



Synthesis, Photophysical, Electrochemical and Thermal Investigation of Anthracene Doped 2-Naphthol Luminophors and their Thin Films for Optoelectronic Devices

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Abstract

A series of novel luminophors of 2-naphthol by doping anthracene were prepared using conventional solid state reaction technique. The photophysical, electrochemical and thermal properties were studied by Fluorescence spectroscopy, XRD, SEM, TGA-DSC and by Cyclic Voltammetry techniques. The thin films were characterized by Fluorescence spectroscopy. XRD study of fine grained powders exhibited sharp peaks which specify crystallinity and homogeneity of the doped luminophors. The fluorescence spectra of doped 2-naphthol exhibited emission of anthracene at 413 nm i.e. blue emission with instantaneous fluorescence quenching of 2-NP due to excitation energy transfer (EET). Electrochemical data specify that the HOMO and LUMO energy levels of the synthesized luminophors are in the range of 5.55–5.71 eV and 3.03–3.24 eV, respectively. TGA-DSC study confirmed thermal stability of prepared luminophors. Hence, overall study proposes that these luminophors seems applicable to be used as n-type materials for Optoelectronic devices.

Keywords n-type materials · Fluorescence quenching by EET · Organic luminophors

Introduction

Nowadays organic semiconductors have attracted more attention for their application in optoelectronic devices such as organic solar cells, organic light emitting diodes (OLEDs), organic photovoltaic devices, etc. [1–3]. Furthermore, demand from optoelectronic industries for these materials encouraged researchers to go for it. As compared to the metals doped in inorganic materials, organic doped materials find greater applications in LEDs with respect to effortless synthesis, reasonable, lightweight property, flexibility, etc. and embrace a productive field. These crucial facts encouraged their applications

in solid-state reactions for lightening. Hence, these mesmerizing properties attracted various researchers and added more to existing literature which throws light on purely organic materials based luminophors and their use in optoelectronics [4–9]. But many of the methods used by researchers in organic synthesis are very tedious, time consuming and need expensive catalysts [10]. Vapour phase method, crystal growth method from solution, melt growth method and solid state growth method by heating have also been employed for the same purpose [11, 12]. Amongst which, doping technique turns efficient method named as conventional solid state reaction technique to get the emission of fluorescent materials due to its simple processing, informal heating and proficient output with great purity materials [13]. In conventional solid state reaction technique, selection of host and guest materials play a dynamic role. Intermolecular energy transfer in between host and guest is considered because of intramolecular interactions [14, 15]. In present article, monoclinic host material has been chosen and purposely doped with blue light emitting guest as an effective donor of excitation energy with the D-type (diffusion spectrum) crystal lattice which trap the excitation energy of host and attain alteration in the fluorescence spectrum of the host material [16–19]. Hence, in this study, 2-naphthol is preferred as a host material which solubilize anthracene as a

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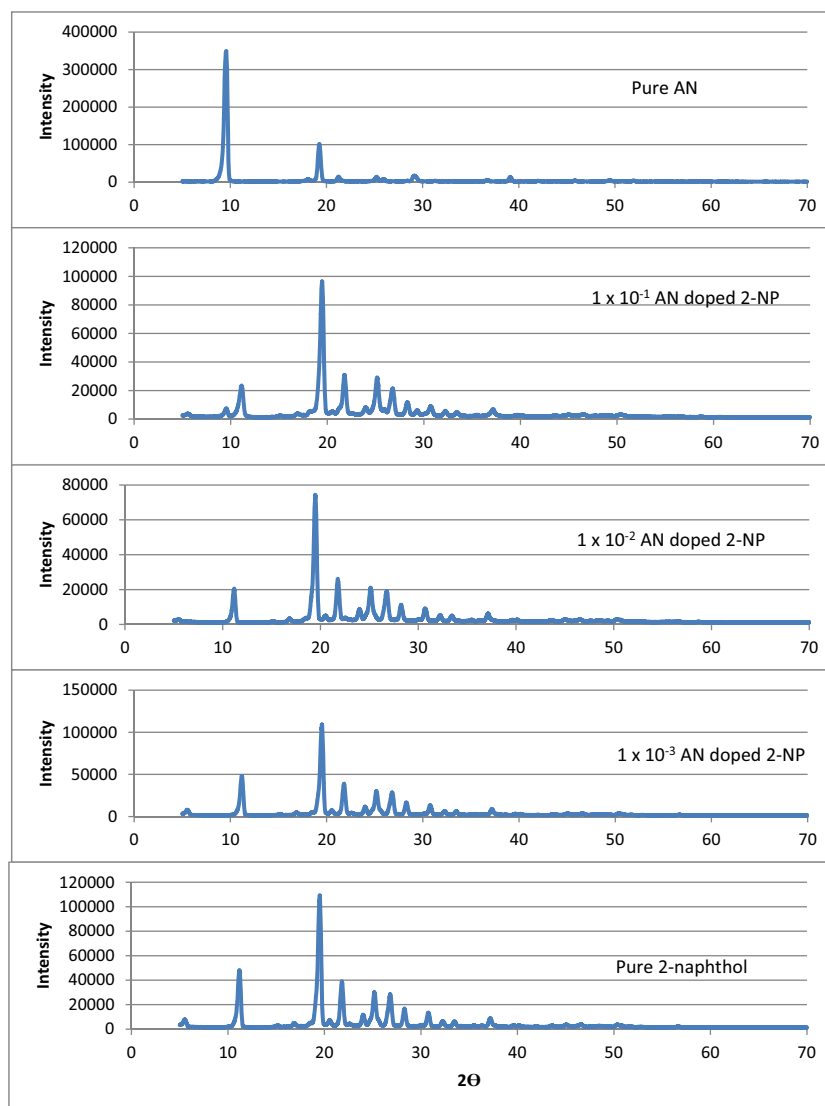
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guest material and transfer electronic excitation energy to the guest molecules via EET process, because of two benzene rings of 2-naphthol which are not co-planar in ground state but oriented in the plane in an electronically excited state by absorbing UV radiations. Aim of current article is to improve emission of 2-naphthol by integrating selected dopant with different concentrations and to make it applicable for optoelectronic devices.

Experimental

Pure 2-naphthol and anthracene of scintillation grade were procured from Merck-Schuchardt. The same were recrystallized and purified by the sublimation method. The similarity in the fluorescence spectra at different excited wavelength in the UV region confirmed the purity of these substances.

Fig. 1 XRD study of pure 2-NP and AN doped 2-NP. **a** 1×10^{-3} M, **b** 1×10^{-2} M, **c** 1×10^{-1} M of AN per mole 2-NP and **e** pure AN



Preparation of Doped 2-Naphthol Luminophors

The conventional solid-state reaction technique was employed to prepare polycrystalline luminophors of 2-NP containing AN [20, 21]. Different concentrations of AN doped 2-NP solid solutions were formed by mixing appropriate amount of these two in silica crucible with heating at the temperature just above the melting point of 2-NP (122 °C). Then the obtained melt was cooled slowly to get polycrystalline luminophors of AN doped 2-NP with fine crushed powder. Finally, the fine powder of doped 2-NP was used to study the photophysical, thermal and electrochemical properties.

Characterization Techniques

The fluorescence spectra of doped 2-naphthol was recorded by JOBIN YVON Fluorolog-3-11 spectrofluorimeter, at IIT Madras. The XRD analysis of doped and undoped crystals

Table 1 Structural parameters of 2-naphthol luminophors

Conc. of AN,(M) Per mole of 2-NP	Pure AN	1×10^{-3}	1×10^{-2}	1×10^{-1}	Pure 2-NP
Glancing Angle, (2θ) degree	9.550	19.510	19.170	19.460	19.445
FWHM, $\beta_{2\theta}$	0.471	0.447	0.424	0.482	0.446
Microstrain, $\epsilon \times 10^{-3} \text{ l}^2/\text{m}^{-4}$	2.047	1.921	1.824	2.072	1.917
GrainSize, (D) Å^0	428.9	267.1	281.4	247.8	266.9
Dislocation Density, $\rho \times 10^{15} \text{ cm}^{-2}$	3.129	4.730	4.264	5.501	4.725
Stacking Fault	0.4122	0.2727	0.2587	0.2945	0.2725

was carried out by Philips Diffractometer (PW-3710 model, Holland) with $\text{CrK}\alpha$ radiation (2.28 \AA). (TGDTA-DSC) TA Inc. SDT- 2790 with heating rate $10 \text{ }^\circ\text{C}$ per minute under the nitrogen atmosphere was employed to carry out Thermogravimetric analysis, while FEI Quanta FEG 200 - Scanning Electron Microscope was used to study surface morphology of samples.

Results and Discussion

Structural Studies of Doped 2-Naphthol Luminophors by XRD

X-ray diffraction spectra of pure and anthracene doped 2-naphthol is shown in Fig. 1. XRD profile of fine grained powder exhibited sharp peaks which specify crystallinity and homogeneity of the doped luminophors. No additional peak for AN was observed in the spectrum of 2-NP luminophors. This reflection specify that, the mixed crystals of two components are homogenous. Along with this, the structural parameters like microstrain, dislocation density, grain size and stacking fault were also calculated and tabulated in (Table 1). Classical Sherrer formula has been used to estimate the average grain size of 2-naphthol luminophors [22]. The addition of AN as a guest material into 2-NP showed highest grain size for 1×10^{-2}

concentration. On doping of a pure crystal into host, it deforms by producing defects and imperfection into host lattice. Hence, this deformation changes microstrain marginally and dislocation density as per the expectation [23]. It has been calculated and tabulated in (Table 1). Also Stacking fault observed to be improved with guest anthracene in 2-naphthol host material. This result concluded to consider close packed structure of both host and guest molecules. SEM micrographs (Fig. 2) of doped and undoped 2-naphthol exhibits well separated, identical crystallites of monoclinic form. Also, SEM micrographs noted average crystallite size of 133 nm which is the range desired in optoelectronic devices.

Photophysical Properties

2-naphthol which is monoclinic unit cell when excited at 330 nm radiation exhibits fluorescence in the UV region [24]. Anthracene is well identified for it's emission like naphthalene matrix by EET process.

The fluorescence spectrum of 2-NP and AN doped 2-NP are shown in Fig. 3. It has been observed that, fluorescence spectra of anthracene doped 2-naphthol is structured and appears to be blue shifted viz. 413 nm which differ completely from fluorescence spectrum of 2-naphthol. The absence of 2-naphthol emission bands clearly specify that the excitation energy of 2-naphthol exciton is trapped by anthracene due to

Fig. 2 SEM images of **a** pure AN and **b** 1×10^{-1} M of AN per mole 2-NP

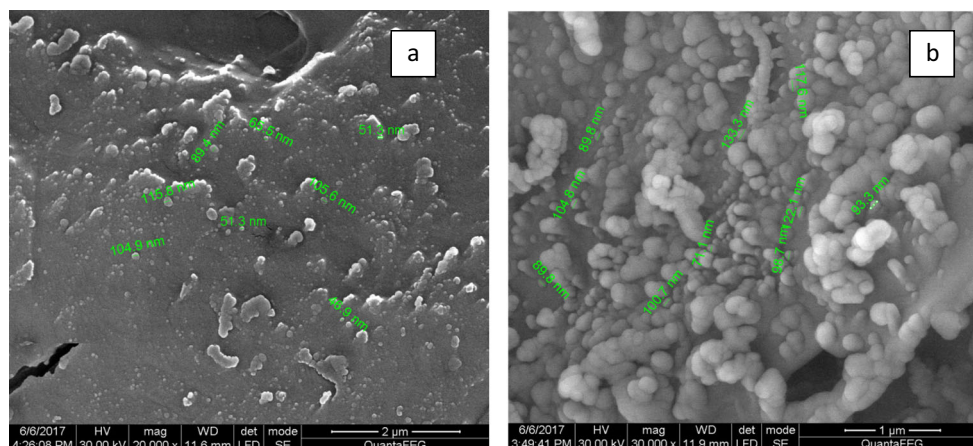
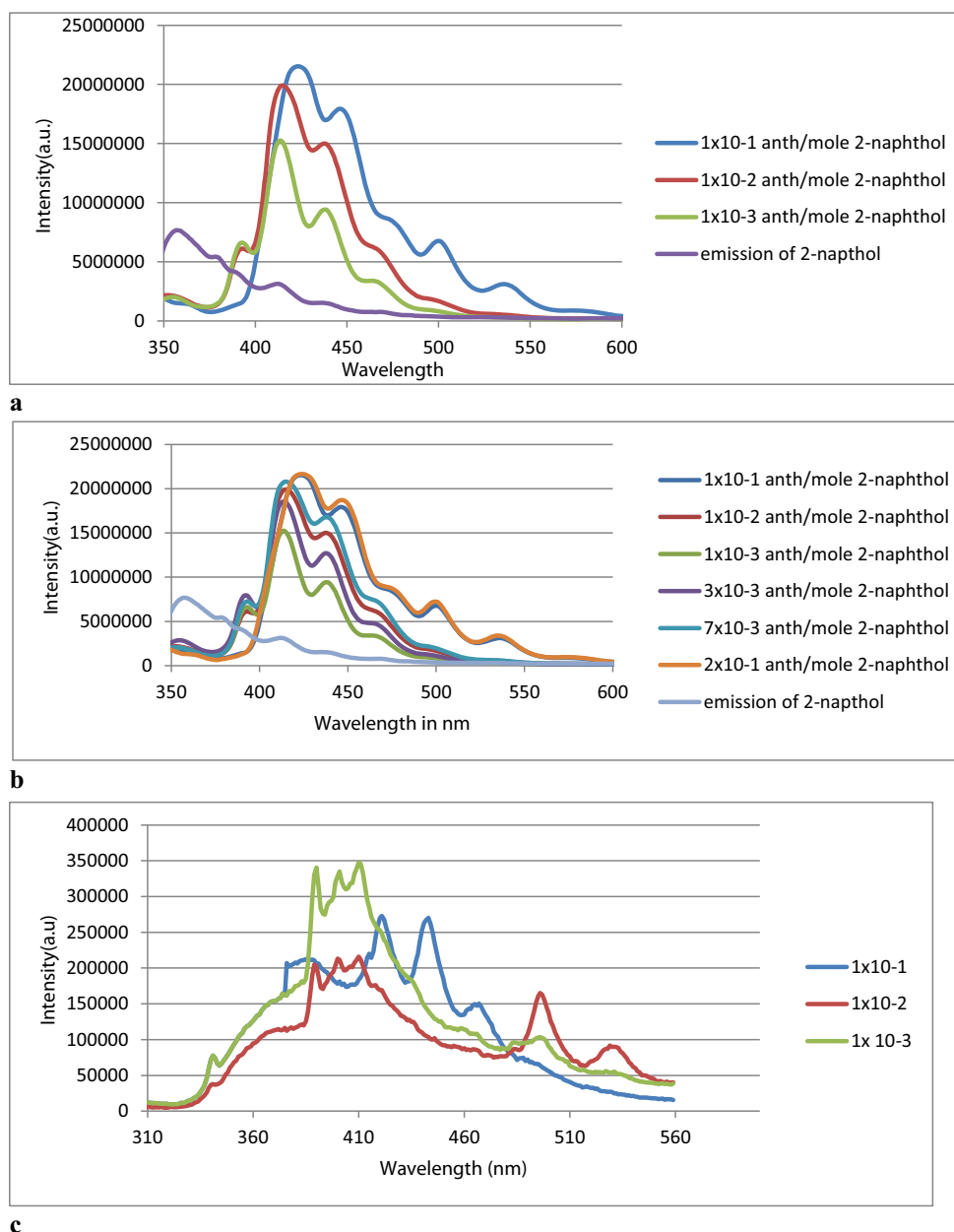


Fig. 3 **a** Fluorescence spectra of pure 2-NP and 1×10^{-1} , 1×10^{-2} , 1×10^{-3} AN doped 2-NP **b** Fluorescence spectra of pure 2-NP and 1×10^{-1} , 1×10^{-2} , 1×10^{-3} , 3×10^{-3} , 7×10^{-3} , 2×10^{-1} AN doped 2-NP **c** Fluorescence spectra of thin film AN doped 2-NP



excitation energy transfer (EET) with immediate fluorescence quenching of 2-NP. Hence, for 1×10^{-3} and 1×10^{-2} anthracene doped 2-naphthol, the peak appeared at 412 nm and

413 nm. As the concentration of anthracene increased, peak shift towards longer wavelength with increase in intensity of peak.

Table 2 Emission data of solid material and their thin films with optical band gap of doped 2-NP luminophors

Compounds	$\lambda_{\text{emi}}^{(a)}$, nm	$\lambda_{\text{emi}}^{(b)}$, nm of thin Films	$E_g^{\text{Opt (c)}}$ (eV)
1×10^{-1} AN/mol 2-NP	421	420	2.94, (2.95)
1×10^{-2} AN/mol 2-NP	415	413	2.98, (3.00)
1×10^{-3} AN/mol 2-NP	415	414	2.98, (2.99)
3×10^{-3} AN/mol 2-NP	415	–	2.98, (–)
7×10^{-3} AN/mol 2-NP	414	–	2.99, (–)
2×10^{-1} AN/mol 2-NP	420	–	2.95, (–)

^a Recorded, ^b Recorded, ^c ($E_g^{\text{Opt}} = 1240.8/\lambda_{\text{opt edge}}$) eV,

Also the fluorescence study of thin films of anthracene doped 2-naphthol by employing spin coating technique was carried out as shown in Fig. 3c and result listed in Table 2. The results fulfilled our expectations.

Thermal Properties of Doped 2-Naphthol Luminophors

To exhibit optical applications, materials need to be thermally stable. To examine alteration in thermal properties of 2-naphthol doped anthracene, thermogravimetric analysis has been done. Figures 4 and 5 show TGA and DSC thermographs of 2-naphthol doped anthracene under the nitrogen atmosphere within temperature range of 0–300 °C. From Fig. 4, it is observed that, the anthracene doped 2-naphthol remains thermally stable up to 125 °C and after that the decomposition starts. The complete process of decomposition proceeds in three stages. The stage one from 125 °C to 230 °C, the stage two from 230 °C to 250 °C in which maximum weight loss is observed while decomposition of remaining compound indicate weight loss in third stage. The Fig. 5 show DSC curve which exhibits one endothermic peak at 120 °C.

From thermogram it is clear that doped 2-naphthol is suitable for device fabrication and to facilitate an enhanced lifetime of the devices.

Electrochemical Properties

Electrochemical properties of AN doped 2-NP luminophors were studied by Cyclic Voltammetry technique (CV) in dichloromethane solution using ferrocene as an internal standard. On anodic sweep, two quasi-reversible waves were observed near 0.2 and near 0.4 in the first and third curve

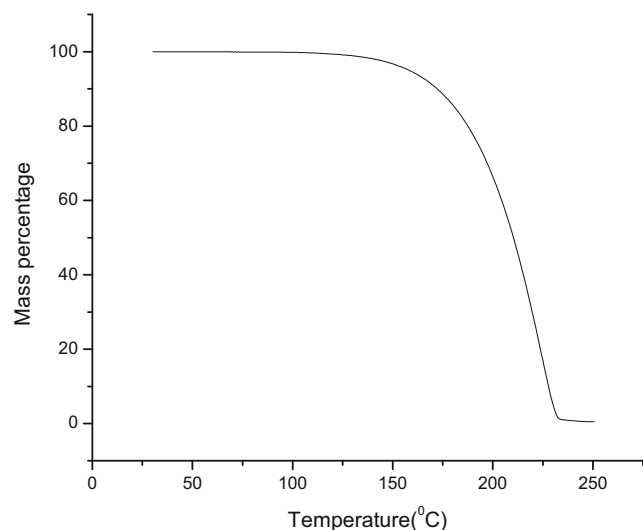


Fig. 4 TGA curve of 2-naphthol containing anthracene

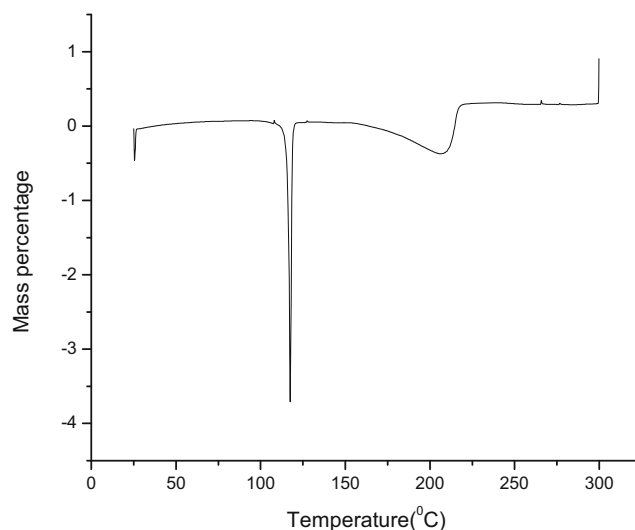


Fig. 5 DSC curve of 2-naphthol containing anthracene

which may be due to two electron process in anthracene impurity doped in 2-naphthol (Fig. 6). For the synthesized luminophors the HOMO and LUMO energy levels were observed in the range of 5.55–5.71 eV and 3.03–3.24 eV respectively. The E_g calculated from the CV were in the range of 2.25–2.82 eV which found in close proximity with optical band gap [25, 26]. Thus, the prepared luminophors are good applicants as n-type materials used in optoelectronic devices.

The observed parameters are tabulated in Table 3.

Conclusion

The structural, emission, electrochemical and thermal properties of the synthesized luminophors are significantly influenced by the concentration of guest material with emission

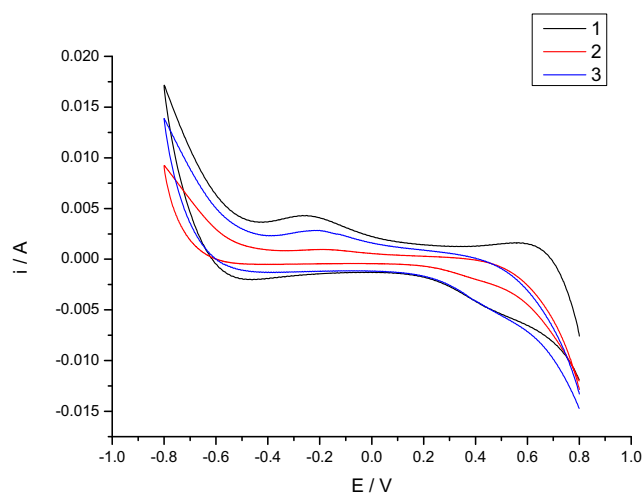


Fig. 6 Cyclic voltammogram of 2-NP doped AN

Table 3 Electrochemical data of doped 2-NP luminophors

Compound	$E_{\text{Ox}}^{\text{peak(a)}}$	$E_{\text{Red}}^{\text{peak(b)}}$	HOMO ^(c)	LUMO ^(d)	$E_g^{\text{(e)}}$
1) 1×10^{-1} AN/mol 2-NP	0.71	-0.53	-5.71	-3.24	2.74
2) 1×10^{-2} AN/mol 2-NP	0.52	-0.74	-5.52	-3.03	2.49
3) 1×10^{-3} AN/mol 2-NP	0.55	-0.68	-5.55	-3.09	2.46

^a $E_{\text{Ox}}^{\text{peak}}$ Oxidation peak potential (V), ^b $E_{\text{Red}}^{\text{peak}}$ Reduction peak potential (V), ^c HOMO, $E_{\text{HOMO}} = -(E_{\text{Ox}}^{\text{peak}} - E_{\text{Ox}}(\text{Fc/Fc}^+) + 4.8)\text{eV}$, ^d LUMO, $E_{\text{LUMO}} = -(E_{\text{Red}}^{\text{peak}} - E_{\text{Red}}(\text{Fc/Fc}^+) + 4.8)\text{eV}$, $E_g^{\text{(e)}} = E_{\text{HOMO}} - E_{\text{LUMO}}$ ²⁷

at blue region. The electrochemical and thermal study of the synthesized luminophors confirmed their use as n-type material for Optoelectronic devices.

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