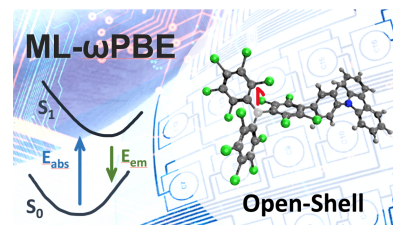


# ACCURATE PHOTOPHYSICS OF ORGANIC RADICALS FROM MACHINE LEARNED RANGE-SEPARATED FUNCTIONALS

CHENGWEI JU, *Pritzker School of Molecular Engineering, The University of Chicago, Chicago, IL, USA*; YILI SHEN, *College of Software Engineering, Tongji University, Shanghai, China*; AARON TIAN, *N/A, Massachusetts Academy of Math and Science, Worcester, MA, USA*; ETHAN FRENCH, HONGSHAN BI, ZHOU LIN, *Department of Chemistry, University of Massachusetts, Amherst, MA, USA*.

Luminescent doublet-spin organic semiconducting radicals are emergent and unique candidates for organic light-emitting diodes because their internal quantum efficiency is not limited by intersystem crossing into any non-emissive high-spin state. The multi-configurational nature of their electronic structures challenges the usage of single-reference density functional theory (DFT), but the problem can be mitigated by designing more powerful exchange–correlation (XC) functionals. In an earlier study, we developed a molecule-dependent range-separated functional, referred to as ML- $\omega$ PBE, using a stacked ensemble machine learning framework.<sup>a</sup>

In the present study, we assessed the performance ML- $\omega$ PBE for 64 organic semiconducting radicals from four categories, when similar radicals are absent from the training set. Compared to the first-principles OT- $\omega$ PBE functional, ML- $\omega$ PBE reproduced the molecule-dependent range-separation parameter,  $\omega$ , with a small mean absolute error (MAE) of **0.0214**  $a_0^{-1}$ . Using single-reference time-dependent DFT (TDDFT), ML- $\omega$ PBE exhibited outstanding behaviors in absorption and fluorescence energies for most radicals in question, with small MAEs of 0.22 and 0.12 eV compared to experimental sources, and approached the accuracy of OT- $\omega$ PBE (0.22 and 0.11 eV). Our results demonstrated excellent generalizability and transferability of our ML- $\omega$ PBE functional from closed-shell organic semiconducting molecules to open-shell doublet-spin organic semiconducting radicals.



<sup>a</sup>Ju et al. *J. Phys. Chem. Lett.*, **2021** 12, 9516.