## Tailoring molecular fluorescence by polymerization-mediated charge transfer

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Charge transfer is a fundamental process in both natural systems and synthetic molecules. It has been widely used for tuning the excited states of organic fluorescent molecules. In recent years, through-space charge transfer (TSCT) has emerged as a novel mechanism for the design of highly emissive molecules.<sup>[1]</sup> However, multi-step organic syntheses and special chemicals are usually involved for these molecules, coming at high cost. Recently, we discovered a structurally remote through-space charge transfer process in well-defined polymer systems, which enabled continuous color tuning of polymer fluorescence in solid state via controlled polymerization.<sup>[2]</sup> Using a single-acceptor fluorophore as the initiator for atom transfer radical polymerization, a series of electron-donor groups containing simple aromatic moieties were introduced by facile copolymerization or post-functionalization. Guided by a machine learning model, the resulted TSCT polymer library showed precisely tailorable emission wavelength.<sup>[3]</sup> This was achieved by fine-manipulation of donor-acceptor interplay via simple controlled polymer synthesis. Theoretical investigations confirmed the structurally dependent TSCT-induced emission redshifts. We further demonstrated this TSCT polymer platform can be used to design stimuli-responsive materials with highcontrast photochromic fluorescence. This study revealed that polymerization-mediated charge transfer can be employed as a general approach for tuning molecular fluorescence with easy synthesis and lowcost chemicals.

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## References

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