

# Synthesis and investigation of photonic properties of surface modified ZnO nanoparticles with imine linked receptor as coupling agent- for application in LEDs

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**Abstract** Wet chemical precipitation route is developed for the synthesis of ZnO nanoparticles using a dipodal receptor as capping agent to control the size and shape of ZnO nanoparticles and also to passivate the surface defects. The capping of ZnO nanoparticles with dipodal receptor is characterized with NMR and IR spectroscopy. EDX analyses also confirmed the presence of organic receptors together with ZnO nanoparticles. The morphology and size of surface modified ZnO nanoparticles is checked by SEM, TEM and DLS spectroscopic techniques. The surface decorated ZnO nanoparticles demonstrate emission peak at 333 nm. The emission peak at 333 nm in case of surface capped ZnO demonstrate fewer surface defects present in comparison to their bulk counterpart, where blue, red, green, yellowish green emission peaks are present. The photophysical studies of ZnO nanoparticles are further carried in presence of metal ions where it is observed that the binding with Mn(II) result in increase in fluorescence intensity. The three fold increase in fluorescence intensity of ZnO nanoparticles in presence of Mn(II) can be utilized in case of lighting devices, where high quantum yield is desirable. To the best of our knowledge, this manuscript

represents the first surface decorated ZnO nanoparticles for their application in lighting devices.

## 1 Introduction

The fabrication of light emitting diodes and the design of high speed optoelectronic device desire a semiconductor material with direct band gap, high carrier mobility, high carrier velocity, high breakdown field strength and so suitable for optoelectronic applications. ZnO possessing all these properties and due to its versatility and multifunctionality has created interest in the research field [1]. Even though operated for a very long time, it is only during the last decade that zinc oxide (ZnO) has been the focus of research in relation to promising optoelectronic applications of this material. Much of the research effort these days is focused in finding the materials to realize UV lighting device. ZnO with band gap 3.37 eV, exciton binding energy 60 meV (2.4 times that of GaAs) can find extensive photonic applications especially for UV light emitting diode (LED) [2–4]. In addition, the application of lead and cadmium chalcogenides in lighting devices (and other electronic applications) is not feasible because of environmental regulations [5–7]. The concerns about the potential toxicity and environmental impact of these compounds, desires the hunt for alternative materials. ZnO with large exciton binding energy is able to persist at room temperature and higher too [8]. Other advantage of ZnO based materials is that it is a non-toxic, biodegradable and a cheap material [9, 10]. ZnO nanoparticles are chemically stable, have high optical transparency and are easy to synthesize. The easy synthesis, cheap fabrication and enhanced optical properties of ZnO nanoparticles have led its use as next generation LEDs [11–14]. The researchers worldwide are

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making effort to enhance luminous efficiency of inorganic LED, so that its performance can approach that of organic light emitting diodes (OLEDs). ZnO materials exhibit two types of emissions: UV emission due to excitonic transitions and broad emission in the visible region due to the deep level transitions [15, 16]. The deep level emission given by ZnO covers the wide range of visible spectrum due to green, blue, yellow, bluish yellow luminescence in the PL spectra, and theoretically, white emission can be obtained [17–20]. The deep level emission appearing in the visible region is owed to the presence of defects on the surface of ZnO [21–23]. In order to improve the luminescence of ZnO nanoparticles and for the device application in UV ranges, the emission due to the deep level transitions need to be censored. As the surface-to-volume ratio of nanoparticles is very high, the surface states play a key role on optical absorption, luminescence and detection in determining the electrical and optoelectronic properties of ZnO nanoparticles based nano-devices [24–29]. ZnO can be synthesized using different techniques, importantly the surface defects are required to be noticed which increases as the size of nanoparticle reduces. The high surface energy also leads to the agglomeration in nanoparticles [30]. The surface modification using capping agent leads to the passivation of both radiative and non-radiative recombination sites on the surface of nanoparticle. The capping monolayer of organic receptor over ZnO nanoparticle surface can also avoid agglomeration and thus reduces the defects on its surface as it stops the growth of ZnO nanoparticles immediately soon the nucleation stage [31–36]. In this research paper, we propose an imine linked dipodal organic receptor that is used to modify the surface of ZnO nanoparticles and provide new insight into the emission of surface functionalized ZnO nanoparticles for their application in lighting devices. The photo physical properties of surface modified ZnO nanoparticles were studied. The effect of metal nitrate salts on the photophysical properties of imine linked ZnO nanoparticles was further explored. Reduction in the band gap is observed in the case of receptor directed ZnO nanoparticles. Theoretical investigation of the system is also carried out using DFT computational calculations in order to explain the experimental data. The geometry of organic receptor was optimized using DFT Gaussian 03 software. DFT calculations were run again to study the effect of capping agent on the ZnO nanoparticles and it was observed that the interaction of organic receptor with the surface of ZnO nanoparticles has resulted in static conformal geometry as the free rotation of the ligand is restricted, which ultimately led to the increase in the selectivity of nanoparticles. So, an increase in the fluorescence intensity was observed when Mn(II) was added to surface modified ZnO nanoparticles. Surface modified ZnO nanoparticles functionalized with Mn(II) for high quantum yield and narrow

emission line width are proposed as an emitter to achieve pure UV electroluminescence.

## 2 Experimental section

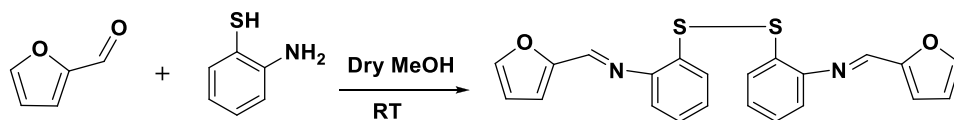
### 2.1 Chemicals and methods

Zinc nitrate hexahydrate, Sodium hydroxide, 2-furan-carboxaldehyde and 2-aminothiophenol were purchased from Sigma Aldrich and were used without further purification.  $^1\text{H}$  NMR spectra of organic receptor and ZnO coated with organic receptor were obtained from JNM-ECS400 (JEOL) NMR spectrophotometer at 400 MHz. An Agilent 7700 Series ICP-mass spectrometer was used for the determination of the masses of the compounds. The elemental and morphology analysis were carried out with scanning electron microscope (SEM JEOL JSM-6610LV) at 15 kV voltage. TEM images were recorded on Hitachi instrument (H-7500) at 100 kV. For TEM measurements the organic receptor coated ZnO nanoparticles were dispersed homogeneously in methanol solvent using ultrasonic treatment. A tiny drop of this solution was direct on to a carbon-coated copper grid followed by subsequently drying in air before transfer it in to microscope. The particle size was determined using Dynamic Light Scattering (DLS), with the external probe feature of a MetrohmMicrotrac Ultra Nanotracer Particle Size Analyzer. FTIR spectrophotometer Thermo Fisher Scientific Inc., USA was used to confirm the functional groups of organic receptor and to observe shift in the bands on surface modified ZnO nanoparticles. The sample used for this measurement was in the form of pellets prepared by mixing 1% weight of nanoparticles with KBr. Perkin Elmer LS55 Fluorescence spectrophotometer was used to carry out the fluorescence measurements. DFT calculations were performed on Gaussian 03 program by using B3LYP/6-311G basis set.

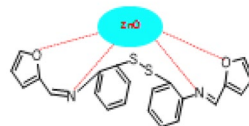
### 2.2 Synthesis of organic receptor and coating on ZnO

The organic receptor was synthesized by condensation reaction between 2-furan-carboxaldehyde (0.83 ml, 10 mmol) and 2-aminothiophenol (1.07 ml, 10 mmol) in dry methanol (30 ml) under  $\text{O}_2$  and basic conditions (Scheme 1). After completion of reaction, the precipitates were filtered and washed with methanol a number of times to get rid of impurities. The resultant yellow solid fine particles were dried for 40 h. ZnO nanoparticles (Scheme 1) were synthesized by taking an alcoholic solution of zinc nitrate hexahydrate (0.2472 mmol, 0.073 g) along with organic receptor (0.4944 mmol, 0.2 g) in round bottom flask. The reaction was kept on continuous stirring at room temperature. Alcoholic solution of sodium hydroxide

**Scheme 1** ZnO nanoparticles capped with receptor 1



**Synthesis of organic receptor 1**



(0.3708 mmol, 0.0148 g) was then added drop by drop. The stirring of the solution was kept continuous for 8 h and a dispersion of ZnO nanoparticles were gradually formed in the solution. The as prepared dispersion of ZnO nanoparticles was filtered and washed with methanol and water several times. The resultant fine nanoparticles were then dried for 40 h.

### 3 Results and discussion

The ligand was fully characterized by mass spectroscopic technique ESI-MS, which shows  $m/z=427.5 [M+Na]^+$ , where  $M=C_{22}H_{16}N_2O_2S_2$  (Fig. 1a) and  $^1H$  NMR.  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 6.6 (t, 2 H, ArH,  $J=1.72$  Hz), 7.1 (d, 2 H, ArH,  $J=6.08$  Hz), 7.16–7.18 (m, 6 H, ArH), 7.66 (t, 4 H, ArH,  $J=1.56$  Hz), 8.3 (s, 2 H,  $-CH=N-$ ) (Fig. 1b). DFT calculations were performed using Gauss View 03 software. DFT calculations were made to realize the optimized structure of the organic receptor and also to find the band gap. The optimized structure (Fig. 1c) has band gap of 3.59 eV.

#### 3.1 Characterization of surface passivated ZnO nanoparticles

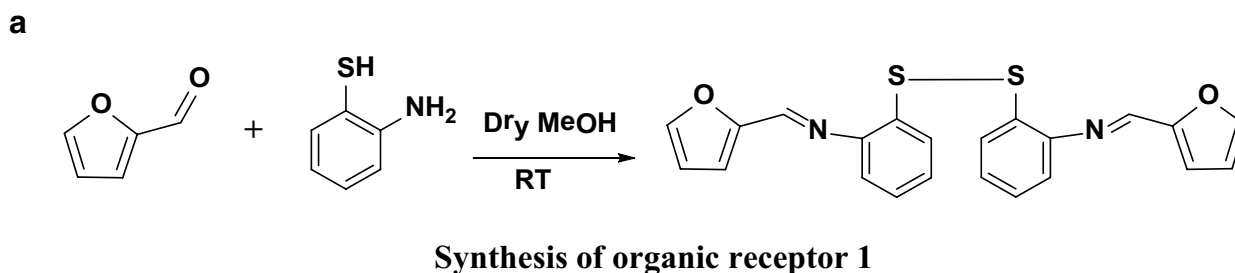
The surface of ZnO nanoparticles was coated with an organic receptor in order to get rid of the surface defects. The capping monolayer improved the photoluminescence characteristics of ZnO nanoparticles which otherwise demonstrated broad emission. The surface passivated ZnO nanoparticles were characterized using  $^1H$  NMR, where shift in the peaks were observed (Fig. 2).

The imine linked dipodal receptor used as capping monolayer over ZnO nanoparticle must have attached in a symmetrical manner. Scanning Electron Microscopy (SEM) was used to study the morphology of the ZnO nanoparticles. The SEM image demonstrated that the synthesized ZnO nanoparticles are spherical in shape. Inset shown in Fig. 3b clearly demonstrate the spherical nature of ZnO

nanoparticles. The elemental analysis was done using energy dispersive X-ray spectrum (EDX), which confirmed the coating of organic receptor over the surface of ZnO nanoparticles (Fig. 3c). The image demonstrated the presence of elements C, N, S of organic compound along with Zn and O. The structure and size of ZnO nanoparticles was obtained using Transmission Electron Microscopy (TEM), which demonstrated the spherical ZnO nanoparticles with average size 50 nm (Fig. 3d). The distribution of particle size of organic ligand directed ZnO nanoparticles (1.ZnO), showing average particle size of 67 nm, was measured with DLS based particle size analyzer (Fig. 3d) by dissolving the compound in DMSO:H<sub>2</sub>O (70:30; v/v). DLS was showing somewhat larger particle size as compared to TEM analysis due to hydro- dynamic radius of nano- aggregates during DLS analysis. The structural analysis of surface passivated ZnO nanoparticles was also supported through the IR spectrum, where a series of peaks were observed from 400 to 4000  $cm^{-1}$  (Fig. 3f). The IR spectrum of imine-linked organic ligand 1 (above) exhibits a band at 1618  $cm^{-1}$  due to the stretching of imine linkage ( $-CH=N$ ) and a band at 1620  $cm^{-1}$  was observed which is assigned as the band due to imine linkages of organic receptor-coated on ZnO (below). Shift in the peaks was observed in the IR spectra of surface decorated ZnO nanoparticles (below) in comparison to the IR spectra of organic receptor (above). These shifts may be related to the change in the bond length of Zn–O in the nanoparticles. Broadening of all signals also substantiate the binding of receptor 1 on the surface of ZnO. So, it was clear that the influence of capping agent exists and ZnO electronic environment has been modified.

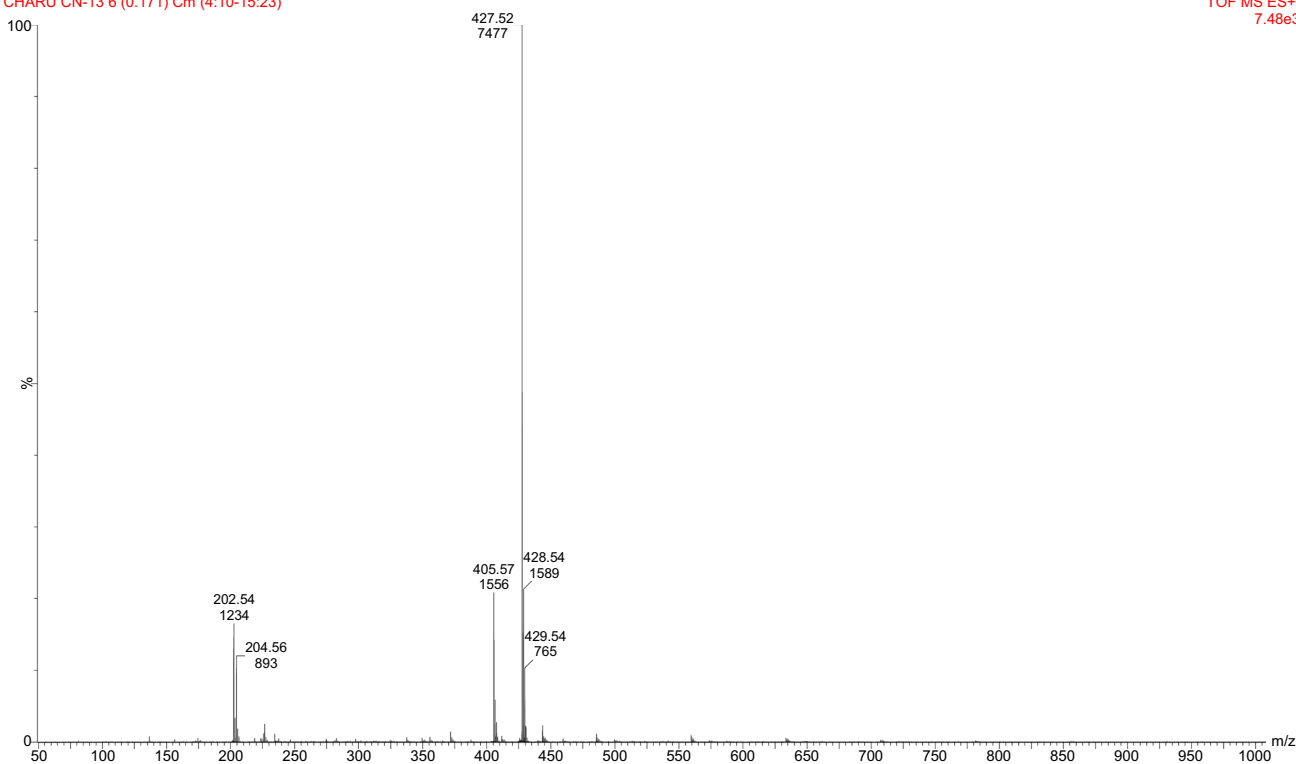
#### 3.2 Theoretical investigation of surface modified ZnO using DFT

To demonstrate the influence and interactions of imine linked capping agent with ZnO nanoparticles surface, DFT calculations were run. A comparison is made between the optimized geometry of an organic receptor and organic receptor with ZnO cluster. A clear change in the geometry



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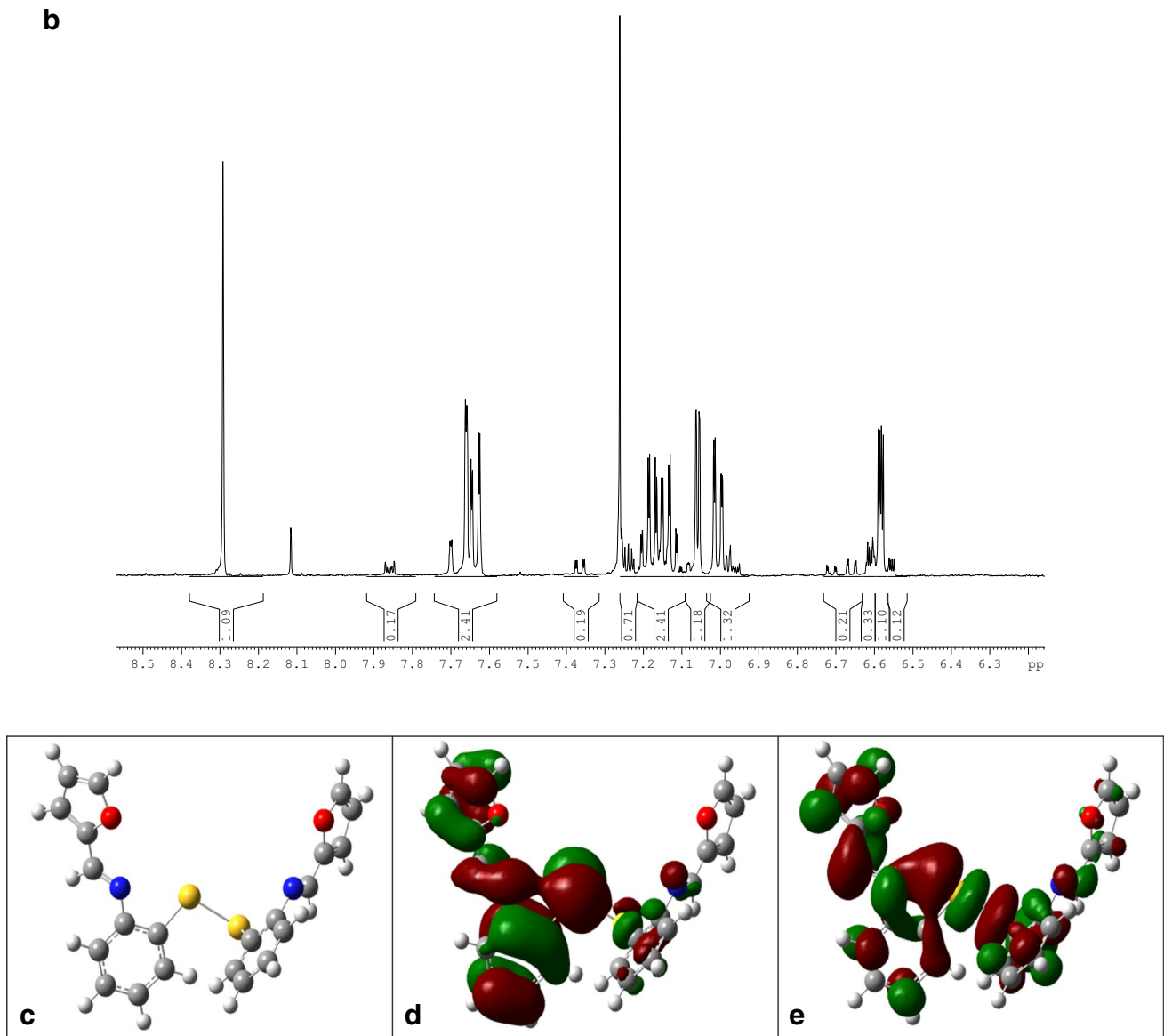


**Fig. 1** **a** Mass spectra of organic ligand showing peak at 427.52, **b**  $^1\text{H}$  NMR of organic ligand, **c** DFT optimized structure of organic receptor, **d** HOMO of organic receptor, **e** LUMO of organic receptor

is demonstrated (Fig. 3a, b). The optimized geometry of dipodal receptor used as capping monolayer had both arms perpendicular to each other in the absence of ZnO nanoparticles represented by a small cluster ( $\text{ZnO}$ )<sub>5</sub>.

Change in the geometry was observed when dipodal receptor was taken in environment of ZnO nanoparticles. Both arms of the organic receptor came closer in the presence of ZnO nanoparticles (Fig. 3b). The optimized geometry clearly demonstrated the development of a fix cavity between the two arms closer to the disulphide bond. So, ZnO offers a size-specific preorganized cavity

for ion interaction. It can be inferred that the interaction of organic receptor with the surface of ZnO nanoparticles has resulted in static conformal geometry as the free rotation of the ligand would have restricted, which ultimately may lead to the increase in the selectivity of nanoparticles. The HOMO densities are completely concentrated on ( $\text{ZnO}$ )<sub>5</sub> cluster with LUMO densities concentrated on the organic receptor. The DFT optimized geometry also showed that the two arms of organic receptor which were initially perpendicular to each other now came closer to one another.

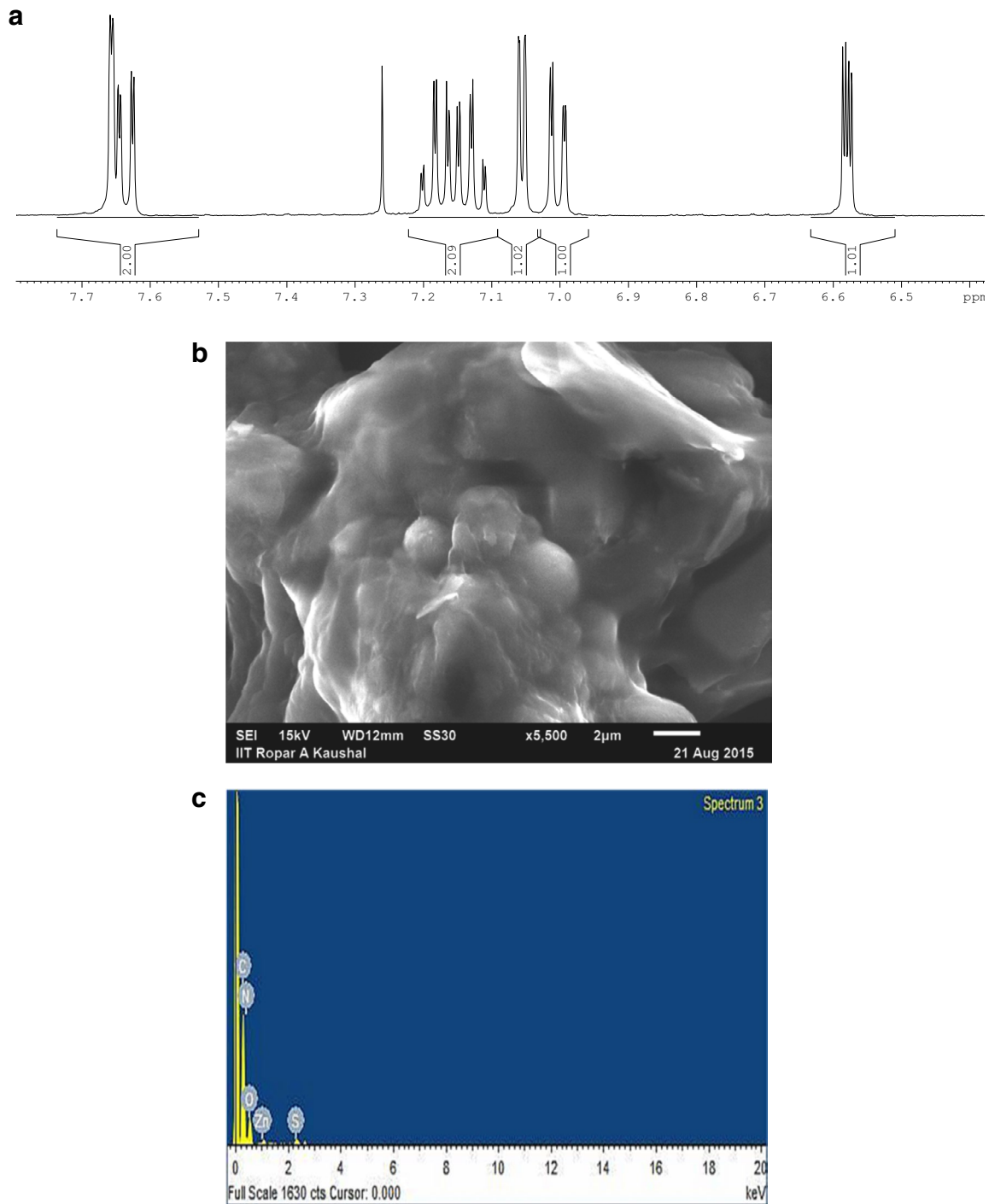


**Fig. 1** (continued)

### 3.3 Photoluminescence studies of surface passivated ZnO nanoparticles

ZnO semiconductor nanoparticles demonstrate two types of emission: the emission in the visible region due to the deep level transitions and the emission in the UV region due to the excitonic transitions. The presence of defects on the surface of pure ZnO nanoparticles result in deep level transitions. The presence of defects introduces different electronic levels within the band gap, which result in electronic transitions by these levels. The optoelectronic property of metal oxide semiconductor will improve if the broad emission in the visible region due to the surface defects could get censored. The PL emission spectrum of surface

modified ZnO nanoparticles excited at 293 nm was obtained and it showed emission at 333 and 350 nm. A single peak at 333 nm was observed in the case of surface improved ZnO nanoparticles with a shoulder at 350 nm, whereas the pure ZnO nanoparticles demonstrate broad emission due to green, blue, yellow, bluish yellow luminescence in the PL spectra. The visible emission band is explained on the basis of formation of a recombination center ( $\text{Vo}^{**}$ ), where the valence band hole is trapped by the surface state and then tunnels back into oxygen vacancies containing one electron ( $\text{Vo}^*$ ). This recombination of a shallow trapped electron with a deeply trapped hole in a  $\text{Vo}^{**}$  center is responsible for visible emission [37]. For the use of ZnO nanoparticles in devices like LEDs, the selectivity factor is



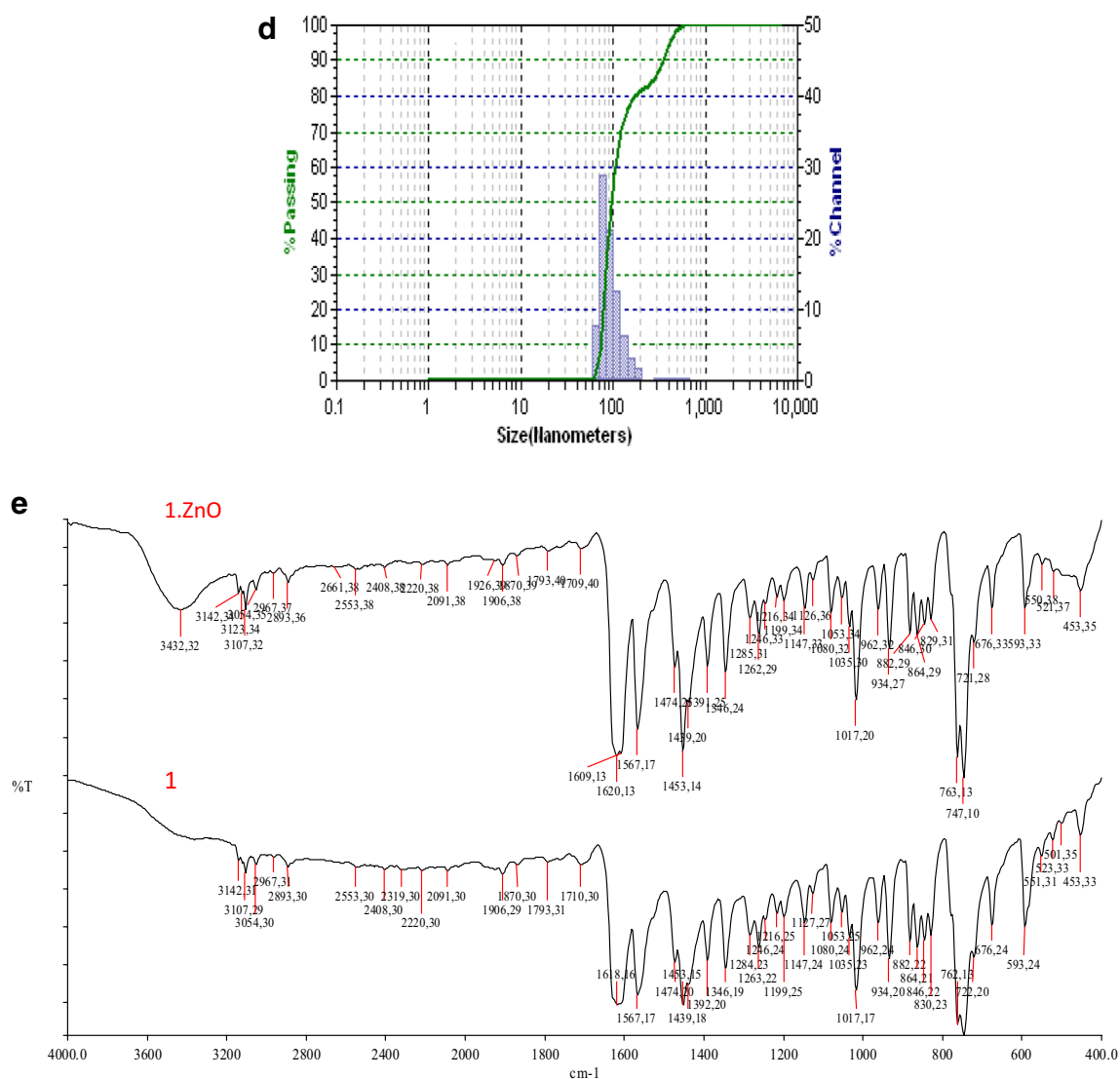
**Fig. 2** **a**  $^1\text{H}$  NMR of ZnO capped with an organic ligand (1.ZnO), **b** SEM image of 1.ZnO showing spherical structure, **c** EDX image of 1.ZnO showing the presence of organic compound together with

Zn and O, **d** DLS based particle size analyzer showing particle size of 67 nm, **e** A comparison of FTIR spectrum of organic receptor 1 (below) and ZnO capped with organic receptor 1 (above)

important. The broad emission in the visible range owing to the presence of surface defects may result in the white light by combination of all the emitted colors from pure ZnO nanoparticles [38–41]. However, if the specific color is desired, the broad emission in the visible region needs

to be improved. The capping monolayer of organic receptor was used to decorate the surface of ZnO nanoparticles, so that the defect originated emission could be avoided. Figure 4a showed the room temperature PL spectra with emission at 333 and 350 nm from surface improved ZnO



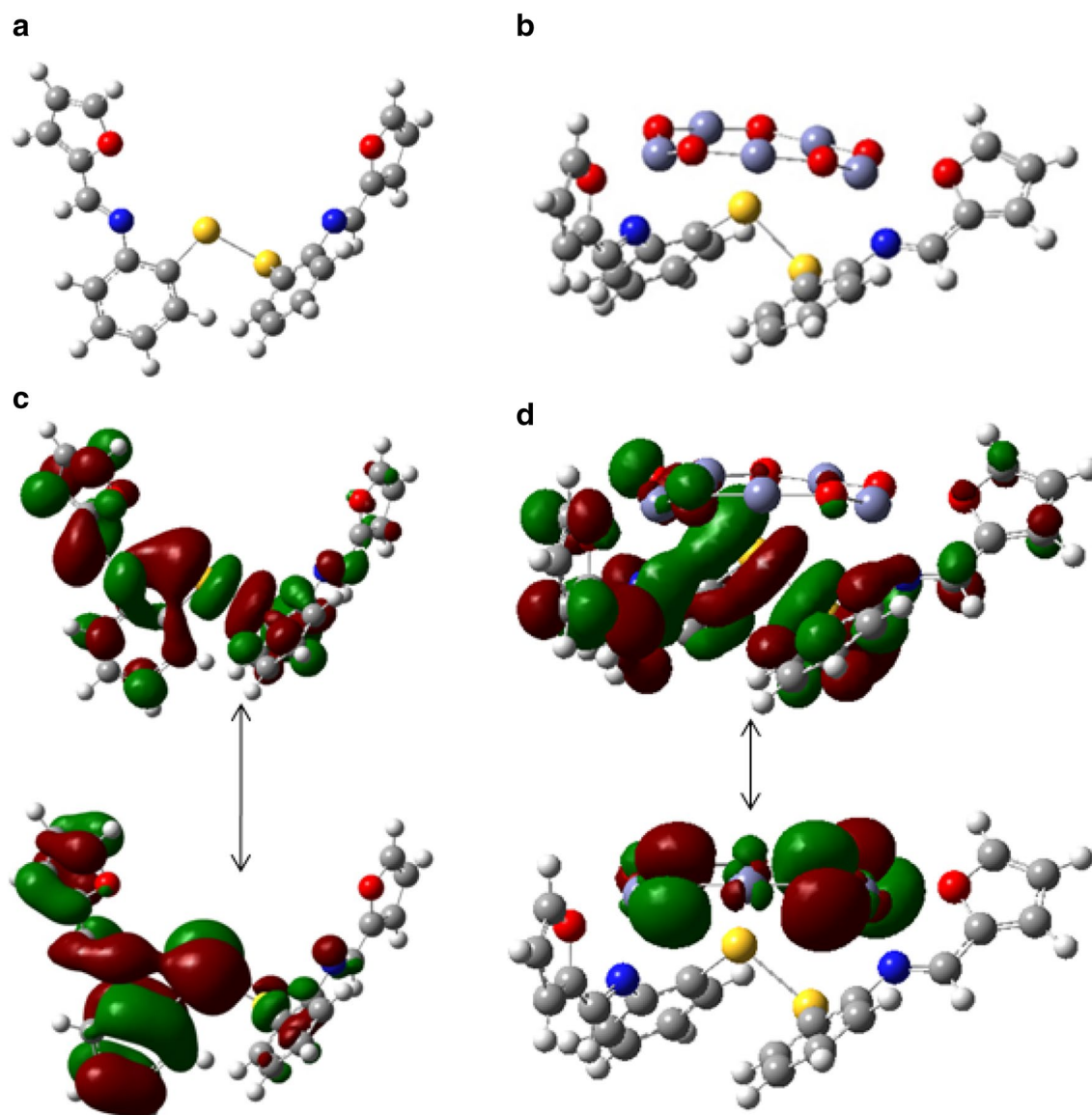


**Fig. 2** (continued)

nanoparticles. The PL spectrum was recorded in the range of 300–800 nm. Clearly the figure shows that the defect related emission and dangling bonds available at the surface of uncapped ZnO nanoparticles is reduced and also the selectivity factor is achieved as the modified ZnO nanoparticles resulted in emission at only 333 nm. The oxygenated zinc defects at the grain boundaries of ZnO may facilitate the conjugation with  $-\text{CH}=\text{N}$  group of organic ligand 1. As a result, the interface defects decrease in surface modified ZnO (1.ZnO). Dijken et al. also presented a model where it was showed that capping of the metal oxide semiconductor nanoparticles resulted in passivation of surface defects. From the existing literature, it is observed that the organic receptors are good capping agents for metal oxide nanoparticles, as they can nicely passivate the surface defects and thus lessens the defect related visible emission [42–45].

Thus, the surface properties of uncapped ZnO nanoparticles with high electron affinity were modulated by coating it with electron donating organic material such as imine linkages.

Apart from decreasing the interface defects of ZnO, the coating of the organic receptor on the surface of ZnO leads to selectivity. The coating of ZnO nanoparticles with the receptor resulted in static conformal geometry as the free rotation of the receptor is restricted which may lead to increase in the selectivity of ZnO nanoparticles. Thus, the optoelectronic properties may change in vicinity of a particular metal nitrate salt. In order to observe the changes in the optoelectronic properties on the receptor capped ZnO nanoparticles, change in the emission profile of ZnO nanoparticles is practiced upon addition of a particular metal nitrate salt as the photophysical properties of

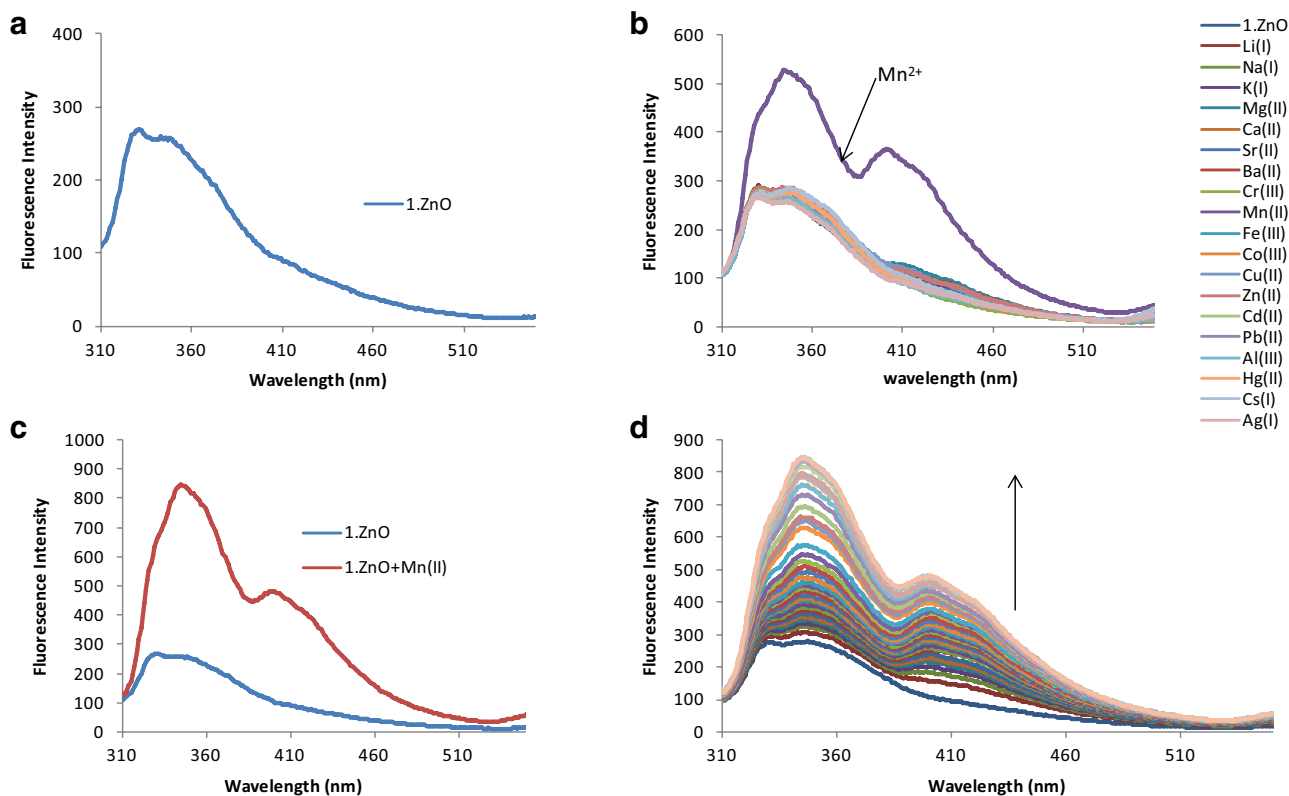


**Fig. 3** **a** DFT optimized structure of organic receptor 1, **b** DFT optimized structure of surface modified ZnO nanoparticles 1.ZnO, **c** LUMO(above) and HOMO (below) of organic receptor 1, **d** LUMO(above) and HOMO (below) of 1.ZnO

the fluorescent chemosensors changes upon its interaction with the chemical species in such a way that its fluorescent signatures are observed [46]. All the recognition studies were carried out at  $25 \pm 1$  °C, and before recording any spectrum, sufficient time was given for shaking to ensure the uniformity of the solution. The metal nitrate salts of different cations were added to the compound 1.ZnO to study the effect of the presence of different cations, including  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cs}^+$  and  $\text{Al}^{3+}$ , on ZnO coated with receptor through the changes in emission spectra of 1.ZnO (Fig. 4b). The metal binding test was carried out by mixing standard solutions of the sensor 1.ZnO (5 ml) along with fixed amounts of a particular metal nitrate salt (20  $\mu\text{M}$  in

HEPES-buffered in DMSO/  $\text{H}_2\text{O}$  (7:3, v/v)). The changes in the PL spectra were recorded to monitor any change in the emission profile of 1.ZnO (host) in presence of the metal nitrate salts. The emission spectra (between 333 and 350 nm) of host has not shown any significant change with most of the metal ions tested, however the addition of  $\text{Mn}^{2+}$  resulted in the enhancement in the fluorescence intensity in emission spectra (Fig. 4c). The increased fluorescence intensity caused by the addition of  $\text{Mn}^{2+}$  cation in 1.ZnO conjugate resulted in the increase in quantum yield. The possible reason for increase in fluorescence intensity upon binding of 1.ZnO with Mn(II) is the binding of metal ion with  $-\text{CH}=\text{N}-$ . The coordination of Mn(II) with the nitrogen atoms, led to increase in fluorescence intensity.





**Fig. 4** **a** PL spectra of surface improved ZnO (1.ZnO) nanoparticles, **b** Changes in the PL spectrum of host upon addition of 2 equivalents of host, **c** Comparison shown between PL spectra of 1. ZnO and

1.ZnO along with Mn(II), **d** Changes in the emission spectrum of host in the presence of different concentrations of Mn(II) (0–35  $\mu\text{M}$ )

So, cancellation of PET is a possible mechanism for fluorescence enhancement. However, a close binding to fluorophore led to shift in  $\lambda_{\text{max}}$  due to modulations in charge transfer transitions. For the application of nanomaterials in the electronic device like LED, the quantum yield is a very important parameter to monitor. The increased quantum yield was observed by adding  $\text{Mn}^{2+}$  to the conjugate 1.ZnO as the conjugate became selective for a particular metal ion. The quantum yield was calculated for 1.ZnO and 1.ZnO + Mn(II) separately using,  $Q.Y = N_E / N_A$ , where  $N_E = (E_{\text{sample}} - E_{\text{blank}})$  and  $N_A = (A_{\text{sample}} - A_{\text{blank}})$ .  $E_{\text{sample}}$ ,  $E_{\text{blank}}$ —sample and blank integrated spectra of emission beam and  $A_{\text{sample}}$ ,  $A_{\text{blank}}$  - sample and blank integrated spectra of excitation beam. The calculated quantum yield for 1.ZnO and 1.ZnO + Mn(II) was 31 and 87% respectively. To observe further change in the emission spectra and thus the quantum yield, small aliquots of  $\text{Mn}^{2+}$  were added and changes were observed using Photoluminescence spectroscopy (Fig. 4d). The successive addition of  $\text{Mn}^{2+}$  ion (0–35  $\mu\text{M}$ ) to the host solution taken in 5 ml volumetric flask confirmed to the changes observed during the metal binding tests as an increase in the fluorescence intensity was observed upon addition of  $\text{Mn}^{2+}$  ion. The PL intensity has increased three-folds approximately upon

surface binding with  $\text{Mn}^{2+}$  ions. The receptor itself was checked for the metal binding studies with the metal nitrate salts but the ligand showed no selectivity for any of the metal ion. The Imine linked ZnO biocompatible nanoparticles functionalized with  $\text{Mn}^{2+}$  ion can be used in electronic devices like light emitting diodes as an improved quantum yield was observed. Also, ZnO being safe, biocompatible, nontoxic considering environmental issues can be picked for electronic devices. Thus, both pure and narrow line blue emission with enhanced quantum yield can be achieved with this proposed material. The introduced findings open a path towards low cost, bio safe, lighting applications with excellent color selectivity.

## 4 Conclusion

ZnO Semiconductor nanoparticles are very promising candidates for light emitting diodes. Environmentally safe, biocompatible, stable alternative to conventional quantum dots utilized in existing LEDs is proposed as active light emitting material with both pure and narrow emission at 333 nm. The photophysical studies were carried out for organic receptor capped ZnO nanoparticles which

established the emission at 333 nm. The photophysical studies were further investigated for ZnO nanoparticles capped with organic receptor in the presence of metal ions. The luminescent property of ZnO nanoparticles is optimized to achieve maximum quantum yield. Three fold improvements in the fluorescent intensity is achieved.

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**Author contributions** The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Compliance with ethical standards

**Conflict of interest** The authors declare no competing financial interest.

## References

- M. Ahmad, J. Zhu, ZnO based advanced functional nanostructures: synthesis, properties and applications. *J. Mater. Chem.* **21**, 599–614 (2011)
- S. Xu, C. Xu, Y. Liu, Y. Hu, R. Yang, Q. Yang, J.H. Ryou, H.J. Kim, Z. Lochner, S. Choi, R. Dupuis, Z.L. Wang, Ordered nanowire array blue/near-UV light emitting diodes. *Adv. Mater.* **22**, 1–5 (2010)
- S. Xu, Z.L. Wang, One-dimensional ZnO nanostructures: solution growth and functional properties. *Nano Res.* (2011). DOI:10.1007/s12274-011-0160-7.
- H. Li, X. Zhang, N. Liu, L. Ding, J. Tao, S. Wang, J. Su, L. Li, Y. Gao, Enhanced photo-response properties of a single ZnO microwire photodetector by coupling effect between localized Schottky barriers and piezoelectric potential. *Optics Expr.* **23**, 21204–21212 (2015)
- Y. Shirasaki, G.J. Supran, M.G. Bawendi, V. Bulović, Emergence of colloidal quantum-dot light-emitting technologies. *Nat. Photonics.* **7**, 13–23 (2013)
- M.J. Anc, N.L. Pickett, N.C. Gresty, J.A. Harris, K.C. Mishra, Progress in Non-Cd quantum dot development for lighting applications. *ECS J Solid State Sci. Technol.* **2** (2), R3071–R3082 (2013)
- L. Protesescu, S. Yakunin, M.I. Bodnarchuk, F. Krieg, R. Caputo, C.H. Hendon, R.X. Yang, A. Walsh, M.V. Kovalenko, Nanocrystals of cesium lead Halide perovskites (CsPbX<sub>3</sub>, X = Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. *Nano Lett.* **15**, 3692–3696 (2015)
- M. Opel, S. Geprägs, M. Althammer, T. Brenninger, R. Gross, Laser molecular beam epitaxy of ZnO thin films and heterostructures. *J. Phys. D.* **47** (3), 034002 (2013)
- A. Kołodziejczak-Radzimska, T. Jesionowski, Zinc oxide—from synthesis to application: a review. *Materials.* **7**, 2833–2881 (2014). doi:10.3390/ma7042833
- Z.L. Wang, ZnO nanowire and nanobelt platform for nanotechnology. *Mat. Sci. Eng. R* **64**, 33–71 (2009)
- N.L. Tarwal, P.R. Jadhav, S.A. Vanalakar, S.S. Kalagi, R.C. Pawar, J.S. Shaikh, S.S. Mali, D.S. Dalavi, P.S. Shinde, P.S. Patil, Photoluminescence of zinc oxide nanopowder synthesized by a combustion method. *Powder Technol.* **208**, 185–188 (2011)
- A. Punnoose, K. Dodge, J.W. Rasmussen, J. Chess, D. Wingett, C. Anders, Cytotoxicity of ZnO nanoparticles can be tailored by modifying their surface structure: a green chemistry approach for safer nanomaterials. *ACS Sustain. Chem. Eng.* **2**, 1666–167 (2014)
- P. Kaur, S.K. Pandey, S. Kumar, N.S. Negi, C.L. Chen, S.M. Rao, M.K. Wu, Tuning ferromagnetism in zinc oxide nanoparticles by chromium doping. *Appl. Nanosci.* (2014). DOI:10.1007/s13204-014-0394-2.
- M. Willander, O. Nur, J.R. Sadaf, M.I. Qadir, S. Zaman, A. Zainelabdin, N. Bano, I. Hussain, Luminescence from Zinc oxide nanostructures and polymers and their hybrid devices. *Materials* **3**, 2643–2667 (2010)
- H. Zeng, G. Duan, Y. Li, S. Yang, X. Xu, W. Cai, Blue luminescence of ZnO nanoparticles based on non-equilibrium processes: defect origins and emission controls. *Adv. Funct. Mater.* **20**, 561–572 (2010)
- N. Bano, I. Hussain, O. Nour, M. Willander, P. Klason, A. Henry, Study of luminescent centers in ZnO nanorods catalytically grown on 4 H-p-SiC. *Semiconductor Sci. Technol.* **24**, 125015 (2009)
- M. Willander, N. Bano, O. Nur, Inorganic–organic ZnO based heterostructures for lighting. *ECS Trans.* **19** (12), 1–12 (2009)
- A. Janotti, C.G. Van de Walle, Fundamentals of zinc oxide as a semiconductor. *IOP PUBLISHING, Rep. Prog. Phys.* **72**, 126501 (2009) (29pp).
- P. Uthirakumar, Y.-S. Lee, E.-K. Suh, C.-H. Hong, Hybrid fluorescent polymer–zinc oxide nanoparticles: improved efficiency for luminescence conversion LED. *J. Lumin.* **128**, 287–296 (2008)
- J. McKittrick, M.E. Hannah, A. Piquette, J.K. Han, J.I. Choi, M. Anc, M. Galvez, H. Lugauer, J.B. Talbot, K.C. Mishra, Phosphor selection considerations for near-UV LED solid state lighting. *ECS J. Solid State Sci. Technol.* **2** (2), R3119–R3131 (2013)
- T. Oh, C.H. Kim, Correlation between energy gap and defect formation of Al doped zinc oxide on carbon doped silicon oxide. *Trans. Electr. Electron. Mater.* **15**, 207–212 (2014)
- J. Bollmann, D.K. Simon, Deep level defects in ZnO. *Phys. B* **439**, 14–19 (2014)
- Z.-Z. Li, M. Bao, S.-H. Chang, Z.-Z. Chen, X.-M. Ma, Green emissions and related defects in ZnO:Ga thin films. *Vacuum* **86**, 1448–1451 (2012)
- B. Karthikeyan, T. Pandiyarajan, R.V. Mangalaraja, Enhanced blue light emission in transparent ZnO:PVA nanocomposite free standing polymer films. *Spectrochim. Acta Part A* **152**, 485–490 (2016)
- J. Xu, S. Shi, C. Wang, Y. Zhang, Z. Liu, X. Zhang, L. Li, Effect of surface-to-volume ratio on the optical and magnetic properties of ZnO nanorods by hydrothermal method. *J. Alloys Compd.* **648**, 521–526 (2015)
- T. Liu, X. Fei, L. Hu, H. Zhang, Y. Li, S. Duo, Effect of substrate surface pretreatment and annealing treatment on morphology, structure, optical and electrical properties of sputtered ZnO films. *Superlattices Microstruct.* **83**, 604–617 (2015)
- A. Samavati, Z. Othaman, S.K. Ghoshal, M.K. Mustaf, The influence of growth temperature on structural and optical properties of sputtered ZnO QDs embedded in SiO<sub>2</sub> matrix. *Superlattices Microstruct.* **86**, 134–142 (2015)
- O. Gürbüz, I. Kurt, S. Caliskan, S. Güner, Influence of Al concentration and annealing temperature on structural, optical, and electrical properties of Al co-doped ZnO thin films. *Appl. Surf. Sci.* **349**, 549–560 (2015)

29. J.W. Zhang, G. He, T.S. Li, M. Liu, X.S. Chen, Y.M. Liu, Z.Q. Sun, Modulation of microstructure and optical properties of Mo-doped ZnO thin films by substrate temperature. *Mater. Res. Bull.* **65**, 7–13 (2015)
30. E. Topuz, J. Traber, L. Sigg, I. Talinli, Agglomeration of Ag and TiO<sub>2</sub> nanoparticles in surface and wastewater: Role of calcium ions and of organic carbon fractions. *Environ. Pollut.* **204**, 313–323 (2015)
31. E. Moghaddam, A.A. Youzbashi, A. Kazemzadeh, M.J. Eshraghi, Preparation of surface-modified ZnO quantum dots through an ultrasound assisted sol–gel process. *Appl. Surf. Sci.* **346**, 111–114 (2015)
32. D. Verma, A.K. Kole, P. Kumbhakar, Red shift of the band-edge photoluminescence emission and effects of annealing and capping agent on structural and optical properties of ZnO nanoparticles. *J. Alloys Compd.* **625**, 122–130 (2015)
33. G. Shan, H. Hao, X. Wang, Z. Shang, Y. Chen, Y. Liu, The effect of PVP on the formation and optical properties ZnO/Ag nanocomposites. *Colloids Surf. A* **405**, 1–5 (2012)
34. K. Raja, P.S. Ramesh, D. Geetha, T. Kokila, R. Sathiyapriya, Synthesis of structural and optical characterization of surfactant capped ZnO nanocrystalline. *Spectrochim. Acta Part A* **136**, 155–161 (2015)
35. C. Narula, I. Kaur, N. Kaur, Characterization and optoelectronics investigations of mixed donor ligand directed semiconductor ZnO nanoparticles. *J. Mater. Sci.* **26**, 791–800 (2015)
36. C. Narula, I. Kaur, N. Kaur, Investigation of optical properties of mixed ligand directed ZnO luminescent nanoparticles for application in light emitting diodes. *J Mater. Sci.* **26**, 8167–8175 (2015)
37. A.V. Dijken, E.A. Meulenkamp, D. Vanmaekelbergh, A. Meijerink, The kinetics of the radiative and nonradiative processes in nanocrystalline ZnO particles upon photoexcitation. *J. Phys. Chem. B* **104**, 1715–1723 (2000)
38. V. Kumar, S. Som, V. Kumar, V. Kumar, O.M. Ntwaeaborwa, E. Coetsee, H.C. Swart, Tunable and white emission from ZnO: Tb3 + nanophosphors for solid state lighting applications. *Chem. Eng. J.* **255**, 541–552 (2014)
39. A. Schejn, L. Balan, D. Piatkowski, S. Mackowski, J. Lulek, R. Schneider, From visible to white-light emission by siloxane-capped ZnO quantum dots upon interaction with thiols. *Optical Mater.* **34**, 1357–1361 (2012)
40. Y.-Y. Peng, T.-E. Hsieh, C.-H. Hsu, White-light emitting ZnO–SiO<sub>2</sub> nanocomposite thin films prepared by the target-attached sputtering method. *Nanotechnology* **17**, 174–180 (2006)
41. C.Y. Lee, J.Y. Wang, Y. Chou, C.L. Cheng, C.H. Chao, S.C. Shiu, S.C. Hung, J.J. Chao, M.Y. Liu, W.F. Su, Y.F. Chen, C.F. Lin, White-light electroluminescence from ZnO nanorods/polyfluorene by solution-based growth. *Nanotechnology* **20**, 425202 (2009) (5pp).
42. K. Shijina, G. Varghese, U. Megha, Surface passivation effect on structure, UV and visible emission of ZnNiPdO nanorods. *Mater. Sci. Semiconductor Process.* **34**, 21–26 (2015)
43. K.S. Babu, A.R. Reddy, K.V. Reddy, Controlling the size and optical properties of ZnO nanoparticles by capping with SiO<sub>2</sub>. *Mater. Res. Bull.* **49**, 537–543 (2014)
44. B. Choudhary, S. Chawla, K. Jayanthi, K.N. Sood, S. Singh, Synthesis and surface modification of ZnO:Cu nanoparticles by silica and PMMA. *Curr. Appl. Phys.* **10**, 807–812 (2010)
45. M. Navaneethan, J. Archana, M. Arivanandhan, Y. Hayakawa, Functional properties of amine-passivated ZnO nanostructures and dye-sensitized solar cell characteristics. *Chem. Eng. J.* **213**, 70–77 (2012)
46. A. Saini, J. Singh, R. Kaur, N. Singh, N. Kaur, Naphthalimide-based organic nanoparticles for aluminium recognition in acidic soil and aqueous media. *New J. Chem.*, **2014**, 38, 4580–4586.