

## Tailoring molecular fluorescence by polymerization-mediated charge transfer

Y. Bao<sup>1</sup>

<sup>1</sup>Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zürich, Switzerland. Email: ybao@ethz.ch

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 high-contrast 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 low-cost chemicals.

### Acknowledgements

We acknowledge the financial support for this study from Fondation Claude et Giuliana (no. 1-005137) and Swiss National Science Foundation (no. 190313).

### References

- [1] Tsujimoto, H.; Ha, D.-G.; Markopoulos, G.; Chae, H. S.; Baldo, M. A.; Swager, T. M. *J. Am. Chem. Soc.* 2017, 139, 4894
- [2] Ye, S.; Tian, T.; Christofferson, A. J.; Erikson, S.; Jagielski, J.; Luo, Z.; Kumar, S.; Shih, C. J.; Leroux, J. C.; Bao, Y. *Sci. Adv.* 2021, 7, eabd1794.
- [3] Ye, S.; Meftahi, N.; Lyskov, I.; Tian, T.; Kumar, S.; Christofferson, A. J.; Winkler, D. A.; Shih, C.-J.; Russo, S.; Leroux, J.-C.; Bao, Y. *Chem* 2023, 9, 924.