Supporting Information for Nonlinear Absorption Properties of Phthalocyanine-Like Squaraine Dyes

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Synthetic Scheme and Conditions

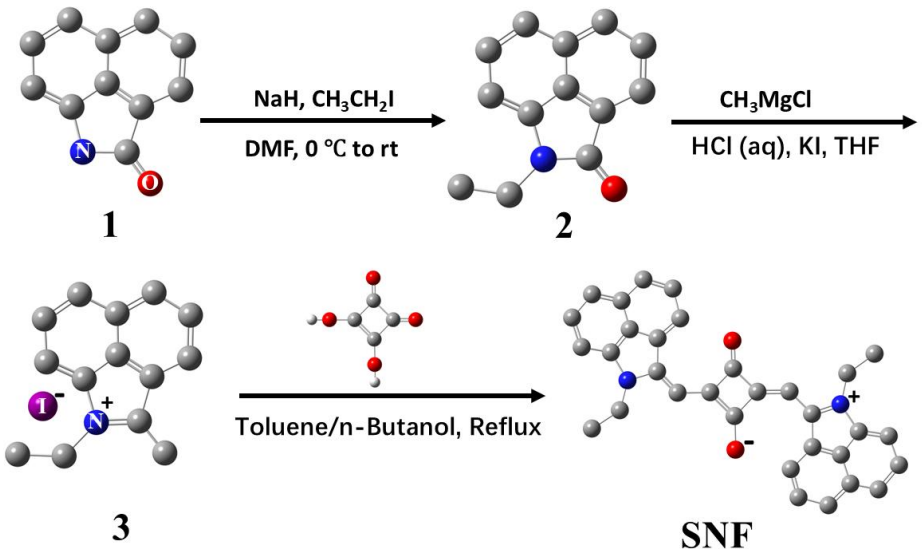

Figure S1. The specific synthetic route of SNF.

Compound 1, Compound 2 were prepared according to previously reported methods

[1]. Compound 3: A solution of methyl magnesium chloride (3.0 ml, 2.0 mol/L in tetrahydrofuran, 9.0 mmol) was added dropwise to a stirred solution of compound 2 (1.35 g, 3.0 mmol) in anhydrous tetrahydrofuran (20 ml) at 0°C. The reaction mixture was then stirred for 2 hours, after which H_2O (0.5 ml) and a 15% aqueous solution of hydrochloric acid (5.0 ml) were introduced. Stirring continued for an additional 15 minutes. Subsequently, an aqueous solution of potassium iodide (3 mol/L, 3.0 ml) was added, resulting in the formation of a dark brown, oily precipitate. The mixture was extracted, filtered, and the solvent was removed by rotary evaporation. After drying, a brown oil was obtained, which was used directly in the subsequent reaction step without further purification.

SNF: A mixture of Compound 3 (3.0 mmol) and 3,4-dihydroxycyclobut-3-ene-1,2-dione (0.17 mg, 1.5 mmol) was added to a solution of n-butanol and toluene (v= 1:1, 20 ml). The reaction mixture was then heated under reflux at 110 °C in a Dean-Stark apparatus for 2 hours. Upon completion, the solvent was removed via rotary evaporation, and the residue was extracted three times with DCM/H_2O. The combined organic phases were concentrated under reduced pressure. The crude product was further purified by column chromatography (10-20% methanol in DCM), yielding Compound 4 as a black solid.

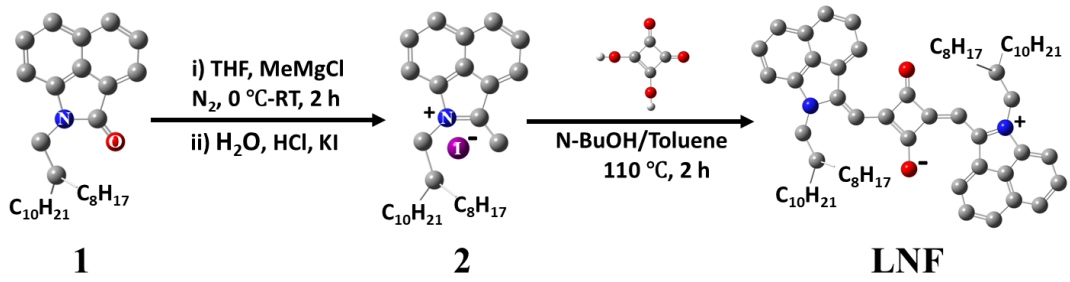

Figure S2. The specific synthetic route of SNF.

Compound 1, Compound 2, LNF were prepared according to previously reported methods [1].

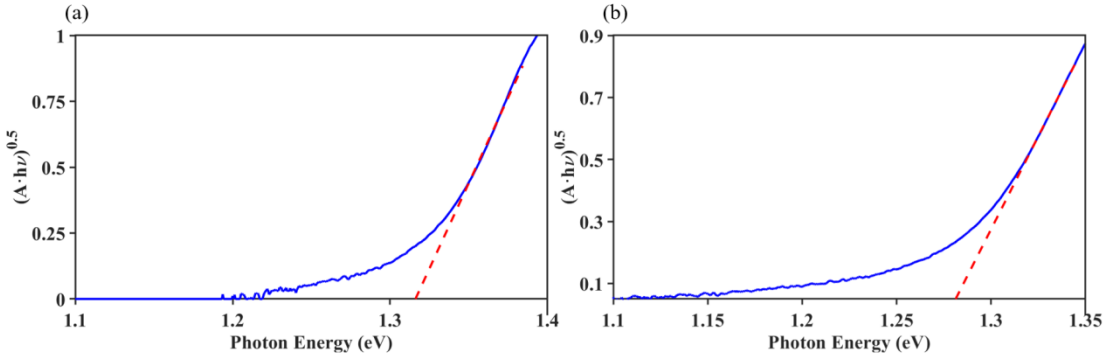

Figure S3. Tauc plots of (**a**) SNF and (**b**) LNF. The estimated optical bandgaps are 1.316 eV and 1.281 eV, respectively

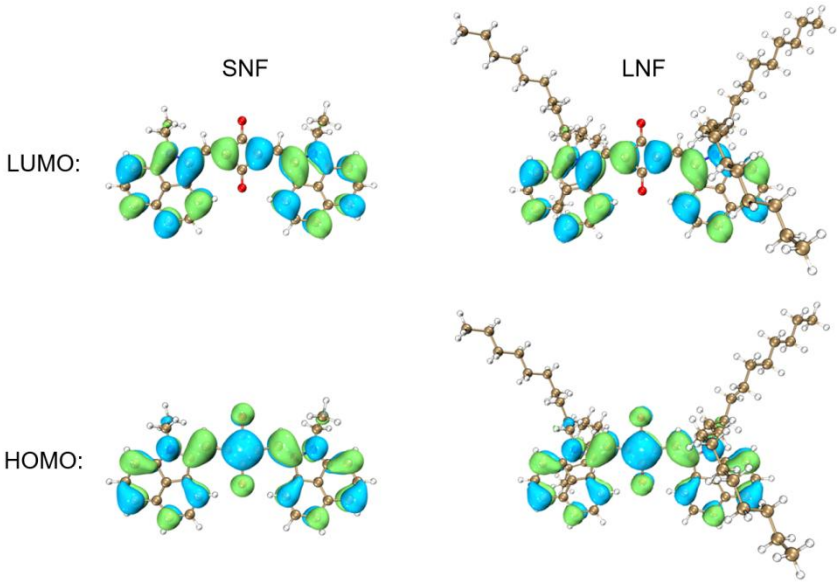

Figure S4. Optimised geometries and frontier-orbital isosurfaces of SNF and LNF(b3lyp/6-311g(d,p), PCM = CH2Cl2). Isosurface = 0.002; blue = positive, green = negative. Average dihedral angle (phenyl–squaraine plane) increases from -3.196° (SNF) to 0.591° (LNF). Calculated HOMO-LUMO gaps: 1.605 eV (SNF) and 1.594 eV (LNF).

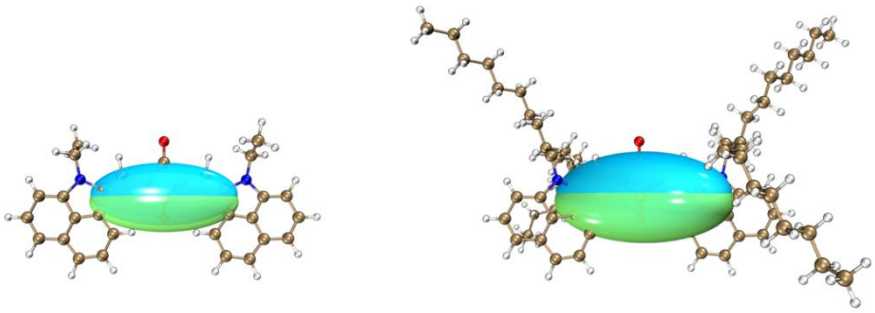

Figure S5. Electron centroid map: the blue circle indicates HOMO, and the green circle indicates LUMO.After alkyl chain substitution, the centroid shift decreases from 0.441 Å to 0.432 Å.

Reference

1. Wang, Y.; Xia, G.; Wang, J.; Wang, M.; Guo, W.; Tan, M.; Si, L.; Yang, Y.; Wang, H.; Wang, H. A synergetic strategy of NIR-II squaraine dyes with ultrahigh photothermal conversion efficiency for photothermal therapy. *Sci. China Chem.* **2024**, *67*, 612–621.