Title

The metallophilic self-assembly of red-shifted cyclometalated palladium photosensitizers

Authors

Lan Wang, Sylvestre Bonnet*

Poster presentation

Photodynamic therapy is a non-invasive and targeted way to treat tumors. Photosensitizers (PSs) have low dark cytotoxicity and good biosafety, and then show light cytotoxicity after light irradiation. [1] Cyclometalated palladium (Pd) PSs were reported that have excellent singlet oxygen or reactive oxygen species generation.[2] [3] The series of cyclometalated Pd(II) complexes with square planar structure can form nano aggregates in cell culture medium with fetal calf serum based on metallophilic interaction and pi-pi stacking. On one hand, the carrier-free nano PSs aggregates with good stability and proper size distribution are proven that have high cellular uptake and tumor therapy efficacy in vitro and in vivo.[3] On the other hand, the metallophilic interaction is also helpful to redshift the compound absorption. However, the blue or green light absorption limits the light penetration depth and hinders the application of these compounds toward solid tumor treatment. Here, we introduce electron-withdrawing groups (EWGs) to the pyridine part of the ligand to lower the LUMO energy of the metal complex to red-shift. For example, the HOMO-LUMO energy gap reduces from PdLF ($\Delta E = -3.49\ eV$) to PdLCF$_3$ ($\Delta E = -3.30\ eV$). Besides, to improve the water solubility, triethylene glycol monoethyl ether (TEG) was introduced, PdLCF$_3$TEG was obtained. PdLCF$_3$TEG shows a very high photo index (PI > 240) with green light PDT for Melanoma A375 cells, which largely improves the PDT efficacy of previous PdL (PI = 72).

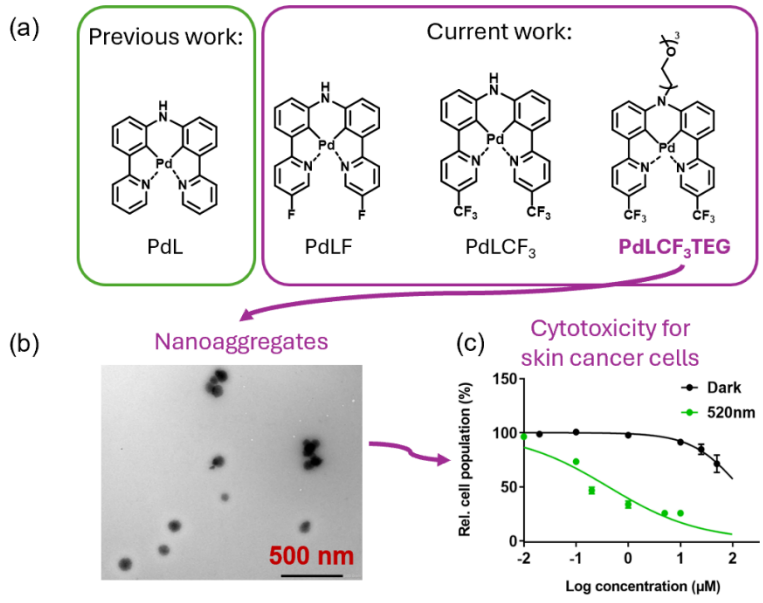

Figure The molecular structures of PdL, PdLF, PdLCF$_3$ and PdLCF$_3$TEG (a); and nano aggregates morphology by TEM (b) and the dark and light cytotoxicity results (520 nm, 8min, 13 J/cm^2) of PdLCF$_3$TEG (c)

References

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