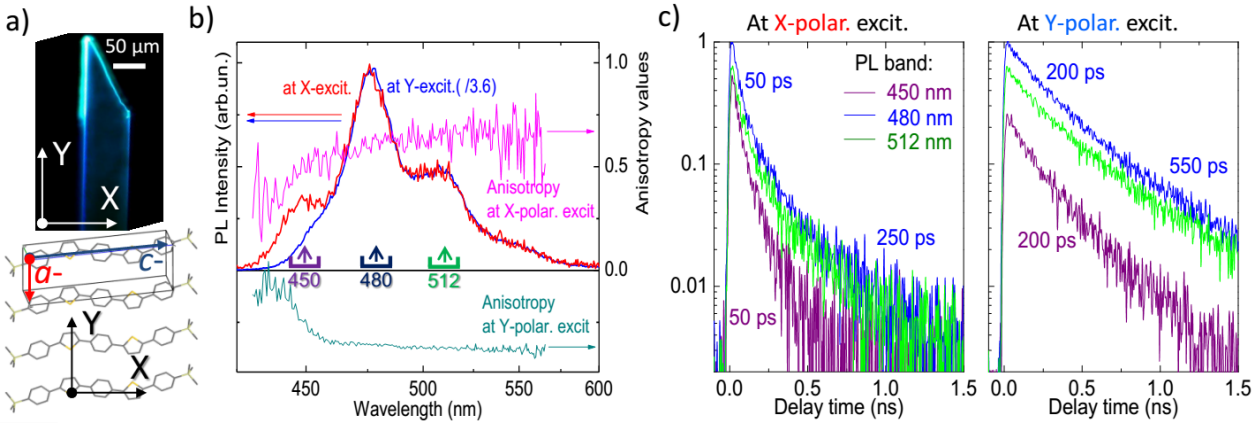

Fig.1 **(a)** Image of the AC5-TMS single crystal (top) and molecular packing (bottom); **(b)** Isotropic PL and anisotropy spectra for X- (red and magenta, respectively) and Y-polarized excitation at 405 nm (blue and cyan, respectively); **(c)** Spectral-resolved PL kinetics for X- (left) and Y-polarized excitation (right). The transients were averaged over the spectral ranges shown in (b).

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[2] L. Kudryashova, *ACS Appl. Mater. Interfaces* (2016), DOI: 10.1021/acsami.5b11967