

Photo-physics of Cu (I) Dipyrrin Complexes: Effect of Substituting Groups and Side Linkages

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Most photo-active transition metal complexes (TMCs) are made from precious metals with very low natural abundance in Earth's crust. Additionally, development of highly efficient near infrared (NIR) emitting TMCs has been under-pursued to date due to our limited understanding of the interplay between radiative and non-radiative relaxation processes leading to extreme variations in photoluminescence quantum yield (PLQY). We use density functional theory (DFT) and time-dependent DFT (TDDFT) to investigate the photo-physics of Cu (I) dipyrrin complexes and Redfield-based non-adiabatic molecular dynamics (NAMD) to compute PLQY. Calculations show a low-energy absorption peak appearing in the red-to-near infrared (NIR) regions (~700 nm) tunable by substituting electron withdrawing (CN, NO₂) and electron donating groups (OCH₃, NPh₂), as well as changing the π -conjugation via side linking groups (H, -CH₂CH₂-, -CH=CH-). The substituent groups change the charge transfer character of the low-energy excitons which is expected to have a large influence on the resulting PLQY, while the side linkages (conjugated connectors) increase the degree of delocalization of the excitons. When non-adiabatic couplings are computed with PBE functional, the splitting between energy levels, including the HOMO-LUMO gap, is smaller, compared to hybrid PBE0 functional. Therefore, PBE likely overestimates non-radiative recombination rates. However, systematic comparison across all models shows that the PLQY increases with the strongest electron-withdrawing group, as well as with enhancement of structural rigidity caused by π -conjugated side linking. Further work will involve computing non-adiabatic couplings with a hybrid functional to improve accuracy of NAMD calculations.