Preparation and Photophysical investigation of methylated 1,5- diaminonaphthalene

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ABSTRACT

The specific aim of this study is to critically evaluate the architectural limits of intramolecular charge transfer (ICT) in naphthalene systems by using 1,5-diaminonaphthalene (1,5-DAN) as a symmetrical, rigid model platform. By systematically executing the orderly structural tuning of this scaffold—progressively evaluating its mono-, di-, tri-, and tetra-methylated derivatives (variants 1–4) we isolate exactly how localized steric hindrance and hydrogen-bonding disruptions govern the "push-pull" dynamic.

Ultimately, this systematic engineering serves as a strict baseline to benchmark alternative substitution patterns. By directly contrasting our expansive multi-solvent photophysical matrices and micro-solvation DFT models with established environmental probes, we definitively demonstrate that the asymmetric 2,6-PRODAN architecture provides an optimized, low-barrier electronic pathway for charge separation that cannot be replicated by symmetric scaling. Through this comparative analysis, we validate 2,6-PRODAN as the fundamentally superior design for next-generation molecular sensing.

SUMMARY

We investigated how changes in solvent environment influence the photophysical behavior of a series of methylated 1,5-diaminonaphthalene derivatives. Absorption and emission measurements were performed in solvents covering a broad range of polarity, and the Stokes shifts were correlated with the Reichardt $E_T(30)$parameter**.** The compounds showed clear solvent-dependent changes in their emission behavior, with the Stokes shift generally increasing as solvent polarity increased. Linear Reichardt plots were obtained for the investigated derivatives, with correlation coefficients ranging from 0.65 to 0.93, indicating a substantial sensitivity of the excited-state properties to the surrounding solvent. The extent of this response also varied with the degree of methyl substitution. In highly polar solvents such as water, particularly large Stokes shifts were observed, reaching approximately 5,700–8,000 cm^{-1}. Overall, the results show that methyl substitution provides a simple way to tune the solvent sensitivity of these naphthalene-based chromophores, highlighting their potential for studying local polarity and microenvironmental effects.

Keywords: Methylated 1,5-diaminonaphthalenes, Solvatochromism, Solvent polarity, Stokes shift

References

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