4. SUMMARY

1. Various styryl phenanthrimidazole derivatives (71-79), viz., (E)-2-styryl-1H-phenanthro[9,10-d] imidazole (71), (E)-1-phenyl-2-styryl-1H-phenanthro[9,10-d] imidazole (72), (E)-2-styryl-1-(p-tolyl)-1H-phenanthro[9,10-d] imidazole (73), (E)-1-(4-methoxyphenyl)-2-styryl-1H-phenanthro[9,10-d] imidazole (74), (E)-N,N-dimethyl-4-(2-styryl-1H-phenanthro[9,10-d]imidazol-1-yl) aniline (75), (E)-2-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)vinyl) phenol (76) (E)-4-(2-(1-(4-chlorophenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)vinyl)-N,N-dimethylaniline (77), 2-(furan-2-yl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (78) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (79). were synthesized by four component assembling of 9,10-phenanthriquinone, arylamine, ammonium acetate, and arylaldehyde with InF₃ or rutile TiO₂ as catalysts.

2. The structures of the styryl phenanthrimidazole derivatives 71-79 have been evaluated using high resolution ¹H NMR, ¹³C NMR and GC-MS spectra. The crystal structure of (E)-1-phenyl-2-styryl-1H-phenanthro[9,10-d] imidazole 72 has been obtained. The ORTEP diagram shows that the imidazole ring is essentially planar. The optimized bond lengths, bond angles and dihedral angles are slightly larger than those obtained by XRD. These deviations can be attributed to the fact that the theoretical calculations are of
isolated molecule in the gaseous phase and the XRD results are of the molecule in the solid state.

3. The nanomaterials namely, TiO$_2$, Fe$_2$O$_3$, phosphated styryl imidazole, phosphated imidazole bound Fe$_2$O$_3$, pristine ZnO, Cu-doped ZnO, Ag-doped ZnO have been characterized by powder X-ray diffractograms (XRD), scanning electron micrographs (SEM), energy dispersive X-ray spectra (EDX) and lifetime spectra. The computational studies (Gaussian-03) have been made in order to supplement the experimental results.

4. Photophysical studies of styryl phenanthrimidazole derivatives 71-79 reveal that the solvatochromic behavior of imidazole derivatives depends not only on the polarity of the medium but also the hydrogen bonding properties of the solvents. The quantum yield decreases in polar protic solvents due to enhancement of nonradiative transition owing to hydrogen bonding interactions. Detailed inspection of the low-energy absorption region of the D-A imidazole derivatives containing styryl moiety as an electron acceptor clearly indicates the presence of additional charge transfer singlet states. A long wave shoulder attributed to the $^1$CT$\leftarrow$ S$_0$ transition is also observed. The magnitude of the shifts suggests that the ground state of the molecule is polar. The absorption data have been analyzed using the solvent comparison method proposed by Kamlet et al.
5. Double linear correlation is observed between the Stokes shift and solvent polarity parameter $E_T$ (30). Polar protic solvents fall on a separate line indicating that the mode of solvation of the emitting state is different from that in the other polar aprotic solvents. For polar protic solvents, gradual increment of Stokes shift is due to intermolecular hydrogen bonding interactions. The studied compounds exhibit overall increase of Stokes shift from non-polar to polar aprotic solvents, mainly due to combined effect of increasing the polarity of the medium and intramolecular charge transfer (CT) state.

6. The radiative ($k_r$) and non-radiative ($k_{nr}$) decay of the excited states have been obtained using the quantum yields and lifetimes. The radiative and non-radiative rate constants show that in most of the cases the radiative emission is predominant over non-radiative transitions. The logarithm of ($k_r/k_{nr}$) is plotted against the solvent polarity parameter $E_T$ (30). Two different straight lines are obtained, one for aprotic solvents and the other for protic solvents. In both the cases, up on increasing the polarity the logarithm ratio of radiative to nonradiative rate decreases but a steeper slope is obtained in the case of protic solvents. It indicates that the radiative and nonradiative rates are more sensitive toward protic solvents. It may be that the hydrogen bonding interaction in polar protic environment enhances the stabilization of excited state.
7. Solvent-induced transformation of the electronic structure of the 
$^1$CT states of selected D–A styryl phenanthrimidazole derivatives 
containing styryl group as an electron acceptor has been 
analysed by combining the Mulliken–Murrell theory of the CT 
complexes and the Marcus theory of the radiative charge 
recombination ($^1$CT→$S_0$). Analysis of the electronic coupling 
elements show that the differences in the photophysical 
properties of the studied molecules can be interpreted in terms of 
the different electronic interactions between the CT state and the 
ground state ($v_0$) and/or $^1(\pi, \pi^*)$ excited state most probably 
localized in the donor moiety. This approach can be used to 
explain the solvatochromic effects observed in the fluorescence 
spectra as well as on transition dipole moment values. The 
conformation of the investigated D–A systems in the fluorescent 
CT states seems to be similar to that in the ground state.

8. The decrease of twisted intramolecular charge transfer (TICT) 
fluorescence of N,N-dimethyl-4-(2-styryl-1H-phenanthro[9,10-d] 
imidazol-1-yl) benzenamine with increasing pH (above 4.01) 
suggests that water molecules become efficient for hydrogen 
bonding interactions only above this pH. This prompts us to 
suggest that styryl phenanthrimidazole may be used as a sensor 
to sense the hydrogen-bonding efficiency of the medium.

9. The electron transfer from excited state of styryl 
phenanthrimidazole to the ZnO and Bi$_2$O$_3$ nanoparticles have
been determined by the conduction band energy position. Mn-doped TiO$_2$/ZnO, BaTiO$_3$/ZnO core/shell and ZnO nanospheres switch on the fluorescence of styryl phenanthrimidazole whereas Mn-doped TiO$_2$ and BaTiO$_3$ nanoparticles switch off the fluorescence. Accidently the wavelength of emission of the fluorophore matches with that of deep level emission of ZnO which results in enhancement of fluorescence. The electron transfer from LUMO to the defect levels of ZnO through the CB of ZnO yields deep level emission. The energy gap between LUMO and CB of BaTiO$_3$ is large and hence quenching of fluorescence is observed. The anatase phase of Mn-doped TiO$_2$ quenches the fluorescence of the fluorophore. The contrasting emission behaviour is also a consequence of the nature of binding of the fluorophore with ZnO and the core nanoparticles.

10. Optical, electrochemical, and thermal properties of bluish-green fluorescent 2-(((E)-2-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl) vinyl) phenol [PPIVP] 76 have been studied. The branched imidazoles are more emissive than their linear 2-phenyl-1H-phenanthro[9,10-d]imidazole analogs, both in solution and aggregated. This is likely to be due to increased π-electron contributions to the electronic structure of the molecule, as well as restricted nonradiative deactivation resulting from less facile rotational deactivation via the interannular C-C bond.
11. The quantum chemical studies reveal that the formation of non-fluorescent isomers (TICT*) of PPIVP 76 was effectively suppressed in the solid state due to the bulky substituents preventing a large conformational change in the excited-state. The ESIPT dye containing branched groups showed excellent thermal properties with high T_g (78.3°C). An efficient large Stokes shifted emission with very high fluorescence quantum yield in the neat solid films free from concentration self-quenching is also observed. The molecular design concept established in this study provides guideline for fine-tuning the emission properties of this class of ESIPT fluorophore, which is beneficial for developing a new class of advanced optoelectronic applications.

12. (E)-4-(2-(1-(4-chlorophenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)vinyl)-N,N-dimethylaniline (CPPIVI) 77, phosphated imidazole (PI) and phosphated imidazole bound to Fe_2O_3 nanoparticles (PSIMN) have been synthesised and was characterized by SEM, TEM, EDX, XRD, VSM, FT-IR, UV-vis absorption, emission and lifetime spectral studies. The mean crystallite size of the imidazole bound nanoparticles (PSIMN) is 30.3 nm. The shift of Fe-O stretching vibration from 1631 cm^{-1} to 1647 cm^{-1} conforms binding of imidazole with the superparamagnetic nanoparticles through oxygen of Fe_2O_3. The intensities of absorption and emission maxima as well as conductance (in DMSO) are of the following
order: PSIMN > PSI > CPPIVI. The life time studies also confirm the formation of PSIMN.

13. The prototropic analysis of \((E)-4-(2-(1-(4-chlorophenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)vinyl)-N,N-dimethylaniline\) (CPPIVI) reveal that the blue shifted absorption and fluorescence bands correspond to the monocation (MC1) whereas the red shifted absorption and fluorescence bands arise out of the monocation (MC2).

14. Photoinduced interactions of 2-(furan-2-yl)-1-phenyl-1H-phenanthro [9, 10-\(d\)] imidazole (FPI) with nanoparticles were investigated using different spectroscopic techniques. Binding constants obtained from the absorption and fluorescence measurements demonstrate that the binding of ZnO nanoparticles with FPI is greatly influenced by the surface modification with Cu and Ag. Electron from the excited FPI is transferred to the conduction band of ZnO and quickly migrated to the Cu\(^{2+}\) or Ag\(^{0}\). All these results put forward that the optoelectronic behavior of FPI with ZnO is influenced by the presence of Cu\(^{2+}\) and Ag\(^{0}\) which implies its potential application in the field of nano-drug carriers.

15. Fluorophore \((E)-1-(4-methoxyphenyl)-2-styryl-1H-phenanthro [9,10-\(d\)]imidazole (MPSPI) 74 is adsorbed on the surface of semiconductor nanoparticles through azomethine nitrogen. The conduction band energy positions determine the electron transfer
from excited state MPSPI to the nanoparticles. The distance between the MPSPI and nanoparticles has been obtained using Forester’s non-radiation energy transfer theory. The negative $\Delta G_{et}$ values reveal that the electron transfer process is thermodynamically favorable. Electron transfer from MPSPI to nanoparticles is explained in detail.

16. The absorption band of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (cationic IL) is red shifted due to binding with nanocrystalline ZnO. Increase of crystal size decreases the shift in the absorption of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (cationic IL) and increases the wavelength of blue as well as yellow emissions. Increase of band gap energy with decrease of crystal size is likely to be the reason for the observed red shift of the emission on increasing the ZnO crystal size. Furthermore, the lifetime is shortened on increase of the ZnO crystal size suggesting smaller is the size or larger is the surface area stronger is the binding. Docking analysis shows that cationic ionic liquid prefers to bind on the minor groove of A-T rich region of DNA molecule.