SYNTHESIS OF 6-AMINO-2-NAPHTHOL BY COPPER CATALYZED ULLMANN-TYPE C–N COUPLING REACTION AND PHOTOPHYSICAL STUDIES

K. U. Jagushte[a], S. Dutta Choudhury[b], and N. Sadhukhan[a]*
[a]*Department of Speciality Chemicals Technology, Institute of Chemical Technology, Mumbai, Maharashtra, 400019, India.*
[b]*Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085.*
(Email: kaustubh.jagushte1996@gmail.com)

Abstract:
6-Amino-2-naphthol (4) is an interesting bi-functional molecule that serves as an intermediate for polariser materials and various pharmaceutics [1]. It is also a photoacid having two protonation sites [2]. We envisioned that synthesis of 4 can be accomplished by copper catalysed Ullmann-type C–N coupling reaction replacing naphthyl bromide with an amine group (-NH_2) [3]. In our approach enroute to compound 4, we followed two protocols, i) direct amination, and ii) protection, amination and deprotection of 6-bromo-2-naphthol. We investigated, two different aminating agents, namely aq. NH_3 (28-30%), and NaN_3 employing various copper catalysts including elemental Cu, CuI, Cu_2O, and $CuSO_4•H_2O$. Extensive method optimization revealed that $CuSO_4•H_2O$ in presence of Na-ascorbate, NaN_3 and NaOH is the superior catalyst. A stable, environmentally friendly, earth abundant and inexpensive catalyst makes the process efficient, sustainable and simple. The photophysics of the 4 was investigated in various solvents. Interesting changes were observed in the absorption and emission spectra with change in pH. Specifically, three pH dependent ground state species were identified: naphtholammonium ion (C), neutral aminonaphthol (N), and aminonaphtholate anion (A). In the excited state, 4 was found to undergo excited state proton transfer (ESPT) leading to formation of the neutral species from the excited cation by deprotonation of amino group. Interestingly, an additional species was observed in the emission spectrum that can be attributed to zwitterion (Z) (Figure 1B). This species is proposed to be formed from the excited cation by deprotonation at the OH site. Thus, presence of NH2 group is found to have significant influence on photoacidity of the naphthol unit [2].

Figure/Scheme (if any):

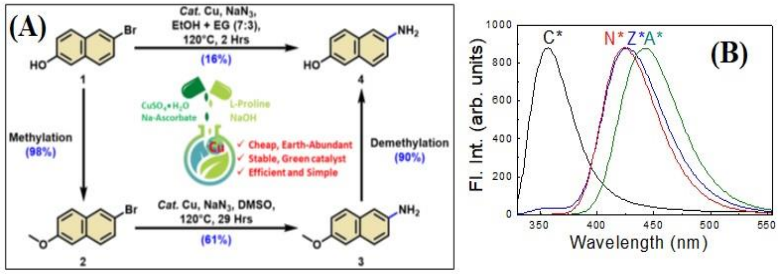

*Figure 1. (A) Synthesis of **4** and (B) its emission spectra at different pH*

References and Notes:

1. Li, X.; Pan, R.; Wang, Z. Dig Tech Pap - SID Int Symp **2019**, 50, 267.
2. Groves, M.S.; Nelson, K.J.; Nelson, R.C.; Takematsu K. Phys Chem Chem Phys. **2018**, 20, 21325.
3. Pearson, J.; Dahal, U.P.; Rock, D.; Peng, C.C.; Schenk, J.O.; Joswig-Jones, C.; Jones, J.P. Arch Biochem Biophys. **2011**, 69, 511.