Switching between coherent coupling modes in mesoscopic conjugated polymer aggregates

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The aggregation of conjugated polymers (CPs) and coherent coupling of chromophores play a central role for a fundamental understanding of light and charge generation processes. The theoretical framework to describe the coherent coupling mechanisms is built upon a combination of J- and H-aggregation between neighboring chromophoric units [1]. Figure 1a depicts three different cases: H-type, J-type and the absence of coherent coupling in CP aggregates and their relationships with chain morphology. However, testing this theory in bulk measurements appears to be very difficult, because of the extraordinarily morphological heterogeneity of CPs. For this reason, we grow isolated mesoscopically sized aggregates of CPs by solvent vapour annealing to overcome the inherent averaging over differently aggregated regions in bulk measurements [2-4]. The dominating coherent coupling in such aggregates can be switched reversibly between H- and J-type coupling by partially drying and swelling the aggregates, as depicted in Figure 1b. This effect is identified by following *in situ* the shifted photoluminescence (PL) wavelengths, changing vibronic peak ratios and PL lifetimes. With this approach, we unravel the internal electronic structure of such mesoscopic aggregates and confirm the theoretically predicted simultaneous H- and J-type coherent coupling in CPs. Finally, we demonstrate how small changes in the molecular structure of side chains of the CPs, as shown in Figure 1c, can be exploited to tune between H-type, J-type and a suppression of coherent coupling in the dried state. These types of coherent coupling are correlated with the morphology, which is measured

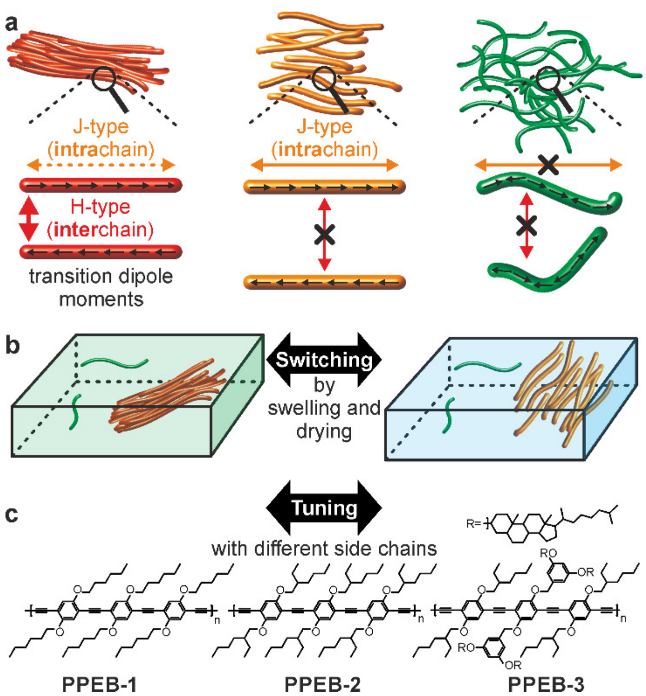

Fig. 1. (a) H-, J-type and suppression of coupling. (b) Switching between H- and J-type coherent coupling by drying and swelling the aggregate. (c) Tuning between H-type (PPEB-1), J-type (PPEB-2) and suppressed coupling (PPEB-3) by changing the side chains.

by excitation polarization spectroscopy, and energy transfer properties within the aggregate which are assessed by obtaining the degree of single photon emission of these mesoscopic aggregates.

References

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