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ORIGINAL ARTICLE

Synthesis, Photophysical, Electrochemical and Thermal Study of Biphenyl Luminophors: Green Light Emitting Materials

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Abstract

Novel luminophors of anthracene (AN) and tetracene (TN) doped biphenyl were prepared using Conventional Solid State reaction technique. Fluorescence spectroscopy, XRD, SEM, TGA-DSC and Cyclic Voltammetry techniques have been employed for photophysical, electrochemical and thermal study. The X-ray diffraction study revealed the formation of homogeneous biphenyl solid solutions with the added guests AN and TN. Fluorescent biphenyl absorbing short wave UV radiation and emitting at long wave UV radiation has been used as a solid matrix. From the fluorescence spectra it is seen that the added guests shifts the UV fluorescence of biphenyl emitting in green region of visible spectrum at 532 nm. SEM images of the prepared luminophors showed the crystallites of average size 140 nm which makes them suitable candidates for their use in Optoelectronic devices. HOMO and LUMO energy levels of the synthesized luminophors from electrochemical data observed in 5.50–5.64 eV and 3.09–3.13 eV with band gap 2.37–2.55 eV, respectively. TGA-DSC study revealed the thermal stability of prepared luminophors.

Keywords Optoelectronic devices · Green light emitting novel luminophors · EET process

Introduction

Recently organic semiconductors got significant attention of researchers because of their ultimate electro-optical properties, technological industrial uses. Many of Organic conjugated molecules have been synthesized for their application as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) [1] and dye-sensitized solar cells [2]. Electroluminescent multifunctional materials consists of donor-acceptor (D-A) molecules which have substantial importance for OLEDs in recent time [3]. These molecules have been found to show fascinating charge-transporting properties in electroluminescent devices [4]. These properties found to be achieved by doping technique known as Conventional Solid State reaction technique [5–7]. The conjugated molecules like anthracene, tetracene, pyrene, perylene, p-terphenyl, etc., have been used as organic scintillators. But the potential of anthracene and tetracene to interact with host molecule is well known [8, 9]. The role of scintillators is to produce light in fluorescent tubes and to transform UV light into visible light [10, 11]. Hence there has been much interest in synthesis, photo-physical, electrochemical and thermal investigation of Organo-luminophors with its utility in solid state electronics emitting in preferred colors.

Mixed crystals of biphenyl doped anthracene in which the fluorescence of biphenyl emission get quenched and shows new anthracene like emission in the spectral region of 400–450 nm. Tetracene exihibits very weak fluorescence in solid state. However, it forms the series of solid solution with anthracene to yield

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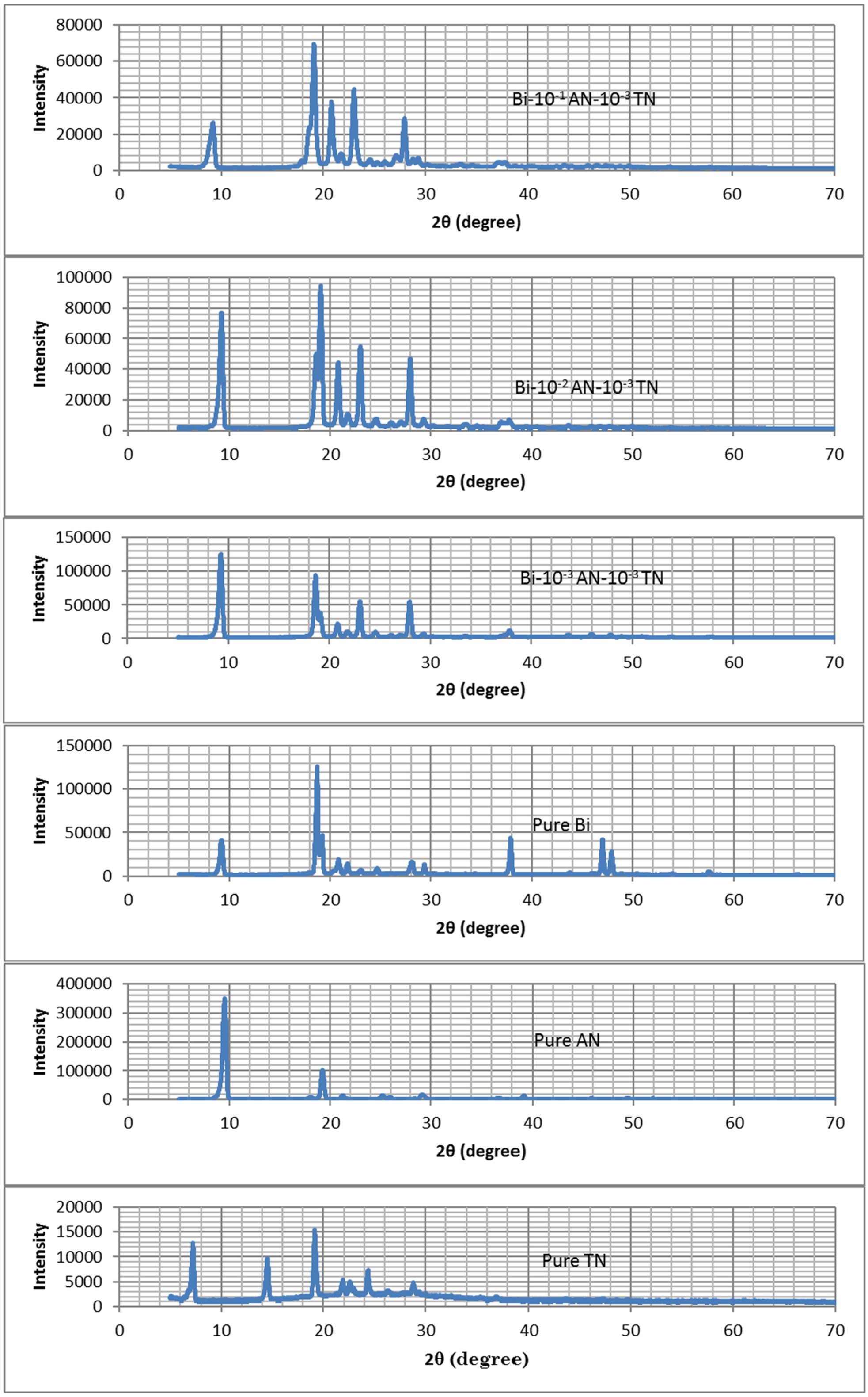

Fig. 1 XRD profile tetracene and anthracene doped biphenyl

green emission [12, 13]. The present work reports, synthesis of tricomponent luminophors of biphenyl doped by anthracene and tetracene with enhancement in fluorescence emission from blue to green light with their photo-physical, electrochemical and thermal properties by selective excitation of host biphenyl.

Experimental

Biphenyl, anthracene and tetracene of scintillation grade were purchased from Merck-Schuchardt and used as received. Biphenyl was used as a host matrix while AN and TN were used as a guests. The series of solid solutions of biphenyl were prepared by conventional solid state reaction method. Different concentrations of AN and TN doped biphenyl solid solutions were prepared by using appropriate amount and mixing all in silica crucible with heating at the melting point of biphenyl. The melt thus obtained was cooled to get polycrystalline luminophors of AN and TN doped biphenyl. The fine powder of doped biphenyl luminophors were then subjected to photophysical, thermal and electrochemical characterization.

Characterization Techniques

JOBIN YVON Fluorolog-3-11spectrofluorimeter, at IIT Madras has been used to record the fluorescence emission of doped biphenyl. For structural analysis of the doped and undoped crystals, X-ray analysis was carried out by Philips Diffractometer (PW-3710 model, Holland) with CrKα radiation (2.28 Å). Thermogravimetric analysis has been done by (TGDTA-DSC) TA Inc. SDT- 2790 with heating rate 10 °C per minute under the nitrogen atmosphere. FEI Quanta FEG 200 -Scanning Electron Microscope was employed to study surface morphology of samples.

Results and Discussion

Structural Studies of Doped Biphenyl Luminophors

X-ray diffraction spectra of pure AN and TN doped biphenyl is shown in Figs. 1, 2 and 3. XRD profile of fine grained powder showed sharp peaks which specified crystallinity. The absence of any new peak in XRD spectra of doped luminophors confirms the homogeneity and formation of solid solution [14]. Microstrain, dislocation density, grain size and stacking fault like structural parameters were calculated from XRD study shown in Tables 1 and 2. Classical Sherrer formula has been used to estimate the average grain size of biphenyl luminophors [15]. We found that, grain size increases with increase in concentration of AN and TN as a dopant into biphenyl material. On doping of a pure crystal into host, it deforms by producing defects and imperfection into host lattice. This deformation changes microstrain marginally and dislocation density as per the hope [16]. The stacking fault observed to be improved with guest moiety in biphenyl host material. These results supports the close packed structure of both host and guest molecules. SEM micrographs of doped and undoped biphenyl showed well separated identical crystallites of monoclinic form. SEM micrographs noted average crystallite size at 140 nm which is in the range desired in Optoelectronic devices.

AN doped biphenyl gives anthracene like emission. The anthracence like emission rules out the possibility of direct excitation of AN. The presence of TN decreases the intensity of AN like emission and new emission appears in the region 480–575 nm. In comparison of the luminophor containing 10^{-3} mol AN and 10^{-3} mol TN per mole biphenyl, the emission intensity of the AN like emission decreases in the luminophor containing 10^{-3} mol AN and 10^{-2} mol TN per mole biphenyl. The observation led us to assume that, energy of excited AN is trapped by TN moiety before it is emitted radiatively. The possibility of two step energy transfer is confirmed on the basis of energy states of biphenyl, AN and TN. The first excited singlet state (S_1) of biphenyl is higher than those of AN and TN while the first excited state (S_1) of AN is lower than biphenyl but higher to that of TN. The TN singlet and biphenyl singlet reveal a wide gap by which the direct transfer of excitation energy to TN is not possible. However, it

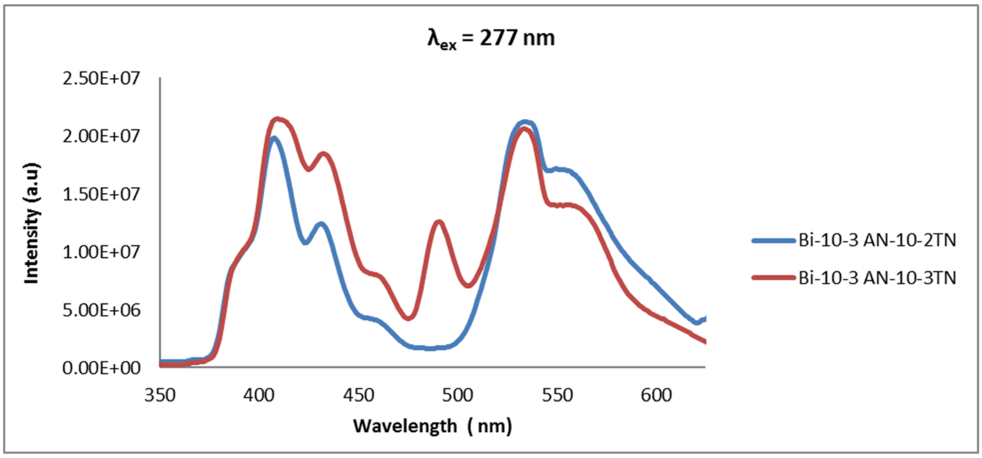

Fig. 2 Fluorescence spectra of biphenyl luminophors containing varying amount of anthracene and tetracene

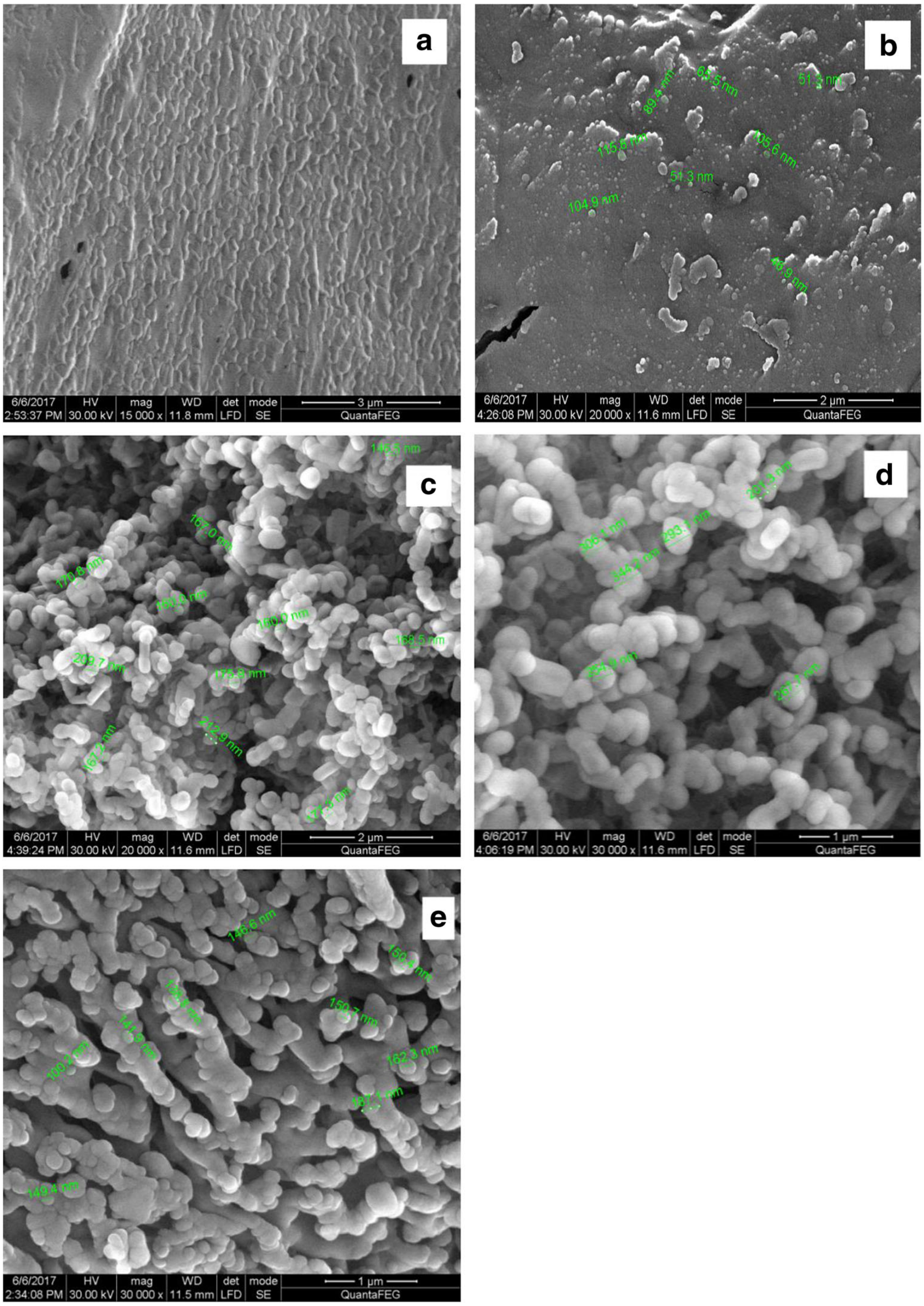

Fig. 3 SEM images of – (**a**) Biphenyl, (**b**) Pure Anthracene, (**c**) 7 × 10^{-3} AN in Bi, (**d**) 1 × 10^{-2}AN in Bi, (**e**) 1 × 10^{-3} TN-10^{-1}AN-Bi

is transferred significantly to AN and then to TN. In the present work we proposed a two step excitation energy transfer from biphenyl to the dopants.

Thermal Properties

The thermal stability of doped materials is important for their applications in optics. To examine thermal properties of biphenyl luminophors, thermogravimetric analysis has been done. Figure 4 shows TGA of doped biphenyl luminophors under the nitrogen atmosphere within temperature range of 0–300 °C. From Fig. 4, it is observed that, the anthracene doped biphenyl remains thermally stable up to 120 °C and after that decomposition starts. The complete process of decomposition proceeds in three stages. The stage one from 120 °C to 185 °C, the second stage from 185 °C to 250 °C in which maximum weight loss is observed while decomposition of

Table 1 Structural parameters of biphenyl luminophors

Conc. of AN, (M) per mole of Biphenyl	Pure TN	Pure AN	Bi-10^{-1} AN-10^{-3} TN	Bi-10^{-2} AN-10^{-3} TN	Bi-10^{-3} AN-10^{-3} TN	Pure Bi
Glancing angle, (2θ) degree	19.480	9.550	19.080	19.090	9.240	18.680
FWHM, $\beta_{2\theta}$	0.447	0.471	0.447	0.464	0.471	0.388
Microstain, $\varepsilon \times 10^{-3}$ l^2/m^{-4}	1.922	2.047	1.923	1.994	2.0483	1.670
Grain Size, (D) A^0	266.89	428.9	266.84	257.20	250.45	307.17
Dislocation Density, $\rho \times 10^{15}$ cm^{-2}	4.738	3.129	4.7411	5.1027	5.380	3.57
Stacking fault, α	0.6106	0.4122	0.617	0.617	0.889	0.6238

Table 2 Electrochemical data of doped biphenyl luminophors

Compound	$E_{Ox}^{peak(a)}$	$E_{Red}^{peak(b)}$	HOMO$^{(c)}$	LUMO$^{(d)}$	$E_g^{(e)}$
1) 1×10^{-1}AN-1×10^{-3}TN per mole Bi	0.50	−0.64	5.50	−3.13	2.37
2) 1×10^{-2}AN- 1×10^{-3}TN per mole Bi	0.61	−0.68	5.61	−3.09	2.52
3) 1×10^{-3}AN- 1×10^{-3}TN per mole Bi	0.64	−0.62	5.64	−3.09	2.55

[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,

$E_g^{(e)} = E_{HOMO} - E_{LOMO}$ [18]

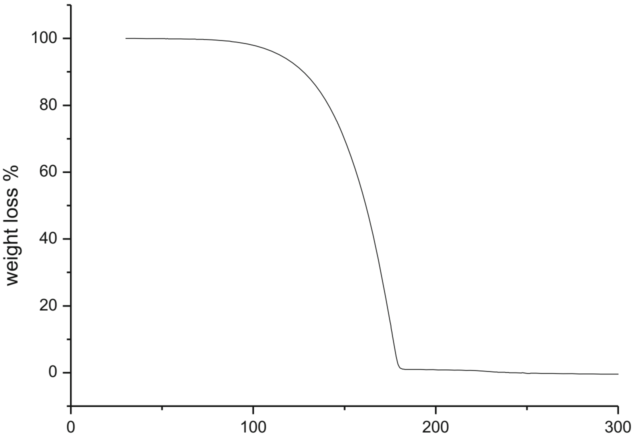

Fig. 4 TGA curve of biphenyl luminophors

remaining compound indicate weight loss in third stage. From this thermal study it is clear that, doped biphenyl luminophors are thermally stable and makes them suitable for device fabrication and lifetime enhancement of the device.

Electrochemical Properties

Electrochemical properties of AN and TN doped biphenyl luminophors were studied by Cyclic Voltammetry (CV) in dichloromethane solution using ferrocene as an internal standard. The cyclic voltamogram is shown in Fig. 5. For the synthesized luminophors the HOMO and LUMO energy levels were observed in the range of 5.50–5.64 eV and 3.09–3.13 eV, respectively. The E_g calculated from the CV were in the range 2.37–2.55 eV which found in close proximity with optical band gap [17]. On anodic sweep, two quasi-reversible waves were observed near −0.3 and near 0.7 in the first and second curve which may be due to two electron transfer processes in AN and TN doped biphenyl luminophors. This data shows the prepared luminophors can be used as a n-type materials in optoelectronic devices.

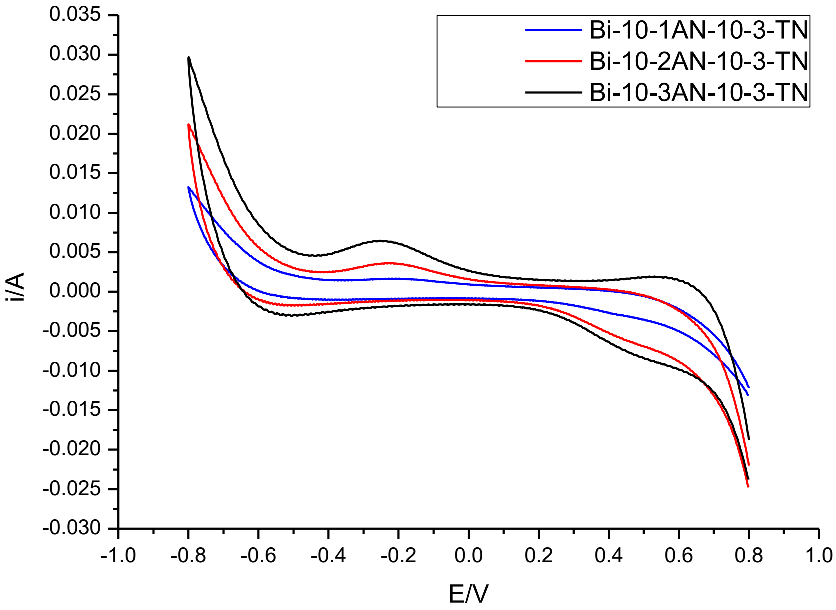

Fig. 5 Cyclic Voltammogram of biphenyl doped AN and TN

Conclusion

The doping of anthracene and tetracene in biphenyl system shifts the fluorescence emission from blue region to green region considerably. The efficient two step excitation energy transfer is proposed from biphenyl host to AN and then to TN. XRD analysis confirms the homogeneous solid solution formation of host and guest material. SEM estimation reveals the average crystallite size of 140 nm. TGA-DSC analysis confirmed thermal stability of compounds. CV analysis showed that, tricomponent luminophors are promising candidates as n-type materials for Organic electronics. So, overall study confirms their use in Optoelectronic devices.

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