3.6. Photoinduced electron transfer from phenanthrimidazole to magnetic nanoparticles

The dynamics of photoinduced electron injection from (E)-1-(4-methoxyphenyl)-2-styryl-1H-phenanthro[9,10-d]imidazole (MP SPI) (74) synthesised using nano TiO$_2$ as catalyst to Fe$_2$O$_3$ nanocrystal has been studied by FT-IR, absorption, fluorescence and lifetime spectroscopic methods. The high resolution $^1$H $^{13}$C NMR spectra of 74 are given in plates 7-8. The corresponding LC-MS spectrum of 74 is displayed in plate 14. The binding between nanoparticle and MP SPI is confirmed by binding constant and binding site. The distance between MP SPI and nanoparticle as well as the critical energy transfer distance has been obtained. The free energy change ($\Delta G_{et}$) for electron injection has also been deduced.

3.6.A. Synthesis of (E)-1-(4-methoxyphenyl)-2-styryl-1H-phenanthro[9,10-d]imidazole (MPSPI)

A mixture of chinnamaldehyde (1 mmol), phenanthrene-9,10-dione (1 mmol), 4-methoxyaniline (1 mmol) and ammonium acetate (1 mmol) with TiO$_2$ (1 mol%) as catalyst was stirred at 120 °C in an ice bath with continuous stirring with a bar magnet. The progress of the reaction was monitored by TLC (Scheme 8). After completion of the reaction, 10 ml of ethyl acetate was added to the reaction mixture and shaken well to dissolve the organic components and the mass filtered to separate out TiO$_2$ and the residue was washed with ethyl acetate. The solid residue of TiO$_2$ was further washed with hot acetone.
and then dried up. The product was purified by column chromatography using benzene: ethyl acetate (9:1) as the eluent. Yield: 79%.

3.6.B. Characterisation of Fe₂O₃ nanocrystal

**Fig. 50** displays the powder diffraction pattern of the imidazole bound magnetic nanoparticles. The recorded XRD is in agreement with that of maghemite cubic Fe₂O₃ with unit cell length as 0.8352 nm. The peaks at 30.2, 35.7, 43.3, 53.7, 57.3 and 62.9° correspond to 220, 311, 400, 422, 511 and 440-planes, respectively [JCPDS card no. 39-1346]. **Fig. 50** (XRD 15-80°) presents the XRD of imidazole bound magnetic nanoparticles. The mean crystallite size (\(L\)) of the imidazole bound nanoparticles is 30.3 nm and the calculated surface area is 50.58 m²/g.

3.6.C. Absorption of MPSPI – nanocrystalline Fe₂O₃

**Fig. 51** display the absorption spectra of MPSPI in presence of Fe₂O₃ nanocrystals dispersed at different loading and also in their absence. Nano Fe₂O₃ enhance the absorbance of MPSPI remarkably without shifting its absorption maximum at 258 nm. This indicates that the semiconductor nanocrystals do not modify the excitation process of the ligand. The enhanced absorption at 258 nm observed with the dispersed nanoparticles are due to adsorption of the MPSPI on surface of nanocrystals. This is because of effective transfer of electron from the excited state of the MPSPI to the conduction band of the semiconductor nanoparticles.
**Scheme 8.** Possible mechanism for catalytic synthesis of phenantrimidazole
3.6.D. FT-IR characteristics of MPSPI –nanocrystalline Fe$_2$O$_3$

The FT-IR spectrum of MPSPI and also that of MPSPI adsorbed on the nanocrystals are recorded. The spectrum of MPSPI shows the $>$C=N stretching vibration at 1602 cm$^{-1}$. This band is shifted to 1632 cm$^{-1}$ allowed to adsorb on the nanocrystals. These observations show that the MPSPI is bound to the surface of nanoparticles.

3.6.E. Fluorescence quenching characteristics

The fluorescence quenching technique is applied to study the interaction between nanomaterials and MPSPI, to infer the association and also the electron transfer between them as indicated in Scheme 9. Addition of nanoparticles to the solution of MPSPI resulted in the quenching of its fluorescence. **Fig. 52** displays the effect of increasing concentration of nanoparticles on the fluorescence spectrum of MPSPI. This quenching behavior is similar to the studies
reported earlier\textsuperscript{193}. The apparent association constants ($K_{app}$) have been obtained from the fluorescence quenching data using the following equation

$$\frac{1}{(F_0 - F)} = \frac{1}{(F_0 - F)} + \frac{1}{K_{app}} (F_0 - F) \text{ [nanoparticles]} \quad (19)$$

where $K_{app}$ is the apparent association constant, $F_0$ is the initial fluorescence intensity of MPSPI, $F$ is the fluorescence intensity of MPSPI adsorbed on nanoparticles. A good linear relationship between $1/(F_0 - F)$ and the reciprocal concentration of nanoparticles is seen. From the slope, the values of $K_{app}$ have been assessed for MPSPI – nano Fe$_2$O$_3$ as $3.68 \times 10^7$.

Fig. 51. Absorption spectra of MPSPI in presence and absence of Fe$_2$O$_3$ nanocrystal with various concentrations

The fluorescence quenching behavior is usually described by Stern–Volmer relation $I_0/I = 1 + K_{SV} [Q]$. Here, $I_0$ and $I$ are the fluorescence intensities in the absence and presence of quencher, $K_{SV}$ is the Stern–Volmer constant related to the bimolecular quenching
rate constant and Q is the quencher. **Fig. 53** presents the Stern-Volmer plot. The ability of the excited state MPSPI to inject its electrons into the conduction band of nanoparticles is determined from the energy difference between the conduction band of nanoparticles and excited state oxidation potential of MPSPI.

**Fig. 52.** Fluorescence spectra of MPSPI in the presence and absence of Fe$_2$O$_3$ nanocrystal with various concentrations

**Fig. 53.** Stern-Volmer plot of MPSPI with Fe$_2$O$_3$ nanocrystal
3.6.F. Energetics

From the onset oxidation potential ($E_{\text{ox}}$) and the onset reduction potential ($E_{\text{red}}$) of the benzimidazole, HOMO and LUMO energy levels have been calculated according to the equations:

$$\text{HOMO} = -e(E_{\text{ox}} + 4.71) \text{ (eV)}, \quad \text{LUMO} = -e(E_{\text{red}} + 4.71) \text{ (eV)},$$

HOMO-LUMO energies of phenanthrimidazole are also calculated theoretically. The theoretically calculated energies are in good agreement with the experimental values. On the basis of the relative positions of phenanthrimidazole derivative and Fe$_2$O$_3$ energy levels shown in Scheme 9, the electron injection would be thermodynamically allowed from the excited singlet of the phenanthrimidazole derivative to the conduction band of nanocrystalline Fe$_2$O$_3$.

From HOMO-LUMO analysis of MPSPI, the oxidation potential of excited singlet state MPSPI is obtained as $-1.84$ V (vs. NHE), using the equation, $E_{s^+/s^+} = E_{s/s^+} - E_s$. Here, $E_{s/s^+}$ is the oxidation potential of 0.20 V (vs. NHE) and $E_s$ is the excited state energy, 2.04 eV. The excited state energy of the MPSPI is calculated from the fluorescence maximum based on the reported method$^{194}$. The energy level of the conduction band of semiconductor nanoparticles is shown in Scheme 9.$^{195}$ It suggests that the electron transfer from excited state MPSPI to the conduction band of nanoparticulate semiconductors is energetically favourable.
3.6.G. Binding constant and number of binding sites

Static quenching arises from the formation of complex between fluorophore and the quencher and the binding constants ($K$) have been calculated by employing the equation

$$\log \left( \frac{F_0 - F}{F} \right) = \log K + n \log [Q]$$

where $K$ is the binding constant of nanoparticles with FPPBI and the calculated value of binding constant value $372.24 \times 10^7$ and the number of binding site ($n$) is 1.20.

3.6.H. Electron transfer between MPSPI – nanocrystalline Fe$_2$O$_3$

The decrease in fluorescence intensity is attributed to electron transfer between MPSPI and the nanoparticles in the case of semiconductors. The excited state energy of the MPSPI is larger than the conductance band energy levels of nanosemiconductors$^{196}$. This makes possible the energy transfer from the excited state of MPSPI to the nanoparticles. The energy transfer efficiency ($E$) is calculated using the equation, $E = 1 - (I/I_0)$, as 0.59 (Fe$_2$O$_3$). Here, $I$ is the emission intensity of donor in the presence of acceptor and $I_0$ is the emission intensity of the donor alone. From the above results it is clear that, in presence of nanoparticles, the fluorescence intensity of MPSPI is reduced (from $I_0$ to $I$) by energy transfer to nanoparticles.

According to Forster’s non-radiative energy transfer theory$^{197}$, the energy transfer efficiency ($E$) is related not only to the distance between the acceptor and donor ($r_0$), but also to the critical energy transfer distance ($R_0$). That is, $E = R_0^6/(R_0^6 + r^6)$, where, $R_0$ is the
critical distance when the transfer efficiency is 50%. \( R_0^o = 8.8 \times 10^{-25} \) K² N⁴ φ J, where, K² is the spatial orientation factor of the dipole, N is the refractive index of the medium, φ is the fluorescence quantum yield of the donor and J is the overlap integral of the fluorescence emission spectrum of the donor and the absorption spectrum of the acceptor. The value of J can be calculated by using the equation, 
\[ J = \frac{\int F(\lambda)\varepsilon(\lambda)\lambda^4d\lambda}{\int F(\lambda)d\lambda}, \]
where, F(\( \lambda \)) is the fluorescence intensity of the donor, \( \varepsilon(\lambda) \) is molar absorptivity of the acceptor. The parameter J can be evaluated by integrating the spectral parameters as 9.76x10⁻¹² cm³ L mol⁻¹. Under these experimental conditions, the value of \( R_0 \) is found to be about 0.69 nm for the nanocrystals; the values of K² (= 2/3) and N (= 1.3467) used are from the literature and the φ value is from the present study. Obviously, the calculated value of \( R_0 \) is in the range of maximal critical distance. This is in accordance with the conditions of Forster’s non-radiative energy transfer theory, indicating the static quenching interaction between nanoparticles and MPSPI. The value of \( r_0 \) (0.91 nm) is less than 8 nm which is larger than that of \( R_0 \) in the present study also reveals the operation of static-type of quenching mechanism.

3.6.I. Free energy change (\( \Delta G_{et} \)) for electron transfer processes

The thermodynamic feasibility of excited state electron transfer reaction has been confirmed by the calculation of free energy change by employing the well known Rehm-Weller expression.

\[ \Delta G_{et} = E^{1/2}_{(ox)} - E^{1/2}_{(red)} - E_s + C \]  
(21)
where, $E^{1/2}_{(ox)}$ is the oxidation potential of MPSPI, $E^{1/2}_{(red)}$ is the reduction potential of nanoparticles, that is, the conduction band potential of nanoparticles, $E_s$ is the excited state energy of MPSPI and $C$ is the coulombic term. Since one of the species is neutral and the solvent used is polar in nature, the coulombic term in the above expression can be neglected.$^{201}$ The values of $\Delta G_{et}$ are calculated as $-3.32$ eV. The high negative values indicate the thermodynamic feasibility of the electron transfer process.$^{190}$

**Scheme 9.** Schematic diagram describing the electron-donating energy level of MPSPI
3.6.J. Fluorescence lifetime measurements

An alternative way to rationalize the binding behaviour in the present study is by considering the fluorescence lifetime of FPPBI with nanoparticles. The experimental decay curves were fit to a biexponentials, \( f(t) = \alpha_1 \exp\left(-\frac{t}{\tau_1}\right) + \alpha_2 \exp\left(-\frac{t}{\tau_2}\right) \), where \( \alpha_1 \) and \( \tau_1 \) are respectively, the pre-exponential factor and lifetime of the various excited states involved. This model is based on the assumption that one, two or three fluorescent substances are present in the solution. The fluorescence decay curves of all nanoparticles with MPSPI were recorded in ethanol. Laser excitation was set at 270 nm and the fluorescence signal was measured at emission wavelength of individual compound. The fluorescence decay was fitted with a biexponential function and the decay time, radiative (\( k_r \)), non-radiative (\( k_{nr} \)) constants and energy transfer rate constants (\( k_{et} \)) are presented in Table 14. Fe\(_2\)O\(_3\) nanocrystals bound to change the fluorescence lifetime. The results can be visualized as shown in Fig. 54. Examination of rate constant of energy transfer shows that energy transfer is more with Fe\(_2\)O\(_3\) nanocrystals which are strongly bound to the ligand. The strongly bound nanocrystal Fe\(_2\)O\(_3\) displays a large electron transfer rate. That is the binding constant and the rate of electron transfer is related.
**Fig. 54.** Fluorescence lifetime spectra of MPSPI in presence and absence of Fe$_2$O$_3$ nanocrystal

**Table 14.** Bi-Exponential fitting parameter for fluorescence decay

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<th>$\tau_2$</th>
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