



Synthesis of Novel Blue and Green Light Emitting 4-Nitrophenol Luminophors for Optoelectronics

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Abstract

The number of anthracene (AN) and anthracene-tetracene (AN-TN) doped 4-nitrophenol (4-NP) luminophors (AN/4-NP and AN-TN/4-NP) were prepared at different proportion by conventional technique called solid state reaction. Excitation energy transfer was observed by fluorescence spectroscopy and cyclic voltammetry. 4-NP acts as an outstanding light emitting matrix. The effect of the donor emission was perceived by changing the dopant concentration; this showed that AN/4-NP and TN-AN/4-NP exhibit fluorescence emission ranging from blue to green i.e. in the range from 400 to 525 nm and 535–550 nm, respectively. Structural properties and thermal stability was studied by XRD, SEM and TGA-DSC techniques. The study reveals that the prepared materials show excellent properties which can meet the demands of optoelectronic devices as well as for light emitting devices.

Keywords Excitation energy transfer · Light emitting devices · Blue and green emission · Doped materials

Introduction

The huge usage of doped organoluminophors motivated their study in organic molecular solids. Nowadays white organic light emitting materials (OLEDs) formed by doped materials have drawn more attention due to their various applications. In recent years many organoluminophors being synthesized and investigated for their properties to meet the demands of phosphors for optoelectronic devices.

The transfer of excitation energy in doped organic aggregates has been widely examined for over half century because of its central role as organic semiconductor materials. One more reason to study the energy transfer in doped organic matrix is sensitized acceptor emissions. This methodology has been applied in numerous studies of doped molecular crystals and thin films [1–4]. The intramolecular charge transfer (ICT) in excited states or excimers or exciplex production [5] are responsible for this type of energy transfer in doped organic matrix.

In last few years, a variety of doped organic semi-conducting materials are being synthesized using different donor-acceptor materials such as tetracene doped p-terphenyl, biphenyl doped pyrene [6], pyrene and perylene doped fluorine [7], tetracene and anthracene doped biphenyl [8], anthracene doped 2-naphthol [9], tetracene and anthracene doped 2-naphthol [10], tetracene and anthracene doped p-terphenyl [11], etc.

Considering the scope of this research, the authors synthesized blue and green light emitting materials by using organic materials viz. AN, TN and 4-NP and the characteristic properties were studied.

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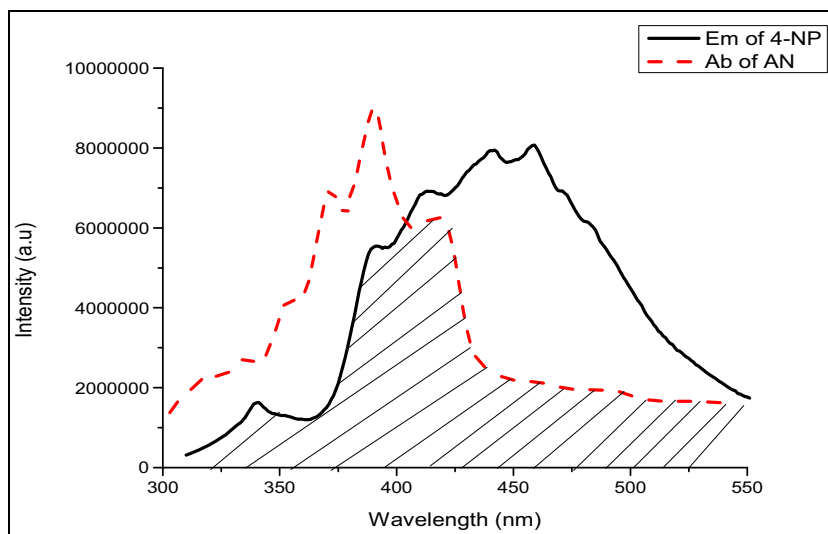
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Fig. 1 Fluorescence spectra of 4-nitrophenol and absorption spectra of anthracene



Experimental

4-nitrophenol of AR grade, anthracene and tetracene of scintillation grade were procured from Merck-Schuchardt. The purchased host and guest materials were further recrystallized before use. The purity of these materials were further confirmed by fluorescence spectra.

Preparation of 4-Nitrophenol Doped Luminophors

The solid state reaction technique had been employed to prepare polycrystalline 4-NP luminophors with varying concentrations of AN and TN [12]. Silica crucibles were used for the preparation of doped materials. The solid solution was heated at the temperature corresponding to

Fig. 2 Fluorescence spectra of 4-nitrophenol and absorption spectra of tetracene

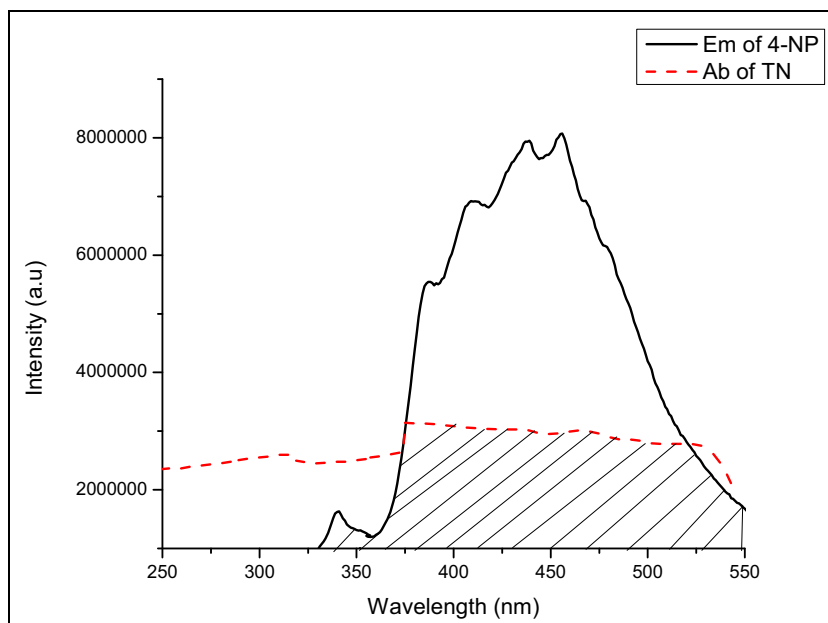


Table 1 Förster energy transfer distance (R_0) in mixed crystals

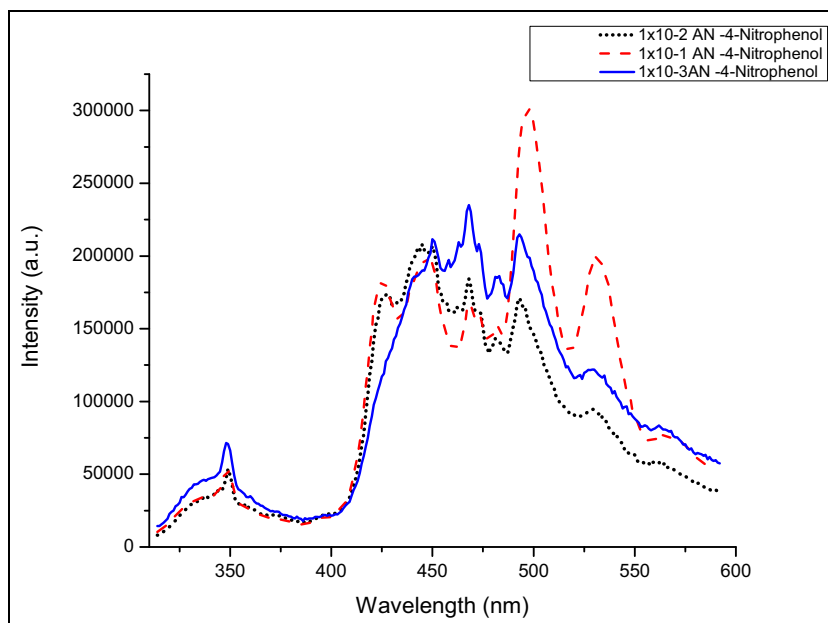
Sr.No	Host (Donor)	Guest (acceptor)	(R_0) Å
1.	4-nitrophenol	Anthracene	37.6 Å
2.	4-nitrophenol	Tetracene	48.9 Å

the M.P. of host 4-NP i.e. at 114 °C. The melt obtained was slowly cooled to get finely grained polycrystalline luminophors of 4-NP. This powder was finally crushed to fine powder and subjected to the characterization.

Characterization

The fluorescence spectra of pure components as well as guest doped 4-NP were recorded by JOBIN YVON Fluorolog-3-11 spectrofluorimeter, at SAIF, Indian Institute of Technology, Madras. The XRD spectra of doped and un-doped crystals were recorded with the Philips diffractometer (model PW-3710, Netherlands) with $\text{CrK}\alpha$ radiation (2.28). (TGDTA-DSC) TA Inc. SDT-2790 with heating rate of 10 °C per minute under nitrogen atmosphere was used to perform thermogravimetric analysis at Solapur University, Solapur, while surface morphology of samples was studied by SEM at SAIF, Indian Institute of Technology, Madras.

Fig. 3 Fluorescence spectra of bicomponent luminophors of 4-NP doped by AN



Results and Discussion

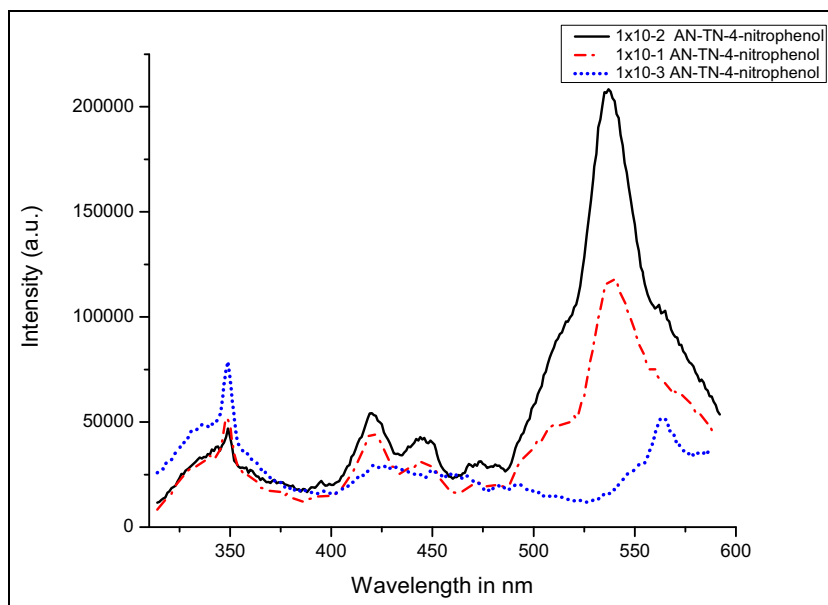
Selection of Guest Materials

The initial studies on anthracene, tetracene and 4-nitrophenol had been performed to choose first and second guest (impurity) in 4-nitrophenol host to prepare bicomponent and tricomponent mixed crystals. Figure 1 shows overlapping region between absorption spectra of AN and emission spectra of 4-NP while Fig. 2 indicates overlapping region between absorption spectra of TN and emission spectra of 4-NP. Shaded area shown in the figure was used to determine Förster energy transfer distance (R_0) values. Calculated values of R_0 are tabulated in Table 1. The values of R_0 are in the range of 37–49 Å indicating the possibility of EET between host and guest [13]. This study further supports to use AN as first and TN as second guest in 4-NP host matrix.

Photophysical Studies of 4-Nitrophenol Luminophors

Figures 3 and 4 shows the fluorescence spectra of AN doped 4-NP luminophors and AN-TN doped 4-NP luminophors at excitation wavelength 301 nm. Fluorescence spectrum of anthracene doped 4-nitrophenol shows partial quenching of host fluorescence with appearance of additional emission bands in the wavelength region

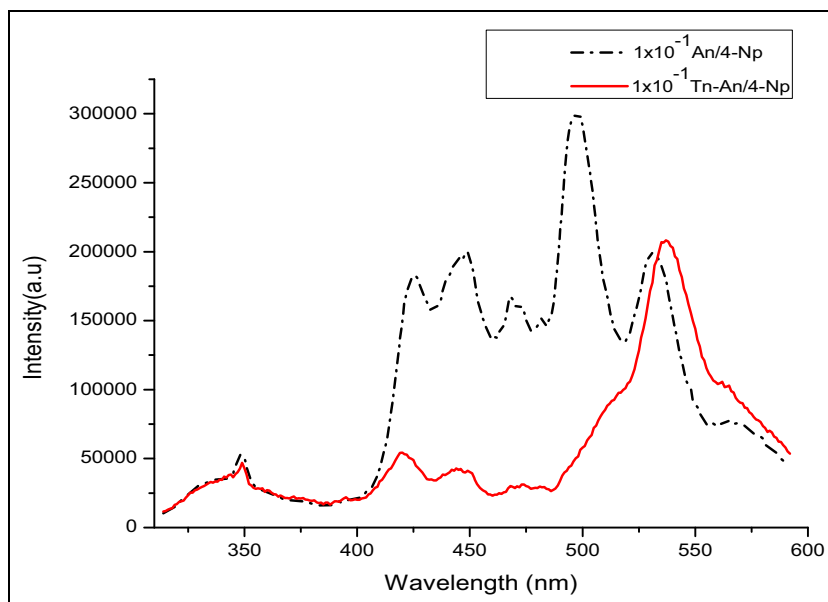
Fig. 4 Fluorescence spectra of tricomponent luminophors of 4-NP doped by AN and TN



335–380 nm. The monomeric peaks of anthracene is seen in the region 400–525 nm. The appeared anthracene emission specifies the transfer of excitation energy of 4-NP to AN either by exciton or by EET process. The quenching of host fluorescence and appearance of guest fluorescence is identified by these processes.

Figure 4 shows monomeric peaks of the tetracene in the wavelength region 480–590 nm [14]. The most intense peak maxima seen at 539 nm. These monomeric emission arises due to the excitation energy transfer from anthracene to tetracene. This bathochromic shift is seen as a result of two step EET from host 4-NP to tetracene via anthracene.

Fig. 5 Comparison between fluorescence spectra of bicomponent 1×10^{-1} AN doped 4-NP and tricomponent 4-NP luminophors containing 1×10^{-1} AN and 1×10^{-1} TN



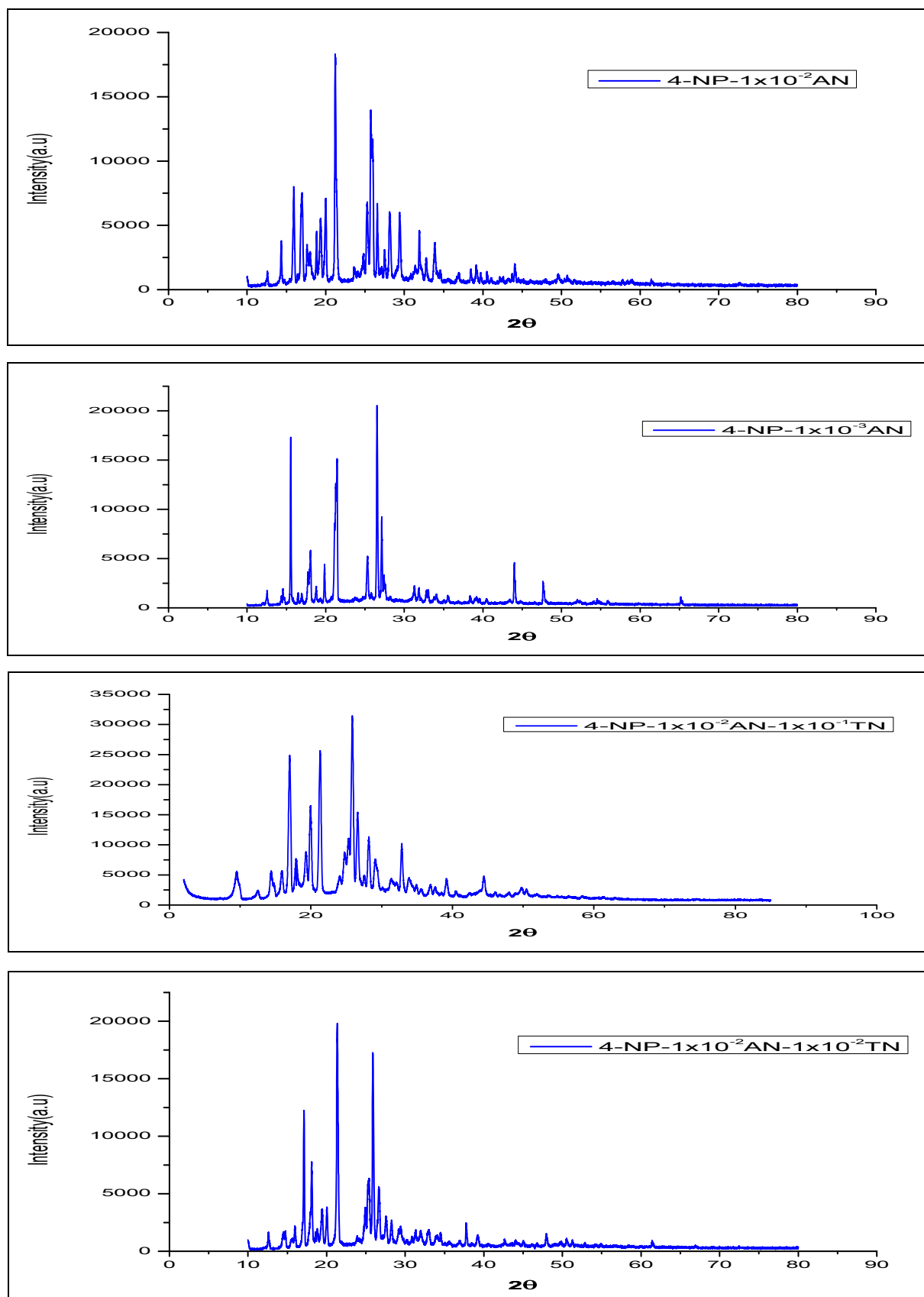


Fig. 6 XRD study of pure 4-NP, pure AN, pure TN and 4-NP luminophors

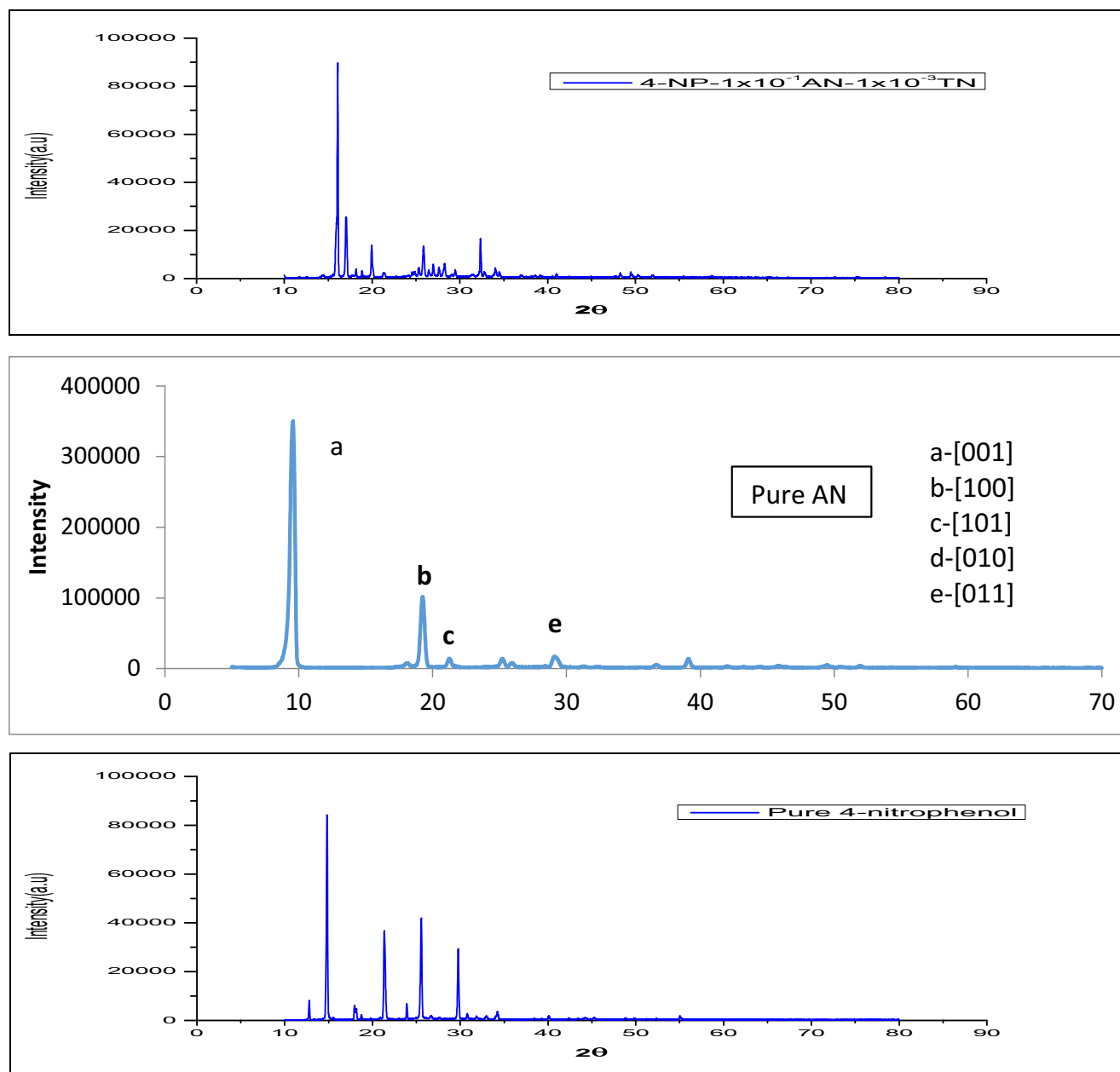


Fig. 6 continued.

The comparison between fluorescence spectra of bi-component luminophors containing 1×10^{-1} mol AN per mole 4-NP and tricomponent luminophors containing 1×10^{-1} mol AN and 1×10^{-1} mol TN per mole 4-NP was shown in Fig. 5. The spectra reveals the fluorescence emission of anthracene doped 4-NP seen in the blue region while tricomponent luminophors emits in the green region peaking at 539 nm.

Structural Studies of Bicomponent and Tricomponent Luminophors of 4-Nitrophenol

Figure 6 shows the XRD spectra of pure 4-NP, AN, TN and doped 4-NP luminophors. The crystallinity of the doped 4-NP luminophors is identified by sharp peaks observed in XRD spectra. Absence of XRD peaks corresponding to AN and TN confirms the homogeneity of

Table 2 Structural parameters of 4-nitrophenol luminophors

Conc. of TN (M) in 1×10^{-1} AN Mole in 4-NP	Glancing Angle, (2 θ) degree	FWHM, $\beta_{2\theta}$	Microstrain, $\epsilon \times 10^{-3} \text{ l}^2/\text{m}^{-4}$	Grain Size, (D) \AA^0	Dislocation Density, $\rho \times 10^{15} \text{ cm}^{-2}$	Stacking Fault, α_{st}
Pure 4-NP	14.822	0.143	0.620	826.3	0.494	0.1006
Pure AN	9.550	0.471	2.047	250.5	5.378	0.8753
Pure TN	19.480	0.447	1.922	266.8	4.738	0.6106
1×10^{-3} AN per mole 4-NP	21.191	0.144	0.617	830.7	0.489	0.0842
1×10^{-2} AN per mole 4-NP	25.824	0.162	0.688	744.7	0.609	0.0855
1×10^{-1} AN per mole 4-NP	26.512	0.138	1.395	367.5	2.500	0.1733
1×10^{-1} TN-AN per mole 4-NP	25.841	0.328	1.395	367.5	2.500	0.1733
1×10^{-2} TN-AN per mole 4-NP	21.335	0.203	0.870	589.1	0.972	0.0842
1×10^{-3} AN-TN per mole 4-NP	16.067	0.092	0.398	1287.3	0.203	0.1733

the doped samples. The prepared luminophors are highly crystalline. The calculated parameters viz., grain size, microstrain, dislocation density and stacking fault are shown in Table 2. These parameters are calculated by

using FWHM value of intense band in XRD spectra. The grain size varies as the dopant concentration changes in the host. The matrix exhibited highest grain size at lower concentration i.e. 1×10^{-3} . The addition of guest

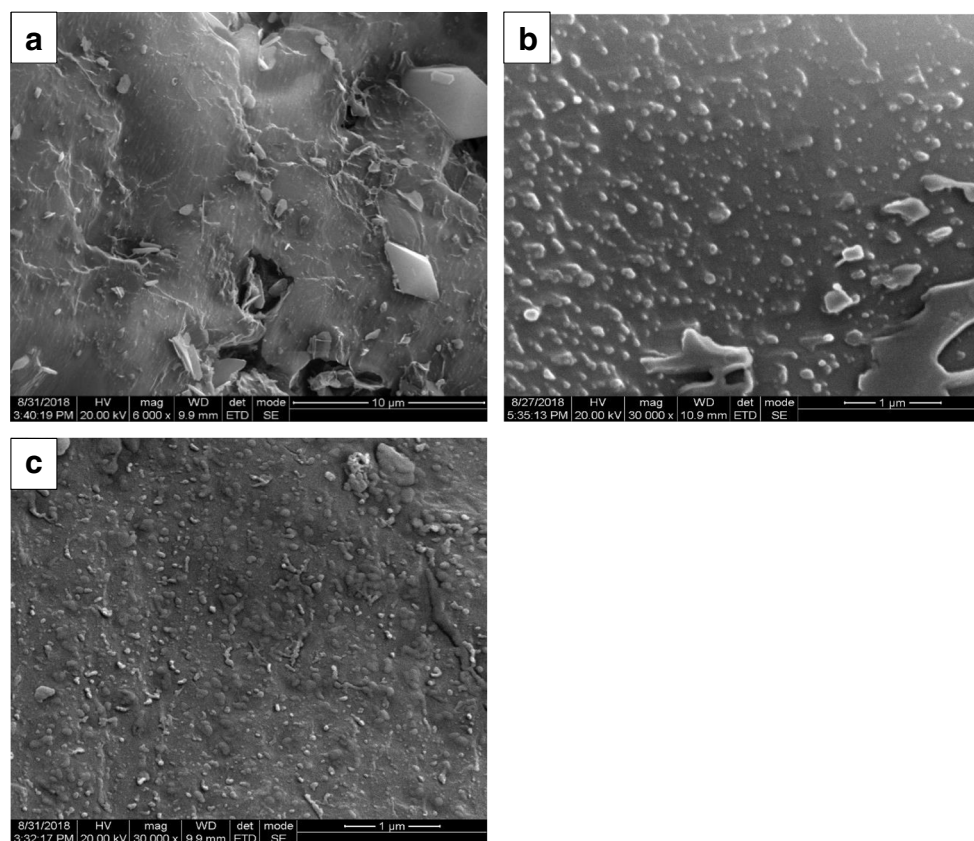


Fig. 7 SEM images of a) Pure 4-Nitrophenol, b) 1×10^{-1} AN mole in 4-NP c) 1×10^{-1} TN- 1×10^{-1} AN mole in 4-NP

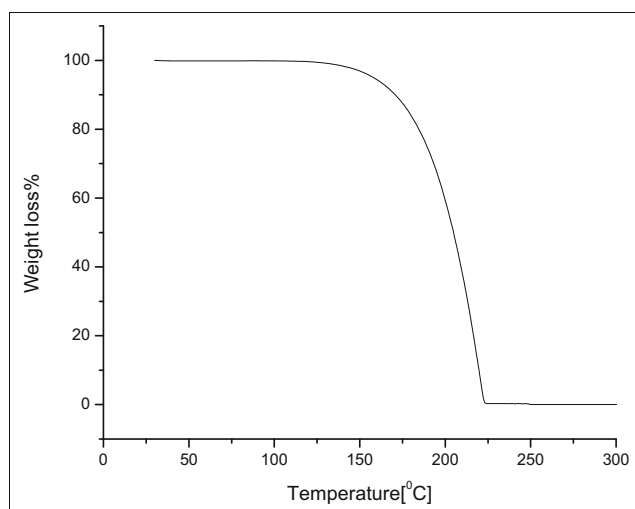


Fig. 8 TGA study of AN-TN doped 4-NP luminophors>

impurities in the host produces defects, imperfections and deformations which affect on other parameters such as microstrain, dislocation density and stacking fault [15].

The SEM images of pure and doped 4-NP luminophors are shown in Fig. 7. The micrographs exhibits identical and finely detached crystallites. It also provides crystallite size which was found as ~95 nm in bicomponent and ~102 nm in tricomponent luminophors. These study reveals that the prepared luminophors in the present investigation can be used in optoelectronics.

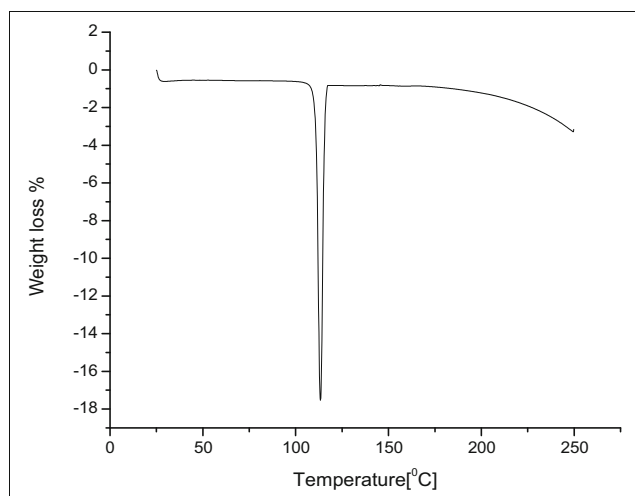


Fig. 9 DSC study of AN-TN doped 4-NP luminophors>

Surface Morphology of Anthracene and Tetracene Doped 4-Nitrophenol Luminophors

Thermal Studies of 4-Nitrophenol Luminophors

For optical applications, thermal stability of the material is essential. Hence, to study the alteration in thermal properties of AN-TN doped 4-NP, thermogravimetric analysis has been done. Figures 8 and 9 shows TGA and DSC thermographs of 4-NP luminophors (1×10^{-1} TN- 1×10^{-1} AN mole in 4-NP) under the nitrogen atmosphere within temperature range of 0–300 °C. From Fig.8, it is observed that the 4-nitrophenol luminophors remains thermally stable up to 225 °C and after that the decomposition starts. The stage one from 195 °C to 225 °C, the stage two from 225 °C to 275 °C in which maximum weight loss is observed while decomposition of remaining compound indicate weight loss in third stage. Figure 9 show DSC curve which exhibits one endothermic peak at 115 °C [16].

Electrical Properties 4-Nitrophenol Luminophors

Electrochemical properties of AN doped 4-NP and TN-AN doped 4-NP luminophors were studied by Cyclic Voltammetry (CV) in dichloromethane solution using ferrocene as an internal standard. On anodic sweep, two quasi-reversible waves were observed near -1.25 and near 1.2 in the first and third curve which may be due to two electron process in anthracene impurity doped in 4-NP and near -1.0 and 1.1 for TN-AN in 4-NP as observed in Figs. 10 and 11, respectively. For the prepared luminophors energy levels of HOMO and LUMO were detected in the range of 5.38–5.85 eV and 2.78–3.08 eV, respectively for both components. The E_g calculated from the CV shown in Table 3 were in range of 2.37–3.07 eV which found in close proximity with optical band gap [18]. This CV data shows that the prepared luminophors may be serve as a good candidates as n-type materials used in optoelectronic devices.

Conclusion

The novel luminophors of 4-NP emitting in the blue and green region are prepared. The two step EET process is observed from host to second guest in 4-NP solid matrix. The XRD analysis indicated the formation of homogeneous solid solutions of the host and guest material. The SEM images evidenced crystals of ~95 nm and ~105 nm size for AN doped

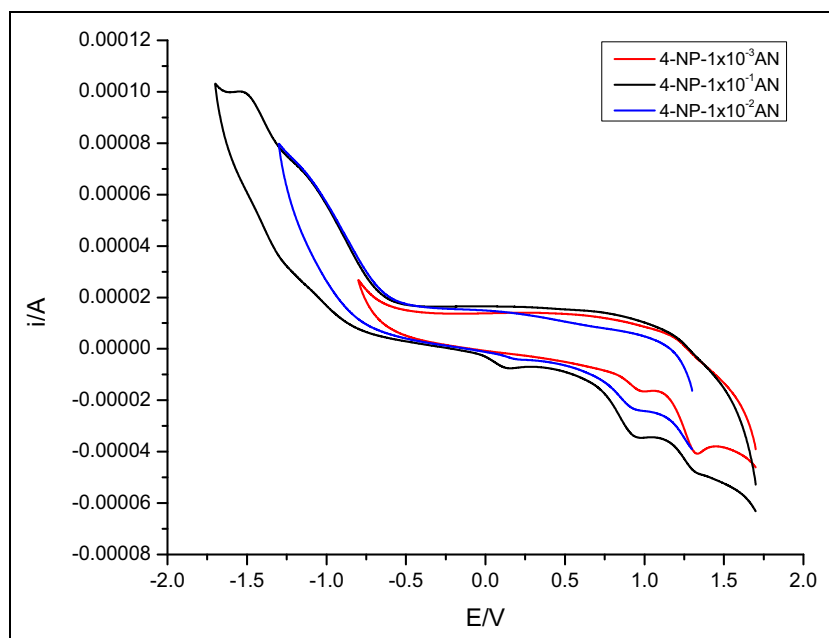


Fig. 10 Cyclic voltammogram of AN doped 4-NP luminophors>

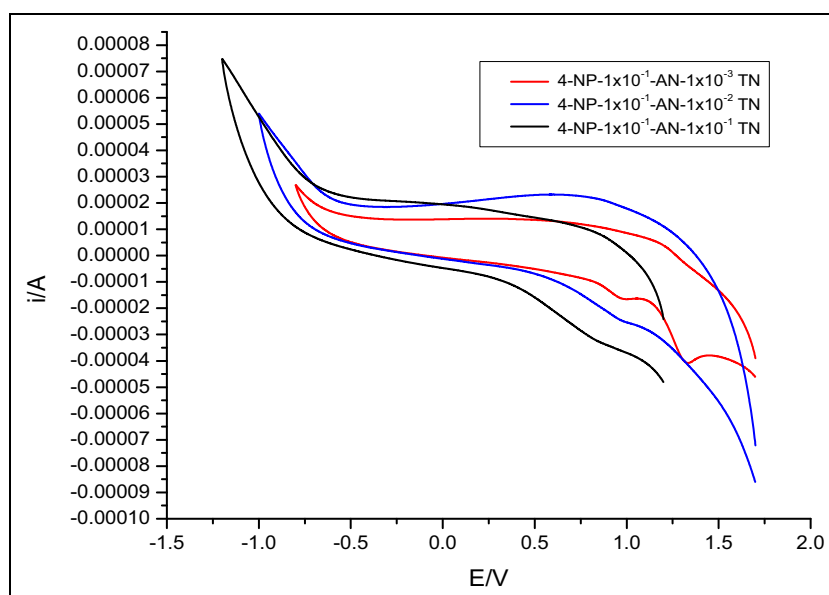


Fig. 11 Cyclic voltammogram of AN and TN doped 4-NP luminophors>

Table 3 Electrochemical data of doped 4-NP luminophors

Compound	$E_{Ox}^{peak(a)}$	$E_{Red}^{peak(b)}$	HOMO ^(c)	LUMO ^(d)	$E_g^{(e)}$
1) 1×10^{-1} AN /mole 4-NP	1.25	-0.99	-5.85	-2.78	3.07
2) 1×10^{-2} AN /mole 4-NP	1.00	-0.75	-5.60	-3.02	2.58
3) 1×10^{-3} AN /mole 4-NP	0.99	-0.96	-5.59	-3.08	2.51
4) 1×10^{-1} AN- 1×10^{-1} TN /mole 4-NP	0.82	-0.98	-5.74	-2.79	2.63
5) 1×10^{-1} AN- 1×10^{-1} TN /mole 4-NP	0.78	-0.76	-5.38	-3.01	2.37
6) 1×10^{-1} AN- 1×10^{-1} TN /mole 4-NP	1.25	-0.70	-5.85	-3.07	2.78

{^a E_{Ox}^{peak} Oxidation peak potential(V), ^b E_{Red}^{peak} Reduction peak potential(V), ^c HOMO, $E_{HOMO} = -(E_{Ox}^{peak} - E_{Ox}(Fc/Fc^+) + 4.8)eV$, ^d LUMO, $E_{LUMO} = -(E_{Red}^{peak} - E_{Red}(Fc/Fc^+) + 4.8)eV$, $E_g^{(e)} = E_{HOMO} - E_{LUMO}$ } [11, 17]

4-NP and AN-TN doped 4-NP luminophors respectively. TGA-DSC and CV study revealed suitability of 4-nitrophenol luminophors in the optoelectronic devices.

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Compliance with Ethical Standards

Conflict of Interest Authors declare that they have no conflict of interest.

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