

*Crystalline triphenylamine substituted arenes: solid state packing and luminescence properties*Ajith R. Mallia¹, Remya Ramakrishnan¹, Niyas M A¹, Mahesh Hariharan¹¹Department Of Chemistry, IISER Thiruvananthapuram, Thiruvananthapuram, India

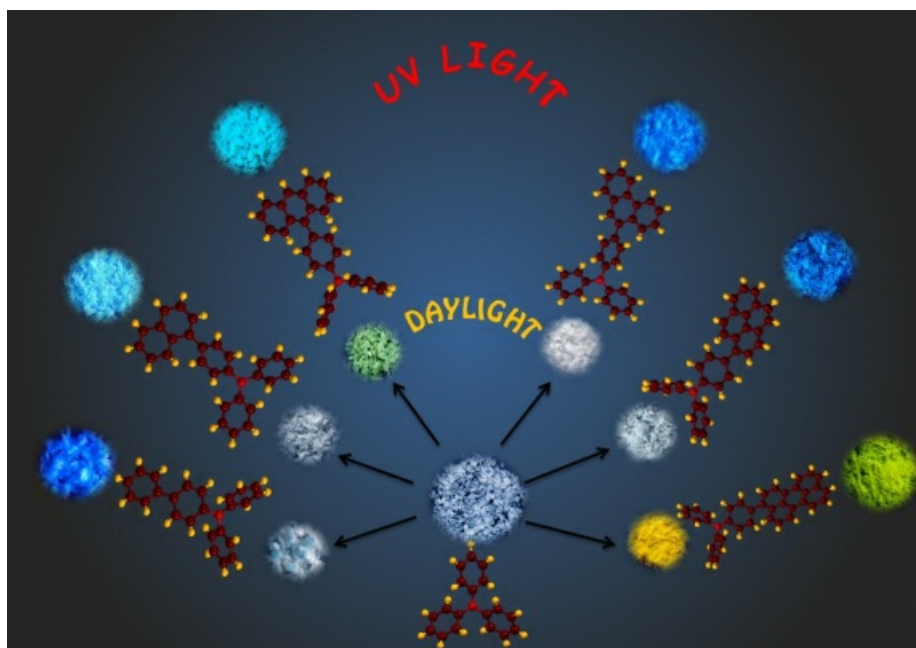
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Structural flexibility and thermal/photostability of crystalline organic materials are promising properties for designing stable and efficient organic functional materials and devices [1]. π - π stacking interaction of polyaromatic hydrocarbons (PAH) that are efficient luminophores leads to the formation of detrimental excimer species that quench fluorescence in crystals. The introduction of the bulky group to prevent the aggregation-caused quenching in the crystalline state is investigated in the current work [2]. Bulky twisted triphenylamine (T), owing to its high hole transporting properties is extensively used in the fabrication of optoelectronic devices [3]. Influence of bulky propeller-shaped T on perturbing the electronic interactions of different aromatic hydrocarbons is investigated by incorporating T into a series of PAHs [ArT where Ar = benzene (Ph), naphthalene (N), anthracene (A), phenanthrene (Phe), pyrene (Py) and perylene (Pe)]. Crystalline state packing and solid state vs solution state photophysical properties are also studied. The qualitative crystal structure and quantum theory of atoms-in-molecules (QTAIM) analyses revealed the dominant role of intermolecular C-H \cdots C interactions in governing the three-dimensional arrangement in ArT crystals. All the ArTs displayed a herringbone packing motif which is revealed from the Hirshfeld surface analyses. A blue shift of ca. 10–28 nm in the emission maxima for PhT, NT, AT, PheT and PyT is observed in the solid state in comparison to that in dichloromethane while the solid state emission maxima is red shifted (ca. 25–71 nm) compared to that in hexane. A 2.40-fold enhancement in the quantum yield of AT is observed in the solid state relative to the solution state (dichloromethane). Solvent polarity dependent absorption and emission measurements of ArT derivatives along with Lippert–Mataga analyses indicated the presence of charge transfer interactions between Ar and T units. A precise and systematic understanding of the Influence of the crystal packing on the photophysical properties is quintessential to achieve highly efficient organic functional materials and devices in the near future.

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[2] Hariharan, M. et al. (2017). CrystEngComm, 19, 817-825

[3] Kabra, D. et al. (2017). J. Mater. Chem. A, 5, 1348-1373

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