

Narrow-Wide Copolymer Design Improving Red-Color-Selective Strong Absorption

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Full-color image sensors for retinal prosthesis and artificial vision require conformable/biocompatible organic RGB-color-selective photodiode components. The most challenging components are those for red-selective absorption because (1) molecular dyes such as phthalocyanine and squaraine require a vacuum deposition, (2) a red-light absorption (625-800 nm) achieved by solution-processed push-pull copolymers is often accompanied by a higher-energy absorption in green/blue regions (400-625 nm), and (3) push-pull copolymers designed to suppress such high-energy absorption show their low-energy absorption in the NIR region (>800 nm) rather than in the red region (625-800 nm), which is useful for photovoltaics but not for sensitive red-color detection. We therefore define the *red selectivity* (RS, %) of a polymer as the ratio of its red-region absorption (625-800 nm) to its total absorption in the visible and near-IR regions (400-1000 nm) and propose a *narrow-wide* (rather than *push-pull*) design rule for RS-enhancing copolymers, (1) HOMO/LUMO localized in the *narrow-band-gap* unit and HOMO-1/LUMO+1 localized in the other *wide-band-gap* unit and (2) hybridization between the two units minimized by introducing a twist in the backbone. Copolymers of thiophene-flanked diketopyrrolopyrrole (T-DPP-T) *narrow* units linked to benzene, naphthalene, or phenanthrocarbazole *wide* units indeed exhibit high RS values up to 75%. Such *minimally-hybridized-narrow-wide-copolymer* design for strong *red-selective* absorption is extended to cover new hypothetical copolymers, utilizing TDDFT calculations on short oligomer models.

