Photophysical properties of near-infrared luminescence of porphyrin array aggregates in thin films

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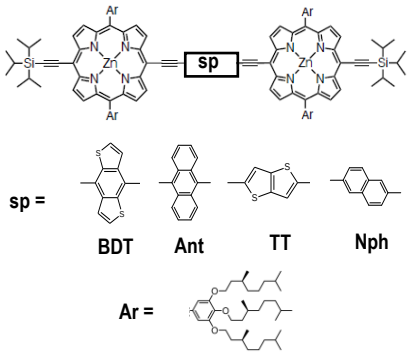
Keywords: porphyrin, aggregate, near infrared luminescence, thin film

Metalloporphyrins bearing 3,4,5-tri((*S*)-dihydrocitronellyloxy) groups at the *meso*-positions form amorphous molecular glass which exhibits near-infrared (NIR) excimer- and/or aggregation induced emission.[1] In this work, the photophysical properties of NIR emissions for Zn porphyrin arrays linked with various arylenes (Scheme 1) in thin neat films.



Scheme 1. Structure of porphyrin arrays linked with arylenes

Figure 1 shows the absorption and emission spectra for a BDT film which was prepared by bar-coating of toluene solutions of BDT onto a quartz substrate. The BDT film exhibited a red-shifted Q-band at 718 nm compared for cyclohexane solutions (685 nm) due to the formation of aggregates through π-staking. At 298 K, the BDT film showed an emission band with the peak at 890 nm and a shoulder at around 770 nm upon irradiation. At 80 K, the intensity at 890nm increased whereas the shoulder at 770 nm diminished.

Emission lifetime was measured by a time-correlated single photon counting with a lab-made picosecond light pulsar (450 nm) and a metal package PMT(R9880U-20). For BDT, the emission intensity decayed nonexponentially with lifetimes (τ) of <40ps, 110 ps, and a very small amount of a few nanosecond components. Similar results were obtained for Ant (τ<40 ps, 168 ps), Naph(τ<40 ps, 128 ps), and TT(τ<40 ps, 199 ps). The shorter lifetime might be ascribable to free exciton in aggregate while the 100~200 ps components to excimers or self-trapped excitons.

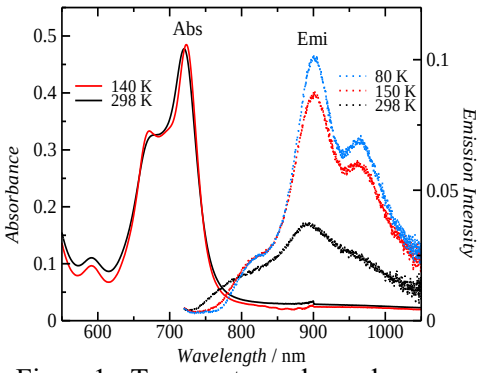


Figure1. Temperature dependence of emission and absorption spectra observed for a BDT film.

[1] M. Morisue *et al., RSC Adv.*, **2017**, 7, 22679-22683.