Donor effect study for azaphenalene derivatives and tuning of its photophysical properties by protonation

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Development of highly efficient organic luminophores is one of the main focus of researchers in photochemistry field, to realize long-lived OLEDs. TADF (Thermally Activated Delayed Fluorescence) is a type of fluorescence which has the potential to achieve this goal. To get TADF emission, traditional molecules are designed to show inverted singlet-triplet energy gaps, efficient Reverse Intersystem Crossing (RISC) via small positive singlet-triplet energy gap(ΔE_{ST}). In 2020, Heptazine, seven-nitrogen substituted phenalene, was reported to exhibit inverted energy gap, $\Delta E_{ST} < 0$[1]. However, azaphenalene emission is usually weak because of small oscillator-strength[2], and there is a need for further investigation of its derivatives.

In this research, we synthesized three penta-azaphenalene derivatives by attaching different donors to penta-azaphenalene core and investigated their photophysical properties (Fig.1). R represents substituents: carbazole, diphenylamine, and phenothiazine. The electron-donor moieties were introduced by a Buchwald-Hartwig reaction. The best yield was 22%, and the substituent was diphenylamine substituents. Also, singlet-triplet energy gap and oscillator strength were calculated for each compound. Moreover, reversible absorbance changes by addition of acid were observed (Fig.2). Acidic condition led to a bathochromic shift of the emission spectra, with a red color fluorescence obtained in diphenylamine-donor derivative.

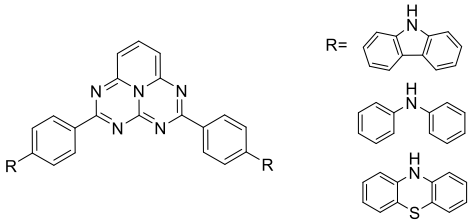

Fig.1 Azaphenalene derivatives

Fig.2 color change of diphenylamine-donor derivative by addition of TFA

1) Aizawa, *Nature. Rev.* **2022**, *609*, 502. 2) R. Okumura, *Angew. Chem. Int. Ed.* **2024**, *64*, 63, e202409670.