



**HAL**  
open science

## Optical and morphological properties of ZnO and Alq<sub>3</sub> incorporated polymeric thin layers fabricated by the dip-coating method

M. Sypniewska, R. Szczesny, L. Skowronski, P. Kamedulski, E. Gondek,  
Aleksandra Apostoluk, B. Derkowska-Zielinska

### ► To cite this version:

M. Sypniewska, R. Szczesny, L. Skowronski, P. Kamedulski, E. Gondek, et al.. Optical and morphological properties of ZnO and Alq<sub>3</sub> incorporated polymeric thin layers fabricated by the dip-coating method. *Applied Nanoscience*, 2023, 13 (7), pp.4903-4912. 10.1007/s13204-022-02647-8 . hal-04138823

**HAL Id: hal-04138823**

**<https://hal.science/hal-04138823>**

Submitted on 21 Mar 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



# Optical and morphological properties of ZnO and Alq<sub>3</sub> incorporated polymeric thin layers fabricated by the dip-coating method

M. Sypniewska<sup>1</sup> · R. Szczesny<sup>2</sup> · L. Skowronski<sup>3</sup> · P. Kamedulski<sup>2,4</sup> · E. Gondek<sup>5</sup> · A. Apostoluk<sup>6</sup> · B. Derkowska-Zielinska<sup>1</sup>

Received: 21 February 2022 / Accepted: 21 September 2022 / Published online: 17 October 2022  
© The Author(s) 2022

## Abstract

In this report, we present the influence of polymer matrix on morphological and optical properties of thin films containing zinc oxide (ZnO), tris(8-hydroxyquinolino)aluminium (Alq<sub>3</sub>) and ZnO:Alq<sub>3</sub>. Polyvinylpyrrolidone (PVP) and poly(methyl methacrylate) (PMMA) dissolved in isopropanol and tetrahydrofuran, respectively, were used as polymeric matrices of fabricated composites. The analysed thin layers were deposited on Si substrates using a dip-coating method and characterized by Fourier-Transform Infrared Spectroscopy (FTIR), Energy-Dispersive X-ray spectroscopy (EDX), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Spectroscopic Ellipsometry (SE) and photoluminescence (PL). It was found that adding the polymer to Alq<sub>3</sub> causes a blueshift in absorption compared to pure Alq<sub>3</sub> layers. We also observed photoluminescence in the region of 2.2–2.8 eV for ZnO:Alq<sub>3</sub>:PMMA and ZnO:Alq<sub>3</sub>:PVP, as well as for Alq<sub>3</sub>:PMMA at room temperature. PL measurements showed that adding ZnO to Alq<sub>3</sub>:polymer matrix did not result in any shift in PL spectra compared to the results of Alq<sub>3</sub>:polymer layer. AFM and SEM measurements show that relatively smooth films were obtained in the case of composites based on PVP and PMMA. Moreover, a change in the size of ZnO agglomerates depending on polymer used is observed for the three-component layers. We also noticed that the values of the refractive index are higher for the samples in the PVP matrix. However, the opposite behaviour was observed in the case of the extinction coefficient.

**Keywords** Zinc oxide · Tris(8-hydroxyquinolino)aluminium · PVP · PMMA · Physico-chemical properties · Spectroscopic ellipsometry · Photoluminescence

## Introduction

In recent years, inorganic/organic hybrid materials have attracted more and more interest, as even though individual materials have distinct physical or chemical properties, the final new composite, instead of adding the properties of the two materials, can show improved properties or entirely new ones (Yoshida et al. 2009; Boeckler et al. 2007; Sanchez et al. 2005). The combination of organic/inorganic hybrid materials provides better transport properties of charge carriers, which offers excellent potential for improving the parameters of optoelectronic devices (Onlaor et al. 2012; Coe et al. 2002).

Tris(8-hydroxyquinolino)aluminium (Alq<sub>3</sub>) is one of the most widely studied organometallic compounds due to its interesting properties and potential applications in optoelectronics. It exhibits features similar to inorganic semiconductors, i.e. relative stability, simple synthesis and good electronic transport (Cuba and Muralidharan 2014a;

✉ B. Derkowska-Zielinska  
beata@fizyka.umk.pl

<sup>1</sup> Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziadzka 5/7, 87-100 Torun, Poland  
<sup>2</sup> Faculty of Chemistry, Nicolaus Copernicus University in Torun, Gagarina 7, 87-100 Torun, Poland  
<sup>3</sup> Institute of Mathematics and Physics, Bydgoszcz University of Science and Technology, S. Kaliskiego 7, 85-796 Bydgoszcz, Poland  
<sup>4</sup> Centre for Modern Interdisciplinary Technologies, Nicolaus Copernicus University, Wilenska 4, 87-100 Torun, Poland  
<sup>5</sup> Department of Physics, Cracow University of Technology, Podchorążych 1, 30-084 Kraków, Poland  
<sup>6</sup> University of Lyon, INSA Lyon, UMR5270, ECL, CNRS, UCBL, CPE Lyon, INL, 69621 Villeurbanne, France

Dalasiniski et al. 2006; Duvenhage et al. 2015). Alq<sub>3</sub> is a metal chelate that is commonly used as an electron transport layer in organic light-emitting diodes (OLEDs) (Cuba and Muralidharan 2014a). Tang and Van Slyke in 1987 described the use of this material in OLED for the first time (Tang and Slyke 1987), and interest in Alq<sub>3</sub> has been growing ever since. In contrast, the hole transport properties of Alq<sub>3</sub> were investigated by Fong and So (Fong and So 2006).

In our previous research (Derkowska-Zielinska 2017) we have shown that Alq<sub>3</sub> has two main absorption bands (called A and B), which are ligand-centered electronic transitions. The A band (visible in the spectral range of 350–450 nm) is associated with the transition from the ground state to the excited one and is also assigned to charge transfer (CT) from the quinolate ring containing oxygen to the pyridyl ring. It corresponds to the  $\pi$ - $\pi^*$  transition of the qH<sup>2+</sup>. Therefore, it is attributed to the excitation of  $\pi$ - $\pi^*$  by the molecular orbitals of quinolate ligands. Whereas B band, which absorption is located in the spectral range of 210–280 nm, suggests the presence of a p-band associated with the central metal atoms, where the transition p- $\pi^*$  is more prominent. It means that the electronic transitions from 3p electronic orbitals to  $\pi^*$  molecular orbitals are allowed (Derkowska-Zielinska 2017). Alq<sub>3</sub> is a green emitter with photoluminescence observed in the range of 520 nm. Its emission occurs due to the transition from the highest occupied molecular orbit (HOMO), lying mainly on the phenoxide ring, to the lowest unoccupied molecular orbit (LUMO) located on the pyridyl ring (Lessmann and Hummelgen 2004). In Alq<sub>3</sub>, the optical transition responsible for PL is centred on the organic ligand, and the luminescent properties of this compound are mainly associated with the metal (Al)-nitrogen bond (Halls and Schlegel 2001).

Zinc oxide (ZnO) is a promising inorganic semiconductor material. Due to its excellent optical and electrical properties, it has the potential applications in light emitting diodes (LEDs), ultraviolet lasers, photodetectors and piezoelectric devices (Sypniewska et al. 2020). ZnO is n-type metal oxide semiconductor, which has a direct band gap (~ 3.37 eV at RT), large exciton binding energy (60 meV), high electron mobility and high optical transmittance (Sypniewska et al. 2020; Abed et al. 2015; Kapustianyk et al. 2007; Sofiani et al. 2007).

A polymeric material with unique properties, such as light weight, high flexibility and the possibility of production at low temperature and at low-cost, can be used to improve the quality of the thin composite layer (Dorranian et al. 2009). One of the most commonly used polymeric material is poly(methyl methacrylate) (PMMA). Its main advantages are excellent mechanical properties, high chemical resistance, simple synthesis, low-cost, good tensile strength, low optical loss in visible spectral range, good insulation properties and thermal stability. PMMA is considered to be

an excellent matrix material due to its good transparency (Suhailath et al. 2017; Derkowska-Zielinska et al. 2016; Ismail et al. 2012). The use of this polymer with Alq<sub>3</sub> was described by Ke-Qin et al. (Ke-Qin et al. 2008), as well as by Mahakhode et al. (Mahakhode et al. 2011). In both studies, the authors observed a blueshift in the luminescence of Alq<sub>3</sub> dispersed in PMMA matrix compared to pure Alq<sub>3</sub> film. The second polymer matrix used in this study was polyvinylpyrrolidone (PVP), which is attractive due to the strong affinity of the pyridine group and its ability to form a hydrogen bond with polar species (Kumar and Buddhudu 2014). Due to the fact that it binds very well with polar particles, it is used in coatings for photo-quality ink-jet papers (Aboud et al. 2009). The formation of transition metal particles inside the polymer system is of interest for some potential applications, such as laser systems, optical lenses and optical planar waveguides (Rzayev et al. 2008). The PVP polymer film has the ability to store charges in response to dopant-dependent optical properties and has a strong tendency to complex with various molecules (Sivaiah et al. 2010).

To develop a new hybrid organic-inorganic structures, which can be used in the production of novel OLED devices, we have prepared thin films containing ZnO, Alq<sub>3</sub> and ZnO:Alq<sub>3</sub> in polymer matrix (PVP or PMMA) by a dip-coating method. Prepared samples were characterized with AFM, SEM, EDX, FTIR spectroscopy, SE and PL. In this studies, we investigated which of the used polymers permits to create more homogeneous and uniform layers, and above all, how (and if) homogeneously Alq<sub>3</sub> and ZnO are embedded in these matrices.

## Experimental

### Materials

Alq<sub>3</sub>, PMMA and PVP (M<sub>w</sub> ~ 40 000 g/mol) powders were purchased from Sigma-Aldrich. PMMA was dissolved in tetrahydrofuran (THF) for 7 days forming a 0.2% solution. The 5% PVP solution was obtained by adding polymer powder to isopropanol (Chempur, pure p.a.) and mixed in an ultrasonic cleaner for 30 min.

To obtain the Alq<sub>3</sub> solution with the polymer, 0.02 g of tris(8-quinolinolato)aluminium powder was added to the previously prepared polymer solutions (10 mL) and placed in an ultrasonic bath for approximately 30 min. In the case of Alq<sub>3</sub>:PVP layers, the solution was left still for 24 h before deposition.

To obtain a ZnO:Alq<sub>3</sub>:polymer suspension, 5 mg of ZnO powder was added to the Alq<sub>3</sub>:polymer solutions (10 mL). Then, the Alq<sub>3</sub>:polymer solution with added ZnO powder was placed in an ultrasonic bath for 30 min. ZnO powder was prepared using the sol-gel method described in detail

elsewhere (Sypniewska et al. 2020) and annealed from the obtained sol at 500 °C. It should be mentioned that to prepare the sol solution, the zinc acetate dihydrate (Merck) and monoethanolamine (MEA, Sigma-Aldrich, 99.5%) were added to isopropanol alcohol (Chempur, pure p.a.). The sol solution was then heated to 70 °C with continuous stirring and maintained at this temperature for 60 min (Sypniewska et al. 2020).

### Thin films preparation

Thin films of polymers, ZnO:polymers, Alq<sub>3</sub>:polymers and ZnO:Alq<sub>3</sub>:polymers were deposited on a p-Si (100) substrate by dip-coating method (Qualtech QPI-168, Denver, CO, USA) at a substrate withdrawal speed equal of 10 mm/min. The obtained layers were dried at room temperature in an ambient atmosphere for 24 h. The thickness of the thin layers was about 100 nm (the exact values are given in Table 2).

### Measurement methods and equipments

The FTIR spectra were measured using FT-IR Vertex 70 V with a Hyperion 1000/2000 microscope by Bruker Optik from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The luminescent properties of prepared thin layers on Si substrates were registered by the spectrometer FP-8200 in the range of 2.1–3.4 eV ( $\lambda_{\text{ex}} = 325$  nm, Xe lamp). The refractive indices ( $n$ ) and extinction coefficients ( $k$ ) were determined by the ellipsometric method using the V-VASE spectroscopic ellipsometer (J. A. Woollam Co., Inc.) (Skowronski et al. 2015). The ellipsometric azimuths  $\Psi$  and  $\Delta$  were recorded at the different three angles of incidence (65°, 70° and 75°). The dispersion properties of extinction coefficient ( $k$ ) and refractive index ( $n$ ) were parameterized using Gaussian oscillators and Tauc–Lorentz oscillators (for ZnO:polymer layers). The analysis of the surface topography of the studied films was performed using Atomic Force Microscopy (AFM, Veeco microscope, Plainview, NY, USA) with the following scan parameters: size 5 × 5 μm<sup>2</sup> with the scan rate of 1 Hz in the tapping mode. The mean surface roughness i.e. the average roughness ( $R_a = \frac{1}{N} \sum_{i=0}^N |y_i|$ ) and the root mean square

roughness ( $R_q = \sqrt{\frac{1}{N} \sum_{i=0}^N y_i^2}$ ) were determined using the NanoScope Analysis software. The quantities  $y_i$  and  $N$  used in  $R_a$  and  $R_q$  are the current surface height value and number of measured points, respectively. Scanning electron microscopy (SEM) studies were performed with a Quanta 3D FEG (FEI, Hillsboro, OR, USA) (EHT = 30 kV) instrument. Energy Dispersive X-ray spectroscopy (EDX) studies were performed with a Quantax 200 with XFlash 4010 detector by Bruker AXS (Germany).

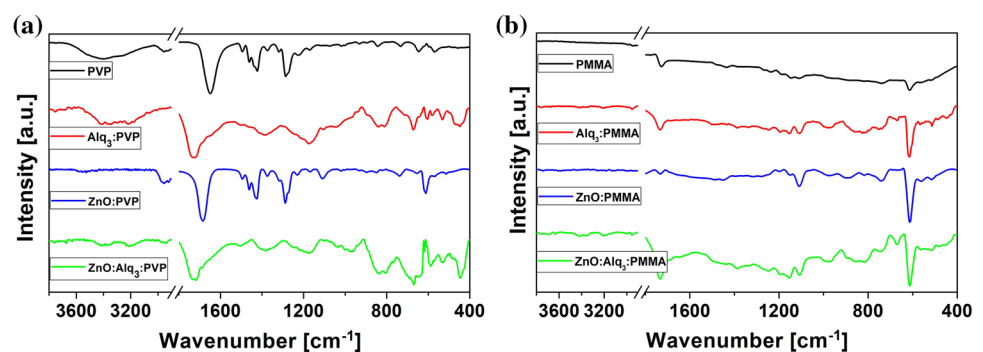
## Results and discussion

Thin films of pure polymers PVP and PMMA, Alq<sub>3</sub>:polymer (PVP or PMMA), ZnO:polymer (PVP or PMMA) and ZnO:Alq<sub>3</sub>:polymer (PVP or PMMA) composites were deposited on silicon substrates by dip-coating method. Isopropanol and tetrahydrofuran (THF) were used as solvents. It was found that isopropanol is a good solvent for PVP and Alq<sub>3</sub>, while THF (Bistac and Schultz 1997) was more suitable for PMMA and Alq<sub>3</sub> samples preparation. It should be noted that dip-coating method used for the production of thin films is not only a simple technique, but also very useful for creating smooth layers of composite materials (Cuba and Muralidharan 2014a; Szczesny et al. 2016).

FTIR spectra measured for thin films of pure polymers, Alq<sub>3</sub>:polymer (PVP or PMMA), ZnO:polymer (PVP or PMMA) and ZnO:Alq<sub>3</sub>:polymer (PVP or PMMA) composites are presented in Fig. 1. The peak positions and the assigned vibration modes are summarized in Table 1.

The characteristic vibration mode for pure Alq<sub>3</sub> layers are: a wide band observed around 3414 cm<sup>-1</sup> (caused by characteristic OH stretching vibrations), a band at 3047 cm<sup>-1</sup> (attributed to (C–H) stretching vibrations in the Alq<sub>3</sub> aromatic ring), a band at 1601 cm<sup>-1</sup> (C=C), bands at 1582 cm<sup>-1</sup>, 1491 cm<sup>-1</sup> and 1425 cm<sup>-1</sup> (result from the conjugated action of aromatic rings in the Alq<sub>3</sub> molecule), bands at 1370–1250 cm<sup>-1</sup> (C–N–C bond), band at 758 cm<sup>-1</sup> (Al–O–Al), bands at 557–644 cm<sup>-1</sup> (Al–O) and band at

**Fig. 1** FTIR spectra of thin layers of **a** pure PVP, Alq<sub>3</sub>:PVP, ZnO:PVP and ZnO:Alq<sub>3</sub>:PVP; **b** pure PMMA, Alq<sub>3</sub>:PMMA, ZnO:PMMA and ZnO:Alq<sub>3</sub>:PMMA



**Table 1** Peak positions and the assigned vibration modes for polymers and Alq<sub>3</sub>, ZnO and ZnO:Alq<sub>3</sub> thin layers in polymer matrices: PVP and PMMA (pp—peak position, vm—vibration mode)

PVP		Alq <sub>3</sub> :PVP		ZnO:PVP		ZnO:Alq <sub>3</sub> :PVP	
pp [cm <sup>-1</sup> ]	vm	pp [cm <sup>-1</sup> ]	vm	pp [cm <sup>-1</sup> ]	vm	pp [cm <sup>-1</sup> ]	vm
735	ρ(CH <sub>2</sub> )	445	ν(Al–N)	512	ν <sub>s</sub> (Zn–O)	436	ν(Al–N)
958	ν(C–O)	557;604;678	ν <sub>s</sub> (Al–O)	738	ρ(CH <sub>2</sub> )	457	ν <sub>s</sub> (Al–O)
996	ω(CH <sub>2</sub> )	585	δ(N–C=O)	1104	τ(CH <sub>2</sub> )	520	ν <sub>s</sub> (Zn–O)
1097	τ(CH <sub>2</sub> )	743	ν <sub>s</sub> (Al–O–Al)	1163	ν(C–O–C)	585	δ(N–C=O)
1172	ν(C–O–C)	813–836	δ(CH <sub>2</sub> )	1287	ν(C–O)	781	ν <sub>s</sub> (Al–O–Al)
1277	ν(C–O)	1032	δ(C–C)	1372	τ(CH <sub>2</sub> )	958	δ(C–C)
1377	τ(CH <sub>2</sub> )	1368	δ(C–H)	1687	ν(C=O)	1023	δ(C–C)
1732	ν(C=O)	3100–3600	ν(OH)	3000–2800	δ(C–H)	1163	ν <sub>s</sub> (C–OH)
2924	δ <sub>as</sub> (C–H)					1368	δ(C–H)
2943	δ <sub>as</sub> (C–H)					1730	ν(C=O)
						2933	ν(CH <sub>2</sub> )
						3200–3600	ν(OH)
PMMA		Alq <sub>3</sub> :PMMA		ZnO:PMMA		ZnO:Alq <sub>3</sub> :PMMA	
pp [cm <sup>-1</sup> ]	vm	pp [cm <sup>-1</sup> ]	vm	pp [cm <sup>-1</sup> ]	vm	pp [cm <sup>-1</sup> ]	vm
750	δ(C–C)	426	ν(Al–N)	512	ν <sub>s</sub> (Zn–O)	463	ν(Al–N)
836	ν(CH <sub>2</sub> )	613	ν <sub>s</sub> (Al–O)	738	ρ(CH <sub>2</sub> )	510	ν <sub>s</sub> (Zn–O)
986	δ(O–CH <sub>3</sub> )	750	δ(C–C)	816	ν(CH <sub>2</sub> )	557–604	ν <sub>s</sub> (Al–O)
1144	ν(C–O–C)	752	ν <sub>s</sub> (Al–O–Al)	970	δ(O–CH <sub>3</sub> )	752	δ(C–C)
1237	ν(C–O–C)	827	ν(CH <sub>2</sub> )	1150	ν(C–O–C)	790	ν <sub>s</sub> (Al–O–Al)
1433	δ(C–H)	995	δ(O–CH <sub>3</sub> )	1279	ν(C=O)	980	δ(O–CH <sub>3</sub> )
1489	ν(CH <sub>2</sub> )	1140	ν(C–O–C)	1448	ν(CH <sub>2</sub> )	1107	ν(C–OH)
1635	ν(C=O)	1218	ν(C–O–C)	1726	ν(C=O)	1144	ν(C–O–C)
1712	ν(C=O)	1256	ν <sub>s</sub> (C–N–C)			1247	ν <sub>s</sub> (C–N–C)
2853	δ(C–H)	1489	δ(C–H)			1386	δ(C–H)
2961	δ(C–H)	1732	ν(C=O)			1741	ν(C=O)
3000	δ(C–H)	2952	δ(C–H)			2961	δ(C–H)
		3100–3600	ν(OH)			3200	ν(OH)

about 460 cm<sup>-1</sup> (Al–N) (Cuba and Muralidharan 2014b). Typical bands for ZnO annealed at 500 °C are presented in Ref. (Sypniewska et al. 2020). From Fig. 1 and Table 1, we can see that in the FTIR spectrum of ZnO:Alq<sub>3</sub>:polymer thin film exists a contribution coming from the polymer matrix and the corresponding Alq<sub>3</sub> and ZnO bands. FTIR measurements thus confirm the presence of all constituent composites.

Figure 2 shows the topographic images for all studied samples obtained by the Atomic Force Microscopy, while Table 2 presents the calculated roughness parameters  $R_a$  and  $R_q$  (see also subsection 2.3).

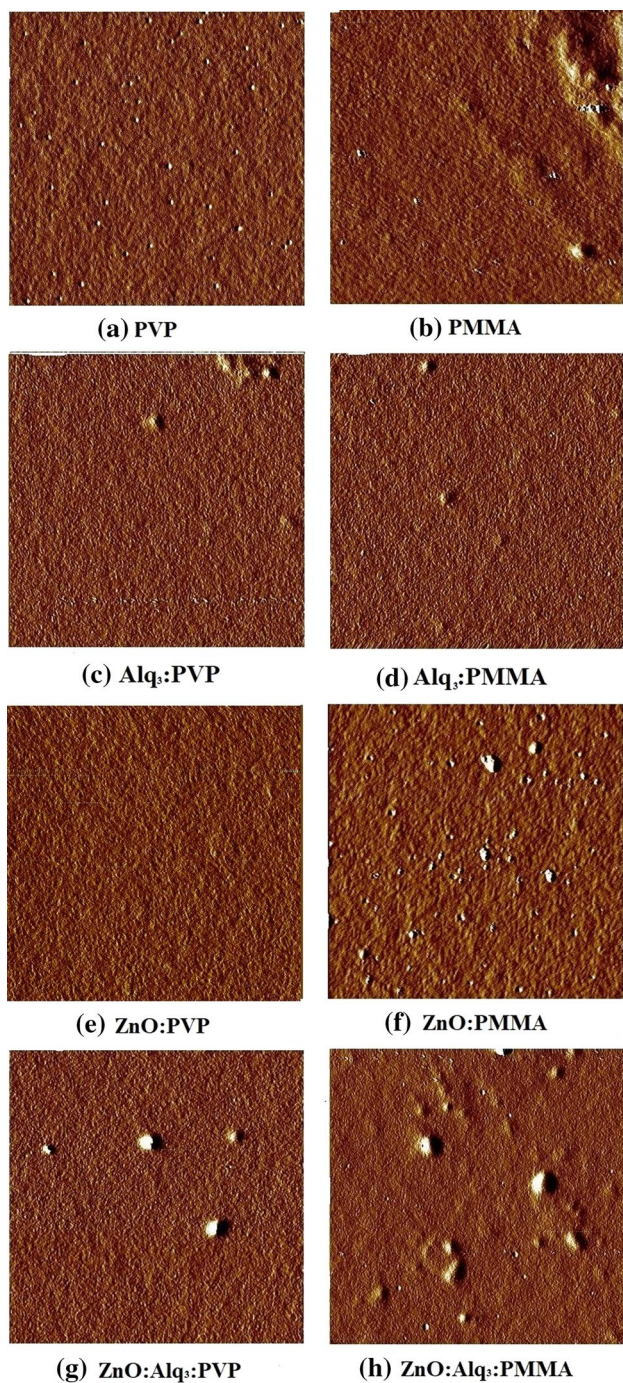
For the pure polymers, the parameter  $R_a$  is in the range of 1.3–2.5 nm, and  $R_q$  takes the values 1.8–3 nm. After adding Alq<sub>3</sub> and ZnO to the polymer matrices, a substantial increase in the  $R_a$  and  $R_q$  parameters is observed. In the case of ZnO:Alq<sub>3</sub> in PVP thin films, the island shape was scattered. Similar behavior was found by Kim et al. (2019). However, their obtained  $R_q$  value for the PVP–ZnO thin layer is 5.0 nm, which is slightly lower compared to our film.

The morphology of the investigated thin layers is shown in Fig. 3. These SEM images confirm that we obtained smooth layers for the PVP and PMMA polymers (see

Fig. 3a, b). ZnO particles visible in Fig. 3h are unevenly distributed on the surface of the samples. We found that for ZnO:polymer and ZnO:Alq<sub>3</sub>:polymer samples, the ZnO crystallite size is the largest for the PMMA polymer. The ZnO agglomerates in the PMMA polymer have a lateral size of about 2–3 μm. This is not evident in the PVP polymer as this polymer prevents the formation of agglomerates (Koczur et al. 2015). SEM micrographs for Alq<sub>3</sub>:PMMA and ZnO:Alq<sub>3</sub>:PMMA show Alq<sub>3</sub> agglomerates with elongated shape, which are not noticeable in the case of the PVP polymer.

EDX mapping analysis of ZnO:Alq<sub>3</sub>:PVP and ZnO:Alq<sub>3</sub>:PMMA are shown in Fig. 4. It should be mentioned that the EDX analysis complements the SEM and AFM studies. From these mapping, we can see how the individual particles containing Zn and Al in their composition are distributed on the sample surface. EDX shows that agglomerates containing Zn and Al are formed for the sample with the PMMA polymer, which is not observed for the PVP polymer matrix.

Spectroscopic ellipsometry (SE) allows determining the optical constants, such as the refractive index ( $n$ ) and the extinction coefficient ( $k$ ). These constants were determined



**Fig. 2** Surface topography obtained from AFM ( $5 \times 5 \mu\text{m}^2$ ) of: pure polymers **a** PVP, **b** PMMA, respectively; Alq<sub>3</sub> in the polymer matrix of: **c** PVP, **d** PMMA, respectively; ZnO in the polymer matrix of: **e** PVP, **f** PMMA, respectively; ZnO:Alq<sub>3</sub> in the polymer matrix of: **g** PVP, **h** PMMA

using the silicon/silicon oxide/Alq<sub>3</sub>:polymer layer/rough layer/ambient or silicon/silicon oxide/ZnO:Alq<sub>3</sub>:polymer layer/rough layer/ambient optical model of the sample. We used the Gaussian and Tauc–Lorentz oscillators (for

**Table 2** Values of roughness parameters  $R_q$  and  $R_a$ , as well as the values of a thickness ( $d$ ) and optical energy band gap ( $E_g$ )

Sample	$R_q$ [nm]	$R_a$ [nm]	$d$ [nm]	$E_g$ [eV]
PVP	3.0	2.5	–	–
Alq <sub>3</sub> :PVP	8.7	7.5	116 ± 1	2.74 ± 0.02
ZnO:PVP	8.9	8.5	135 ± 1	5.14 ± 0.04
ZnO:Alq <sub>3</sub> :PVP	8.8	12.0	110 ± 1	2.79 ± 0.02
PMMA	1.8	1.3	–	–
Alq <sub>3</sub> :PMMA	2.7	2.9	102 ± 1	2.99 ± 0.02
ZnO:PMMA	4.0	2.0	84 ± 1	4.45 ± 0.02
ZnO:Alq <sub>3</sub> :PMMA	10.8	8.6	114 ± 1	3.13 ± 0.03

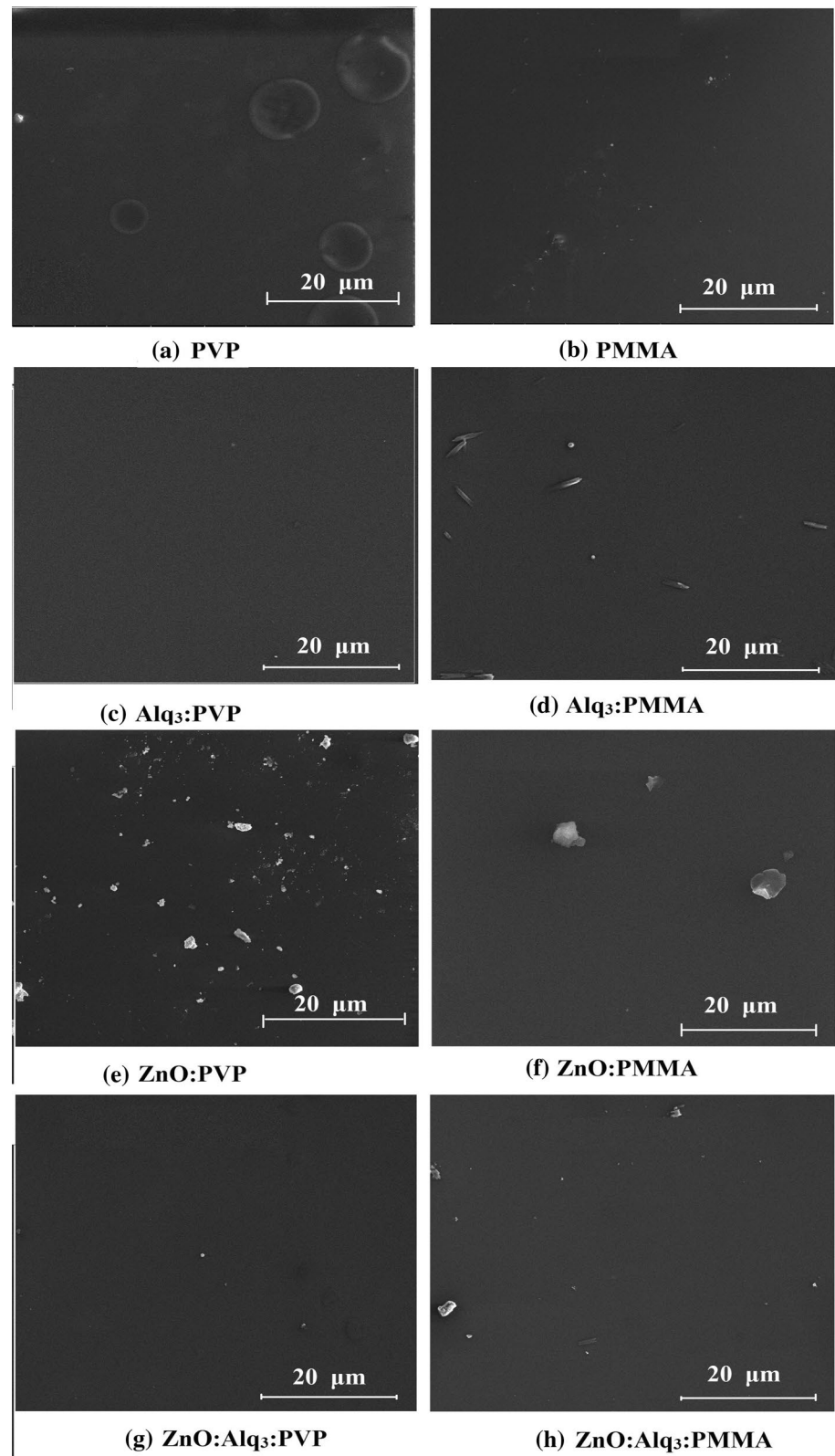
ZnO:polymer layers) to parametrize the dispersion properties of  $n$  and  $k$ .

Figure 5 presents the refractive index ( $n$ ) as a function of photon energy for all studied thin films. One can see that the refractive index exhibits normal dispersion in the spectral range up to 3.0–3.2 eV, and it shows anomalous dispersion at energies above 3.2 eV. Plots for ZnO:polymer show the shapes typical of PVP and PMMA polymers due to insufficient number of ZnO particles on the sample surface. In addition, we can notice that the values of the refractive index of ZnO:Alq<sub>3</sub>:PVP and ZnO:Alq<sub>3</sub>:PMMA are higher compared to Alq<sub>3</sub>:PVP, Alq<sub>3</sub>:PMMA, ZnO:PVP and ZnO:PMMA in normal dispersion region. We also found that the  $n$  values for Alq<sub>3</sub>:PVP, ZnO:PVP and ZnO:Alq<sub>3</sub>:PVP are higher compared to studied materials in PMMA matrix. Similar shapes of refractive index are obtained for Alq<sub>3</sub>:PVP and Alq<sub>3</sub>:PMMA, as well as for ZnO:Alq<sub>3</sub>:PVP and ZnO:Alq<sub>3</sub>:PMMA.

Figure 6 shows the extinction coefficient ( $k$ ) as a function of the photon energy for studied samples. In the spectra for two-component thin layers, Alq<sub>3</sub>:polymers, three bands are observed: two strong ones in the ranges of 2.3–3.7 eV and 4.3–5.2 eV and weak bands in the range of 3.7–4.3 eV. Band in region of 2.3–3.7 eV (called A band) is connected with a transition from a ground state to an excited state and is attributed to the  $\pi$ – $\pi^*$  excitation involving molecular orbitals of the quinolate ligands. The location of the second band 4.3–5.2 eV (B band) suggests the presence of a p-band associated with the central metal atoms, where the transition  $p$ – $\pi^*$  is more prominent. Weak bands in the range of 3.7–4.3 eV (called C and D bands) are identified with vibronic progression due to the deformation mode of the electron transition ring. These bands can be attributed to different electronic transitions than the main strong bands.

From Fig. 6, we can also see a redshift of only A band (i.e. from 3.1 to 3.3 eV) for Alq<sub>3</sub>:PVP compared to Alq<sub>3</sub>:PMMA. For samples ZnO:Alq<sub>3</sub>:polymer we observe only two main bands 2.2–4.3 eV and 4.3–5.3 eV. In addition, we can observe the redshift of extinction coefficient

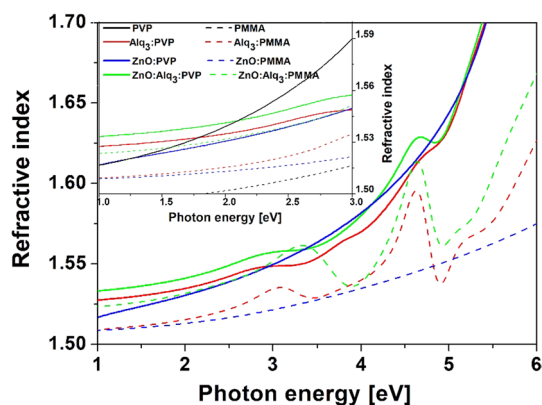
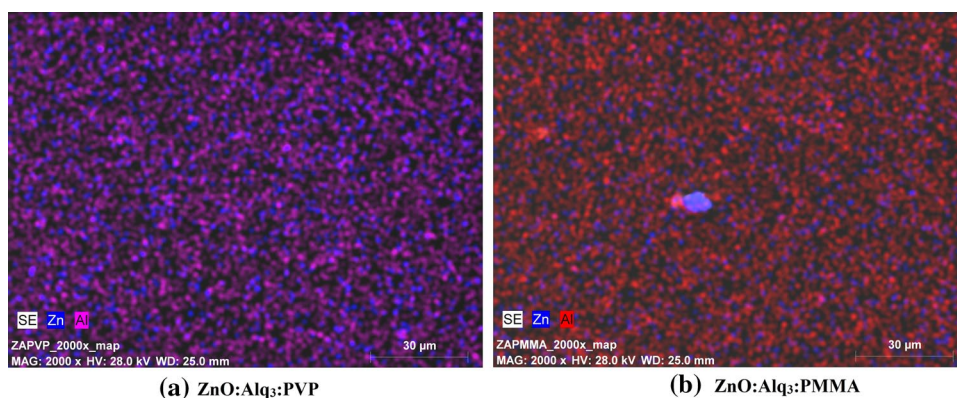
**Fig. 3** SEM micrographs of thin films of: pure polymers **a** PVP, **b** PMMA, respectively; Alq<sub>3</sub> in the polymer matrix of: **c** PVP, **d** PMMA, respectively; ZnO in the polymer matrix of **e** PVP, **f** PMMA, respectively; ZnO:Alq<sub>3</sub> in the polymer matrix of: **g** PVP, **h** PMMA, respectively



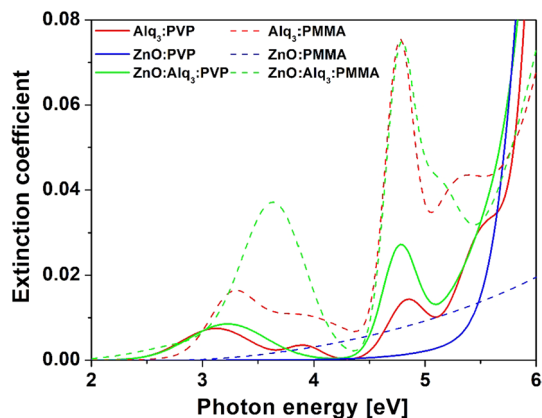
of ZnO:Alq<sub>3</sub>:PVP compared to ZnO:Alq<sub>3</sub>:PMMA. In addition, in the case of ZnO:Alq<sub>3</sub>:PMMA, an additional band at 5.2 eV can be seen due to visible band in Alq<sub>3</sub>:PMMA.

Figure 7 presents the Tauc plots of the studied thin films as a function of photon energy with the extrapolation of the linear part of the  $(\alpha h\nu)^2$  relation (where  $\alpha$  is

**Fig. 4** EDX mapping analysis images for **a** ZnO:Alq<sub>3</sub>:PVP and **b** ZnO:Alq<sub>3</sub>:PMMA thin films. The Zn particles are blue and Al are purple for the ZnO:Alq<sub>3</sub>:PVP sample (**a**) for the ZnO:Alq<sub>3</sub>:PMMA sample, Zn particles are also blue, while Al-containing areas are red (**b**)



**Fig. 5** Refractive index (*n*) versus photon energy for thin films Alq<sub>3</sub>, ZnO and ZnO:Alq<sub>3</sub> in PVP and PMMA polymer matrix, respectively



**Fig. 6** Extinction coefficient versus photon energy for thin films Alq<sub>3</sub>, ZnO and ZnO:Alq<sub>3</sub> in PVP and PMMA matrix

absorption coefficient calculated from  $\alpha = \frac{4\pi k}{\lambda}$ ). The determined values of optical energy band gap ( $E_g$ ) are shown in Table 2. Prepared thin layers of Alq<sub>3</sub> in a polymer matrix were found to exhibit the energy gap of 2.74 eV for PVP

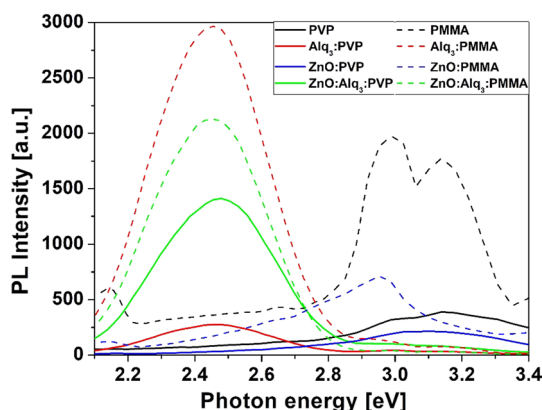
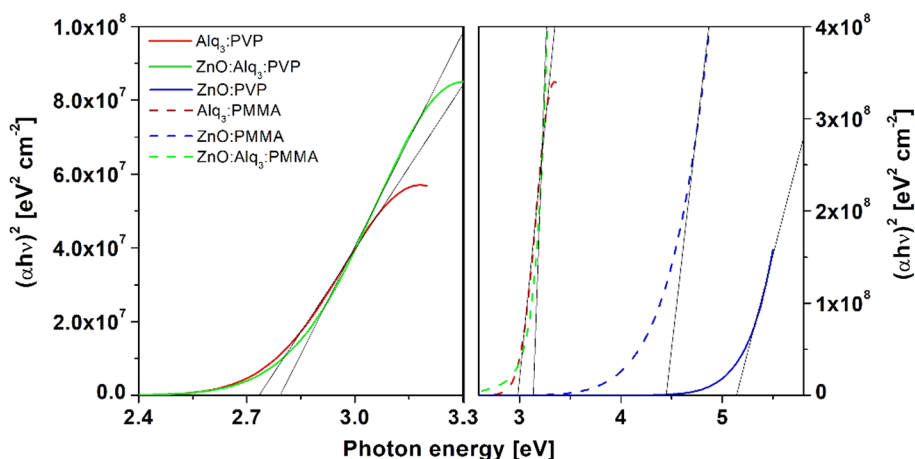
and 2.99 eV for PMMA. These values are similar to those reported by Cuba et al. (Cuba and Muralidharan 2014b), i.e.  $E_g = 2.87$  eV for Alq<sub>3</sub> film prepared by dip-coating method. For ZnO:Alq<sub>3</sub>:polymer thin layers, the energy gap were determined as 2.79 eV for the PVP polymer matrix, and 3.13 eV for the PMMA polymer. Increasing the optical energy gap has the effect of shifting the absorption threshold toward the shorter wavelengths, along with the decreasing particle size. This relationship is called the quantum size effect. It also leads to an increase in the molar absorption coefficient, which is related to the overlapping of the wave functions of the charge carriers (Trindade et al. 2001). We found that the values of  $E_g$  are 5.14 eV and 4.45 eV for the ZnO:PVP and ZnO:PMMA, respectively. These values are approximate for the literature values of energy band gaps in the range given by Baskoutas et al. (~5–7 eV) for the PVP polymer (Vempati et al. 2013; Baskoutas and Terzis 2006) and 4.9 eV for PMMA (Aziz et al. 2017).

Figure 8 shows the photoluminescence spectra for thin films of pure PVP and PMMA, Alq<sub>3</sub>:polymer (PVP or PMMA), ZnO:polymer (PVP or PMMA) and ZnO:Alq<sub>3</sub>:polymer (PVP or PMMA), which were obtained using an excitation wavelength of 325 nm at room temperature.

A typical Alq<sub>3</sub> luminescence spectrum is characterized by a single broad peak in the range of 2.13–2.75 eV with a maximum at ca. 2.38 eV (Cuba and Muralidharan 2014a). On the other hand, PL spectrum of ZnO layer demonstrates two bands: a strong emission band focused around 3.26 eV due to the emission of a free exciton and second band at 2.58 eV to 1.55 eV (yellow–orange emission) (Sypniewska et al. 2020). In the case of Alq<sub>3</sub>:polymer (PVP or PMMA) samples, it can be supposed that the final luminescence spectrum is the combination of the typical spectrum of the Alq<sub>3</sub> and the one of the pure polymer. The addition of polymer to Alq<sub>3</sub> caused the luminescence maximum to shift toward higher energies, 2.46 eV for PVP and 2.45 eV for PMMA. After the addition of ZnO, the maxima for the three-component layers were not changed. In the case of the ternary



**Fig. 7** Tauc plots of the studied thin films



**Fig. 8** PL spectra for PVP, PMMA, as well as Alq<sub>3</sub>, ZnO and ZnO:Alq<sub>3</sub> in PVP and PMMA polymer matrix, respectively

samples for PVP polymers, an increase in the intensity of luminescence can be noticed compared to the samples with Alq<sub>3</sub> alone. Such enhancement may result from compatible energy levels of the organic and inorganic material. They can also be attributed to the distortion caused by the incorporation of ZnO over the Alq<sub>3</sub> molecules (Cuba and Muralidharan 2014b).

## Conclusions

The main object of the present work was to develop a new hybrid organic–inorganic structure, which can be used in the production of innovative OLED devices.

The AFM and SEM measurements show that relatively smooth layers were obtained for the PVP and PMMA polymers. Thin layers with smooth surfaces of Alq<sub>3</sub>, ZnO and ZnO:Alq<sub>3</sub> were also successfully prepared in PVP and PMMA polymer matrices using the dip-coating method. In addition, the sizes of the visible ZnO crystallites in the

three-component samples change. The EDX analysis complements the SEM and AFM analyses showing how the individual Zn and Al particles are distributed on the sample surface. Spectroscopic ellipsometry was used to determine the refractive indices and extinction coefficients of the obtained two- and three-component layers. In the spectral range up to 3.0–3.2 eV, refractive index exhibits normal dispersion and in the energy above 3.2 eV it shows anomalous dispersion. For two-component thin layers, Alq<sub>3</sub>:polymer (PVP or PMMA), three bands are observed in the extinction coefficient: two strong ones in the ranges of 2.3–3.7 eV and 4.3–5.2 eV and weak bands in the range of 3.7–4.3 eV. For samples ZnO:Alq<sub>3</sub>:polymer, we can see two main bands 2.2–4.3 eV and 4.3–5.3 eV. In addition, the optical energy band gaps were determined for the thin layers under study and were equal to 2.74 eV and 2.99 eV for Alq<sub>3</sub>:PVP and Alq<sub>3</sub>:PMMA, respectively. For the three-component layers, we obtained the  $E_g$  values as 2.79 eV for the PVP polymer and 3.13 eV for the PMMA polymer. Measurements of PL of Alq<sub>3</sub> in polymer matrices under 325 nm excitation showed a blue shift in relation to pure Alq<sub>3</sub> layers.

In conclusion, after analysing the produced thin films and examining their optical and structural properties, we found that PVP would be a better polymer for OLED applications.

**Acknowledgements** M.S., A.A. and B. D.-Z. thank the NAWA PHC Polonium Project (No. BPN/BFR/2021/1/00036) for the financial support.

## Declarations

**Conflict of interest** There is no conflict of interest.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are

included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

## References

- Abed S, Bougharrar H, Bouchouit K, Sofiani Z, Derkowska-Zielinska B, Aida MS, Sahraoui B (2015) Influence of concentration of nano particles of Bi on the electrical and optical properties of ZnO thin films. *Superlattices Microstruct* 85:370–378. <https://doi.org/10.1016/j.spmi.2015.06.008>
- Aboud SR, Kareem A, Al-Bermayn J, Megahed N (2009) Effect of Temperature on Some Rheological Properties of Polyvinyl Pyrrolidone (PVP). *Egypt J Solids* 32:81–88. <https://doi.org/10.21608/EJS.2009.148779>
- Aziz SB, Abdullah OG, Hussein AM, Ahmed HM (2017) From Insulating PMMA polymer to conjugated double bond behavior: green chemistry as a novel approach to fabricate small band gap polymers. *Polymers* 9(11):1–15. <https://doi.org/10.3390/polym9110626>
- Baskoutas S, Terzis AF (2006) Size-Dependent Band Gap of Colloidal Quantum Dots. *J Appl Phys* 99(1):013708. <https://doi.org/10.1063/1.2158502>
- Bistac S, Schultz J (1997) Study of solution-cast films of PMMA by dielectric spectroscopy: influence of the nature of the solvent on and/ relaxations. *Int J Adhesion Adhesives* 17:197–201. [https://doi.org/10.1016/S0143-7496\(97\)00001-8](https://doi.org/10.1016/S0143-7496(97)00001-8)
- Boeckler C, Feldhoff A, Oekermann T (2007) Electrodeposited Zinc Oxide/Phthalocyanine Films – An Inorganic/ Organic Hybrid System with Highly Variable Composition. *Adv Funct Mater* 17:3864–3869. <https://doi.org/10.1002/adfm.200700619>
- Coe S, Woo WK, Bawendi M, Bulovic V (2002) Electroluminescence from single monolayers of nanocrystals in molecular organic devices. *Nature* 420:800–803. <https://doi.org/10.1038/nature01217>
- Cuba M, Muralidharan G (2014a) Effect of thermal annealing on the structural and optical properties of tris-(8-hydroxyquinoline) aluminum(III) (Alq<sub>3</sub>) films. *Luminescence* 30:1–6. <https://doi.org/10.1002/bio.2738>
- Cuba M, Muralidharan G (2014b) Enhanced luminescence properties of hybrid Alq<sub>3</sub>/ZnO (organic/inorganic) composite films. *J Lumin* 156:1–7. <https://doi.org/10.1016/j.jlumin.2014.07.008>
- Dalasiniski P, Łukasiak Z, Rebarz M, Wojdyła M, Bała W (2006) Study of optical properties of TRIS (8-hydroxyquinoline) aluminum (III). *Opt Mat* 28:98–101. <https://doi.org/10.1016/j.optmat.2004.10.031>
- Derkowska-Zielinska B (2017) Enhancement of third order nonlinear optical susceptibility of Alq<sub>3</sub> in polar aprotic solvents. *Opt Lett* 42:567–570. <https://doi.org/10.1364/OL.42.000567>
- Derkowska-Zielinska B, Krupka O, Smokal V, Grabowski A, Naparty M, Skowronski L (2016) Optical properties of disperse dyes doped poly(methyl methacrylate). *Mol Cryst Liq Crystals* 639:87–93. <https://doi.org/10.1080/15421406.2016.1254585>
- Dorranian D, Abedini Z, Hojabri A, Ghoranneviss M (2009) Structural and optical characterization of PMMA surface treated in low power nitrogen and oxygen RF plasmas. *J Non-Oxide Glasses* 1:217–229
- Duvenhage MM, Ntwaeaborwa OM, Swart HC (2015) Optical and chemical properties of Alq<sub>3</sub>:PMMA blended thin films. *Mater Today Proc* 2:4019–4027. <https://doi.org/10.1016/j.matpr.2015.08.031>
- Fong HH, So SK (2006) Hole transporting properties of tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>). *J App Phys* 100:1–5. <https://doi.org/10.1063/1.2372388>
- Halls MD, Schlegel BH (2001) Molecular Orbital Study of the First Excited State of the OLED Material Tris(8-hydroxyquinoline) aluminum(III). *Chem Mater* 13:2632–2640. <https://doi.org/10.1021/cm010121d>
- Ismail LN, Zulkefle H, Herman SH, Mahmood MR (2012) Influence of Doping Concentration on Dielectric, Optical, and Morphological Properties of PMMA Thin Films. *Adv Mater Sci Eng* 2012:1–5. <https://doi.org/10.1155/2012/605673>
- Kapustianyk V, Turko B, Kostruba A, Sofiani Z, Derkowska B, Dabos-Seignon S, Barwiński B, Eliyashevskiy Yu, Sahraoui B (2007) Influence of size effect and sputtering conditions on the crystallinity and optical properties of ZnO thin films. *Opt Commun* 269:346–350. <https://doi.org/10.1016/j.optcom.2006.08.034>
- Ke-Qin T, Chun-Xian X, Qiong W, Bao-Xiang G, Ke Z, Li-Hua Y, Xin-Song L (2008) Photoluminescence of Electrospun Poly-Methyl-Methacrylate:Alq<sub>3</sub> Composite Fibres. *Chin Phys Lett* 25:4453–4455. <https://doi.org/10.1088/0256-307X/25/12/075>
- Kim O, Kwon JB, Kim SW, Xu B, Seo KH, Park CE, Do WJ, Bae JH, Kang S (2019) Effect of PVP- capped ZnO nanoparticles with enhance charge transport on the performance of P3HT/PCBM polymer solar cells. *Polymers* 11:3–10. <https://doi.org/10.3390/polym11111818>
- Koczkur KM, Mourdikoudis S, Polavarapu L, Skrabalak SE (2015) Polyvinylpyrrolidone (PVP) in nanoparticle synthesis. *Dalton Trans R Soc Chem* 44:17883–17905. <https://doi.org/10.1039/C5DT02964C>
- Kumar KN, Buddhudu S (2014) Enhanced photoluminescence of Mn<sup>2+</sup>+Tb<sup>3+</sup>Ions doped PEO+PVP blended polymer films. *Proc Indian Nat Sci Acad* 80:345–354. <https://doi.org/10.16943/ptinsa/2014/v80i2/55112>
- Lessmann R, Hummelgen IA (2004) Thin copolymer-cased light-emitting display made with fluorine-foped tin oxide substrates. *Mater Res* 7:467–471. <https://doi.org/10.1590/S1516-14392004003000015>
- Mahakhode JG, Dhoble SJ, Joshi CP, Moharil SV (2011) Blue-shifted photoluminescence of Alq<sub>3</sub> dispersed in PMMA. *Bull Mater Sci* 34:1649–1651. <https://doi.org/10.1007/s12034-011-0372-1>
- Onlaor K, Tunhoo B, Thiawong T, Nukeawa J (2012) Electrical bistability of tris-(8- hydroxyquinoline) aluminum (Alq<sub>3</sub>)/ZnSe organic-inorganic bistable device. *Curr Appl Phys* 12:331–336. <https://doi.org/10.1016/j.cap.2011.07.004>
- Rzayev ZMO, Denizli BK, Denizli H (2008) Bioengineering functional Copolymers. XI. Copper (II)-Poly (N-vinyl-2-pyrrolidone-N-isopropylacrylamide) macro complexes. *J Appl Polym Sci* 109:903–909. <https://doi.org/10.1002/app.26329>
- Sanchez C, Belleville BJP, Popall M (2005) Applications of hybrid organic–inorganic nanocomposites. *J Mater Chem* 15:3559–3592. <https://doi.org/10.1039/B509097K>
- Sivaiah K, Rudramadevi B, Buddhudu S, Kumar G (2010) Structural, thermal and optical properties of Cu<sup>2+</sup> and Co<sup>2+</sup>: PVP polymer films. *Indian J Pure Appl Phys* 48:658–662
- Skowronski L, Krupka O, Smokal V, Grabowski A, Naparty M, Derkowska-Zielinska B (2015) Optical properties of coumarins containing copolymers. *Opt Mat* 47:18–23. <https://doi.org/10.1016/j.optmat.2015.06.047>
- Sofiani Z, Sahraoui B, Addou M, Adhiri R, Alaoui M, Dghoughi L, Fellahi N, Derkowska B, Bała W (2007) Third harmonic generation in undoped and X doped ZnO films (X: Ce, F, Er, Al, Sn) deposited by Spray Pyrolysis. *J Appl Phys* 101:1–5. <https://doi.org/10.1063/1.2711143>

- Suhailath K, Ramesan MT, Naufal B, Periyat P, Jasna VC, Jayakrishnan P (2017) Synthesis, characterisation and flame, thermal and electrical properties of poly (n-butyl methacrylate)/titanium dioxide nanocomposites. *Polym Bull* 74:671–688. <https://doi.org/10.1007/s00289-016-1737-9>
- Sypniewska M, Szczesny R, Popielarski P, Strzałkowski K, Derkowska-Zielinska B (2020) Structural, morphological and photoluminescent properties of annealed ZnO thin layers obtained by the rapid sol-gel spin-coating method. *Opto-Electron Rev* 28:182–190. <https://doi.org/10.24425/opelre.2020.134460>
- Szczesny R, Szlyk E, Wisniewski MA, Hoang TK, Gregory DH (2016) Facile preparation of copper nitride powders and nanostructured films. *J Mater Chem C* 4:5031–5037. <https://doi.org/10.1039/C6TC00493H>
- Tang CW, Van Slyke SA (1987) Organic electroluminescent diodes. *Appl Phys Lett* 51:913–915. <https://doi.org/10.1063/1.98799>
- Trindade T, O'Brien P, Pickett NL (2001) Nanocrystalline semiconductors: synthesis, properties, and perspectives. *Chem Mat* 13:3843–3858. <https://doi.org/10.1021/cm000843p>
- Vempati S, Ertas Y, Uyar T (2013) Sensitive surface states and their passivation mechanism in CdS Quantum Dots. *J Phys Chem C* 117:21609–21618. <https://doi.org/10.1021/jp408160h>
- Yoshida T, Zhang J, Komatsu D, Sawatani S, Minoura H, Pauporte T, Lincot D, Oekermann T, Schlettwein D, Tada H, Wohrle D, Funabiki K, Matsui M, Miura H, Yanagi H (2009) Electrodeposition of inorganic/organic hybrid thin films. *Adv Funct Mater* 19:17–43. <https://doi.org/10.1002/adfm.200700188>

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.