

Role of gadolinium(III) complex in improving thermal stability of polythiophene composite

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This paper involves the preparation of polythiophene (PTP) and its composite by the oxidative polymerisation method by using ferric chloride as an oxidant and thiophene monomer. The gadolinium(III) complex obtained by the refluxing technique was used as dopant in the PTP matrix. On the basis of the spectroscopic characterisation, seven-coordinate geometry is proposed for the complex. Conductance measurement confirms the non-selectrolyte nature of complex. The PTP and its composite were subjected to FTIR, X-ray diffraction and scanning electron microscope techniques. The powder X-ray diffraction pattern showed the high crystalline nature of the complex which in turn developed a good degree of crystallinity in the PTP composite. The average particle size was calculated as 4.655 Å and 3.737 Å for the dopant and PTP composite, respectively, by using Debye Scherrer's equation. Thermal analysis was performed by thermogravimetric (TG) analysis, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) techniques. The TG, DTA and DSC results were well-correlated. The thermal analysis revealed the high thermal stability of the dopant which in turn improved the thermal stability of the PTP composite, revealing the potential of the composite for high temperature applications.

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Keywords: rare earth complex, polythiophene composite, crystallinity, thermal stability

Introduction

Rare earth complexes are potential candidates for molecular electronics; they exhibit ferroelectric properties, are thermally stable and have the ability to incorporate both photoluminescent centres and magnetic properties for developing new multifunctional materials, especially when organic linkers are attached with metal (Want & Shah, 2014). Lanthanide complexes have wide-ranging applications in such diverse fields as organic light-emitting diodes (OLEDs), fluorescent probes, sensors, laser materials, molecular optoelectronic devices, etc. (Taha et al., 2013). The property that renders these complexes functional and applicable is their high thermal stability. Investigation of the thermal stability reveals important information on the physico-chemical properties of the complexes besides affording a greater insight into the bonding and structure of complexes (Zalewicz et al., 2004). Triva-

lent rare earth ions with macrocyclic ligands exhibit liquid crystalline properties (Binnemans & Gündogan, 2002), hence their electrical and optical properties can be explored.

Magnetic resonance imaging (MRI), a medical diagnostic technique based on the principle of the nuclear magnetic resonance (NMR) of water protons in tissues and organs, is used to identify serious and life-threatening diseases. The detection of disease requires contrast agents and most of the contrast agents used in MRI are gadolinium complexes (Riri et al., 2011). Gadolinium complexes take precedence over other rare earth elements complexes for use as MRI contrast agents due to their low toxicity, high stability and high relaxivity (Cohen et al., 2000). Currently, all approved gadolinium-based contrast agents for MRI, are based on ligands having a multidentate character with donor atoms of nitrogen and oxygen (Miéville et al., 2011). Rare earth elements have at-

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tracted the attention of academicians and researchers not only because of their physiological activities but also due to their decreased toxicity after coordination with ligands (Pusz & Wolowiec, 2012).

Apart from the use of gadolinium and its related family as MRI agents, gadolinium(III) has been used as a dopant in titanium materials for photoenergy applications. The photocatalytic activity of Gd^{3+} derives from its important role in the photo-induced electrons transportation mechanism. It decreases the crystallite size, enlarges pore sizes and increases the surface area of the titanium material, thereby enhancing its ability towards photocatalytic reactions (Zalas, 2014). Gadolinium complexes have also exhibited magnetic properties due to the formation of short-lived clusters with non-magnetic ground-state and magnetic excited states. Gadolinium usually exhibits antiferromagnetic coupling with neighbouring complexes that favour the formation of short-lived clusters (Leniec et al., 2007). Gadolinium(III) can introduce an anisotropic property into the polymer matrices to influence the properties of magnetic materials (Zhou et al., 2010).

The coordination chemistry of lanthanide elements is of interest because of their unusual coordination characteristics. The coordination number (C.N.) of lanthanide ions varies from complex to complex. The C.N. of Ln^{n+} is very rarely six and a higher coordination number in the range of 7–12 appears to dominate (Gallardo et al., 2011). Lanthanide ions form stable complexes with macrocyclic ligands (Zhong et al., 2008; Wang et al., 2003). Gadolinium mostly forms complexes with C.N. seven to nine, with seven appearing to be the most common. 1,10-phenanthroline and oxalic acid have been used as ligands due to their good coordination sites and high entropy effect. Chelating ligands such as 1,10-phenanthroline and oxalic acid can impart extra stability to the complex by decreasing the entropy of activation and the overall Gibbs free energy. The ligands with conjugated π -bonds may add a new dimension to the complex in the form of photophysical properties.

A survey of the literature reveals that a large number of metal complexes such as metal bis(salicylaldehyde), copper bisglycinate, mixed ligand ruthenium complex, multiligand urea complex of cobalt(II), cobalt(II) monoethanolamine complex, etc. have been used as dopants in the conjugated polymers of polyaniline and polythiophene (Rasool & Majid, 2014; Rafiqi et al., 2013, 2014). The dopant transmits different characteristics to the polymer matrix under different conditions. Metal complexes embedded in the polymer matrix impart many attractive and useful properties to the polymer composite. The terbium(III) complex not only enhances the luminous intensity of polyaniline and polythiophene composites but also increases their thermal stabilities (Rafiqi & Majid, 2015). Conducting polymers containing metal complexes have attracted the attention of material scientists worldwide

because the insertion of an inorganic phase into the organic material of polyaniline and polythiophene generate the hybrid systems. The composite materials have intrigued a great deal of interest among material scientists as these materials cover a wide range of applications from the industrial sector to research fields. The *p*-conjugated carbon backbone of the polythiophene matrix makes the composites potential candidates for use in microelectronic devices, sensors, catalysts, transistors, EMI shielding, solar cells, light emitting diodes, DNA detection and polymer electronic interconnects (Zhu et al., 2008; Gnanakan et al., 2009; Salatelli et al., 2010; Najar & Majid, 2013). Out of all the heterocyclic conjugated polymers, polythiophenes occupy a special place in photocatalytic applications because of their stability under photoirradiation (Khatamian et al., 2014).

In view of the above, in the present study, the polythiophene was doped with the macrocyclic gadolinium(III) complex with the aim of improving some properties such as the degree of crystallinity, thermal stability, electrical conductivity, etc. and to induce chemical changes which can have a desirable impact on the structural and electronic properties of the final composite material. The polymer composite as prepared was subjected to various spectroscopic and surface-characterisation techniques. Thermal analysis was performed using the thermogravimetric (TG) analysis, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) techniques.

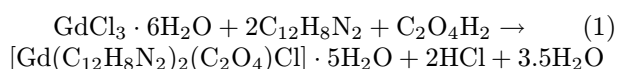
Experimental

Gadolinium chloride hexahydrate was purchased from Chengdu Haoxuan Technology (China). 1,10-Phenanthroline and oxalic acid were from Merck (Germany). All the reagents and solvents used were of analytical grade. Triple-distilled water was used in the gadolinium complex synthesis. Thiophene (Himedia, India) was distilled and stored at -5°C prior to use. Ferric chloride was supplied by Loba chemicals (India). All the reagents and solvents used were of analytical grade.

The FTIR spectra were recorded on a Perkin-Elmer (USA) spectrometer using KBr pellets. The elemental analysis including C, H and N was performed using a Vario (USA) EL elemental analyser. XRD data were collected from a PW 3050 base diffractometer (Germany) with CuK_α radiation of 1.540598 \AA . The conductance measurement was carried out in a 10^{-3} M DMSO solution using a model Labindia Pico⁺ Conductivity Bridge (India). The surface morphology of the samples was studied using a ZEISS EVO series scanning electron microscope model EVO50 (USA). The thermal analysis was carried out on a Perkin-Elmer thermal analyser in a nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ from ambient temperature to 720°C . DSC was carried out using a NETZSCH

DSC 204 F1Phoenix (Germany) using aluminium pan as a reference. The temperature range was from 30 °C to 400 °C at the heating rate of 10 °C min⁻¹. The electrical conductivity of synthesised materials was measured by the standard Four Probe Technique at 25 °C with Keithley mode 2400 (USA).

The procedure involved in the synthesis of the complex of gadolinium(III) involves 0.01 M of gadolinium chloride hexahydrate and 0.01 M of bis 1,10-phenanthroline dissolved in 20 mL of aqueous solutions separately. Both the solutions were mixed and refluxed in a water bath for approximately 0.5 h. Oxalic acid (20 mL of 0.01 M) was added drop-wise to a solution containing both the metal salt and the ligand 1,10-phenanthroline under continuous stirring. The pH of the solution was adjusted to 7.0–8.0 by using sodium hydroxide pellets and refluxing continued for approximately 6 h. The solution was left to stand overnight, then the yellow precipitate resulting from this solution was filtered and washed repeatedly with distilled water and dried in an oven at approximately 50 °C. The following reaction is presumed to take place in the aqueous medium.



Polythiophene was prepared by recognised methods of oxidation with ferric chloride (Majid et al., 2009a). Thiophene (2 mL) was transferred into a titration flask containing CHCl₃ (70 mL). Next, FeCl₃ (9 g) was added to CHCl₃ (180 mL). This mixture was stirred and added to the thiophene solution then the whole mixture was subjected to magnetic stirring. After 24 h of stirring, the black-coloured polymer powder thus obtained was washed first with CHCl₃ and then with CH₃OH. The powder was collected and dried in an oven at 40 °C.

Thiophene (2 mL) was transferred into a titration flask containing CHCl₃ (70 mL) then FeCl₃ (9 g) was added to CHCl₃ (180 mL). This mixture was stirred and added to the thiophene solution. Next, 1.5 g of the thermally synthesised gadolinium(III) complex containing ligands 1,10-phenanthroline and oxalic acid was added and the whole mixture was subjected to magnetic stirring. After 24 h of stirring the black-coloured polymer powder thus obtained was washed first with CHCl₃ and then with CH₃OH. The powder was collected and dried in an oven at 40 °C.

Results and discussion

The empirical formula assigned to the gadolinium complex is [Gd(C₁₂H₈N₂)₂(C₂O₄)Cl] · 2.5H₂O. The percentages of C, H and N observed are 48.00 %, 2.85 % and 8.71 % against the calculated values of 47.96 %, 2.84 % and 8.61 %, respectively. The presence of lattice water in the gadolinium(III) complex is

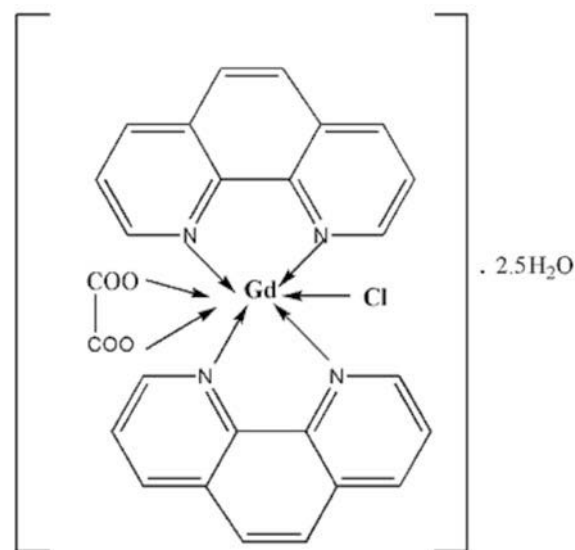


Fig. 1. Seven-coordinate structure of gadolinium(III) complex.

confirmed from FTIR and TG. On the basis of the elemental analysis, FTIR and TG results, a seven-coordinate chelated structure has been proposed for the gadolinium complex as shown in Fig. 1.

The molar conductance value of the gadolinium(III) complex in DMSO solution (10⁻³ M) at ambient temperature is 11.91 cm² Ω⁻¹ mol⁻¹, which is lower than the range reported for electrolytes in DMSO solutions (Zhong et al., 2008). Such a low value of ionic conductance could be because of the chelated structure of the gadolinium complex and the absence of any ionic moiety outside its coordination sphere. As per Kohlrausch's law of the independent migration of ions, at infinite dilution the total conductance is the conductance of all the ions present in the solution. The more ions are in the solution, the greater will be the conductance. The chelated molecules on dissolution supply a very low number of ions in the solution, resulting in a very low value of overall ionic conductance. These results reveal the light electrolyte nature of the complex and indicate that the ligands were successfully chelated by the metal ion.

The FTIR of the gadolinium complex, pure polythiophene (PTP) and PTP composite are shown in Fig. 2. In the gadolinium complex, the presence of a 1,10-phenanthroline ligand is confirmed by the appearance of peaks at 1673 cm⁻¹ due to the C=N stretching vibration, the peak at 3049 cm⁻¹ is because of aromatic C—H stretching, the peaks at 2929 cm⁻¹ and 1593 cm⁻¹ are due to stretching vibrations of C=C (Zhong et al., 2008). The peak at 758 cm⁻¹ is due to the skeleton vibration of the heterocyclic ring containing nitrogen (Jiang et al., 2006). A peak centred at 1525 cm⁻¹ is attributed to the asymmetrical stretching of the coordinated carboxylate group ν_{as}(COO)⁻. Another peak at 1378 cm⁻¹ is due to

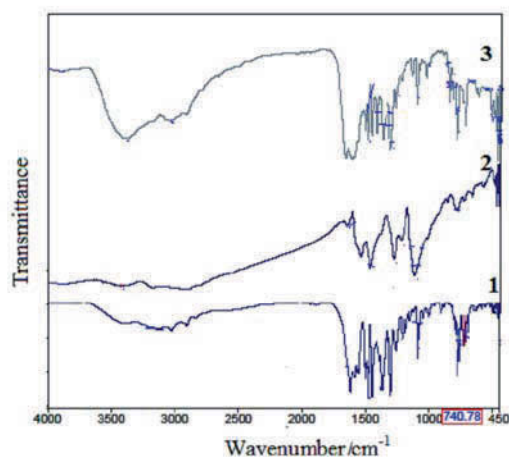


Fig. 2. FTIR of gadolinium complex (1), pure PTP (2), PTP composite (3).

the symmetrical stretching of coordinated carboxylate group $\nu_s(\text{COO})^-$. It is generally believed that $\Delta\nu$ is below 200 cm^{-1} for the bidentate carboxylate moiety (Want & Shah, 2014). The absence of any bands in the region of $1700\text{--}2850\text{ cm}^{-1}$ indicate the replacement of acid hydrogens of the COOH group by a metal cation. The sharp band observed at 1225 cm^{-1} is attributed to the C—C inplane bending of oxalate ligand. The peaks which appeared at 1463 cm^{-1} and 1496 cm^{-1} are due to the C—O, C—C—O stretching vibrations of oxalate moiety (Pusz & Wolowiec, 2012). Gd—O, Gd—N and Gd—Cl peaks are observed below 850 cm^{-1} (Riri et al., 2011; Majid et al., 2009b), which includes peaks at 825 cm^{-1} , 740 cm^{-1} , 736 cm^{-1} , 620 cm^{-1} , 540 cm^{-1} , 490 cm^{-1} and 449 cm^{-1} , confirming the presence of all such bonds. A broad band at 3438 cm^{-1} indicates the presence of lattice water, which is also confirmed by thermogravimetric analysis.

The FTIR spectrum of pure PTP exhibits C—H stretching at 3196 cm^{-1} ; a C=C stretching vibration at 1488 cm^{-1} ; C—H in-plane bending at 1140 cm^{-1} and C—S bending band at 750 cm^{-1} (Najar & Majid, 2013). These bands appear in the polythiophene composite at 3071 cm^{-1} , 1427 cm^{-1} , 1112 cm^{-1} and 724 cm^{-1} , respectively. The shift towards a lower wavenumber in the polymer composite than that of pure PTP indicates a weak van der Waals kind of interaction between the dopant and polythiophene backbone (Rafiqi et al., 2013). In addition, lattice water is present in both the pure PTP and PTP composite as the broad bands at 3446 cm^{-1} and 3414 cm^{-1} have been found in the spectrum of pure PTP and PTP composite, respectively. The lattice water that might have been embedded in the outer layers of polythiophene is also confirmed by thermogravimetric analysis and the loss of these moieties occurs at the very onset of the thermal decomposition process.

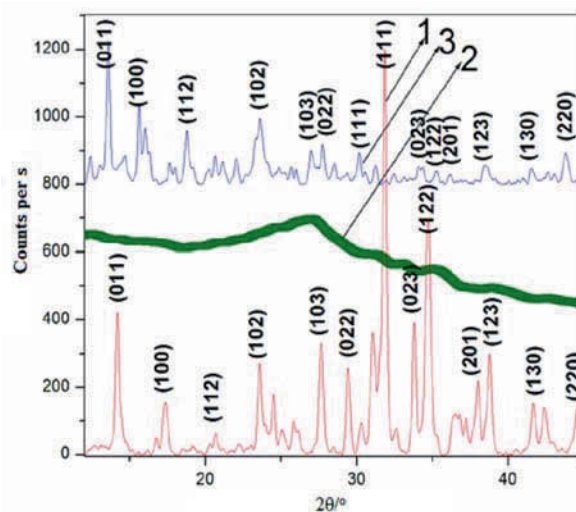


Fig. 3. XRD of gadolinium complex (1) pure PTP (2) PTP composite (3).

The other peaks that appear in the PTP composite are observed at 1673 cm^{-1} , 2929 cm^{-1} , 1605 cm^{-1} , 780 cm^{-1} , 1524 cm^{-1} , 1496 cm^{-1} , 1455 cm^{-1} , 1378 cm^{-1} , 853 cm^{-1} , 817 cm^{-1} , 789 cm^{-1} , 751 cm^{-1} , 545 cm^{-1} and 480 cm^{-1} . These peaks are due to 1,10-phenanthroline, oxalate moiety, $\nu(\text{Gd—N})$, $\nu(\text{Gd—O})$ and $\nu(\text{Gd—Cl})$ vibrations of dopant component. In comparing the spectra of the dopant and the PTP composite, the FTIR peaks showed a significant shift, indicating a strong interaction between the metal complex and the polythiophene *p*-conjugated network, hence successful doping is proved in the composite material.

X-ray diffraction (XRD) analysis was conducted on a PW-3050 base diffractometer with $\text{CuK}\alpha$ radiations (scanning range 2θ : $5\text{--}70^\circ$). The XRD data were analysed by powder-X software (Xpovder, Spain). Fig. 3 presents the XRD diffraction pattern of the gadolinium complex (dopant), pure PTP and PTP composite, respectively. The PTP shows a wide peak covering the angles between 20° to 30° due to intermolecular $\pi\text{--}\pi$ stacking. Pure PTP shows amorphicity in the whole matrix, indicating a level of disorderedness, is also evident from its surface morphology. In the XRD of pure PTP, a peak is centred at about 25.7° which reveals the amorphous nature of PTP. In the PTP composite, the wide peak overlaps with the peaks observed at 23.604° and 27.648° , showing a change in nature from amorphicity to crystallinity. The crystalline substances are characterised by the presence of sharp peaks; the appearance of this type of peak in both the dopant and composite illustrates a good degree of crystallinity (Majid et al., 2009a; Rather et al., 2013b). In comparison, it is evident that all the peaks of the dopant appear in the PTP composite with appreciable shifts, indicating a strong interaction between the components. The lattice parameters of the gadolinium complex obtained after refinement are $a = 5.776\text{ \AA}$,

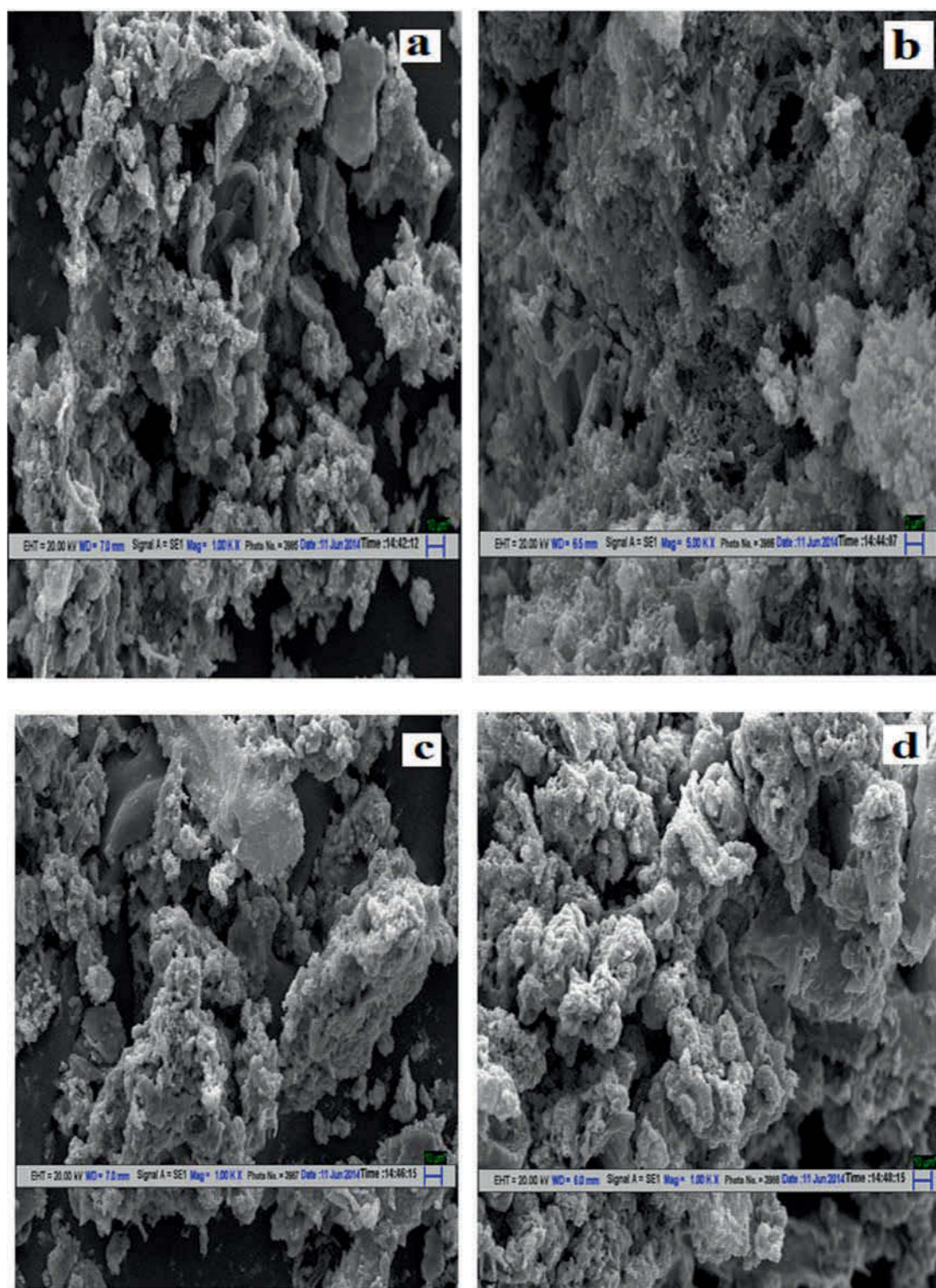


Fig. 4. SEM of pure PTP at magnification 10000 \times (a), 50000 \times (b) and SEM images of PTP composite at 10000 \times (c) and 50000 \times (d).

$b = 6.987 \text{ \AA}$ and $c = 13.543 \text{ \AA}$ and axial angles $\alpha = \beta = \gamma = 90^\circ$ with unit cell volume of 547 \AA^3 . In the case of the composite, the pattern shows $a = 5.753 \text{ \AA}$, $b = 6.959 \text{ \AA}$ and $c = 13.412 \text{ \AA}$ and $\alpha = 90^\circ$, $\beta = 88^\circ$ and $\gamma = 92^\circ$ with unit cell volume of 537 \AA^3 . Particle size L was calculated at various values of 2θ for both

the dopant and PTP composite from the equation:

$$L = \frac{k\lambda}{b \cos \theta} \quad (2)$$

where $\lambda = 1.540598 \text{ \AA}$ is the wavelength of the $\text{CuK}\alpha$ radiation applied, θ is the Bragg angle ($^\circ$), b is the full

width at half the maximum of the diffraction peak and K is the Scherrer's constant (0.89). The average particle size of dopant and PTP composite was calculated as 4.655 Å and 3.737 Å, respectively. The decrease in crystallite size from the gadolinium(III) complex to the PTP composite may be because of the stacking interaction of polythiophene layers and the microstrain in the composite caused by the gadolinium(III) complex.

From the above results and discussion of XRD pattern, the successful synthesis of PTP and its composite with gadolinium complex is confirmed. The structure of the PTP composite improved from an amorphous to a crystalline nature.

The surface morphologies of pure PTP and PTP composites are shown in Fig. 4 at 10000 and 50000 magnifications. The SEM of PTP shows voids, grooves and a spongy nature in its surface, which is also observed in the SEM image of the composite at certain places on its surface, thus confirming its successful formation. The SEM images of the PTP composite show an agglomeration of particles of various sizes and shapes. Cloud-like structures predominantly appear at magnifications of 5000 which agglomerate one above the other, indicating layering in the composite. The bright agglomerated structure depicts the presence of a metallic complex in the polythiophene matrix.

The thermal analysis –differential thermal analysis (TG–DTG) curves of dopant gadolinium complex, pure PTP and PTP composite are shown in Fig. 5. Thermal analysis by TG–DTA technique determines the sequential and overall stability of the metal complex upon decomposition besides providing information on the composition of different moieties. The TG decomposition curve of the gadolinium hydrate complex shows the decomposition in two steps. The first decomposition which occurs in the temperature range of 60–190 °C is related to the dehydration of lattice water. This step amounts to a mass loss of 6.80 % against the calculated value of 6.84 %. The DTG temperature corresponding to this transition step is 65 °C. The second transition occurs in the temperature range of 200–720 °C with DTG maximum temperatures of 179.14 °C and 494.30 °C. This step accounts for the 65.60 % mass loss against the calculated value of 65.63 %, which may be because of the loss of the chloride ion and chelating ligands 1,10-phenanthroline and the oxalate ion from the complex. The thermal decomposition is incomplete even up to 720 °C, due to the formation of thermally stable gadolinium oxide. The residue remaining at 720 °C is Gd_2O_3 that amounts to 27.60 % of total mass against the calculated value of 27.53 %. The scheme of the water release along with other moieties from the complex is as follows:

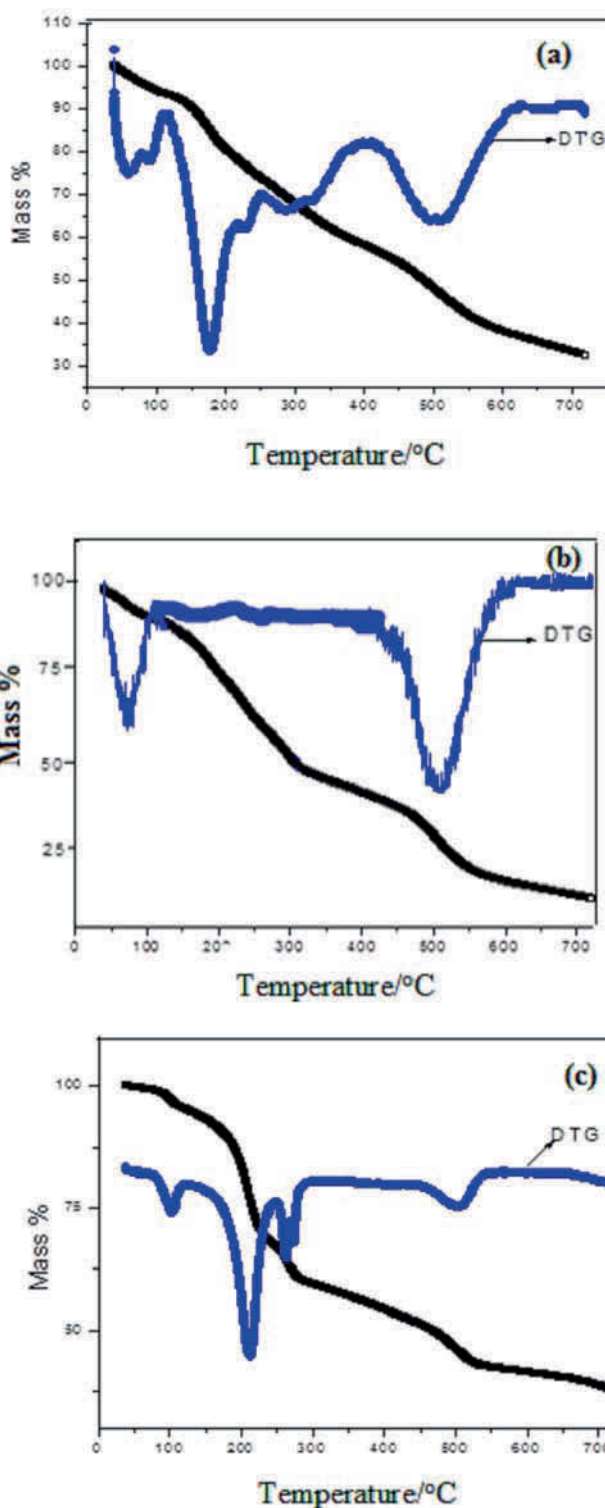
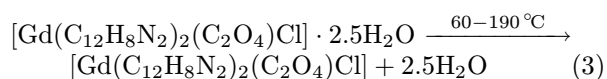
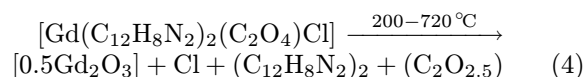


Fig. 5. TG–DTG of gadolinium complex (a), pure PTP (b), and PTP composite (c).



observed mass loss in Eq. 3 was 6.80 % (calculated mass loss 6.84 %) and observed mass loss in Eq. 4 was

65.60 % (calculated mass loss 65.63 %).

The TG of pure PTP shows two transitions. The first transition occurring in the temperature range of 60–130°C with DTG temperature of 74.16°C is attributed to the loss of moisture embedded in the polymer layers. This transition accounts for the 5.4 % mass loss. The second transition occurs in the temperature range of 140–720°C with a DTG maximum temperature of 504.40°C. This transition corresponds to the decomposition of polythiophene chains. About 90 % of the mass loss occurs up to 720°C leaving the residue of 10 %.

The TG of the PTP composite shows three transitions. The first one due to the loss of moisture occurs in the temperature range of 100–120°C, with DTG maximum of 103.82°C. The second transition starts at 160°C and ends at 290°C with mass loss of 40 %. This step could be because of degradation of the organic part of the dopant and PTP polymer. The third transition that occurs in the temperature range of 300–720°C with a DTG maximum of 502.63°C is exclusively because of decomposition of the acquired crystallisation state of the PTP amorphous material. The crystallisation of PTP is also discussed in the differential scanning calorimetric analysis below. This step amounts to a 30 % mass loss. The residue remaining at 720°C is approximately 25 % of total mass which could be due to the presence of gadolinium oxide.

On comparing the TG of the pure PTP and the PTP composite, the 10 % and 25 % residues left at 720°C indicate that the dopant was inserted in the polymer matrix and had increased its thermal stability. The improved thermal stability of PTP composite is because of the strong interaction of polythiophene with the gadolinium(III) complex. The gadolinium(III) complex may have restricted the thermal motion of polythiophene, once the samples were subjected to heat treatment. It is the strong interaction between the dopant and polythiophene which provides stability to the composite material.

Another parameter that compares the thermal stability of molecules is T_i (T_i is the temperature at which the transition occurs). A higher value of T_i indicates a higher thermal stability (Rather et al., 2014). Setting aside the transition of lattice water loss, T_i for pure PTP is 140°C and 160°C in the case of the composite. This 20°C increase in T_i indicates a higher thermal stability of the PTP composite than pure PTP.

Fig. 6 shows the thermogram of polythiophene composites with dopant concentrations of 15 %, 20 % and 25 %. The residue remaining at 700°C of different polythiophene composites with 15 %, 20 % and 25 % dopant concentrations are 33.32 %, 37.10 % and 47.83 % of total mass, respectively. The results show that the thermal stability of the polythiophene composite increased upon doping with the gadolinium(III) complex. This could be because of the strong

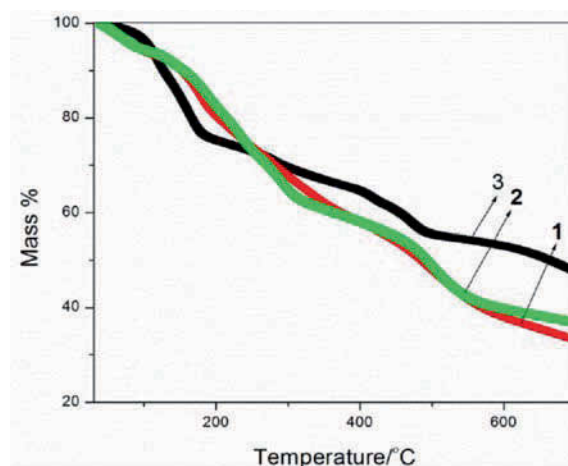


Fig. 6. TG curves of PTP composite with different dopant concentrations 15 % (1), 20 % (2) and 25 % (3).

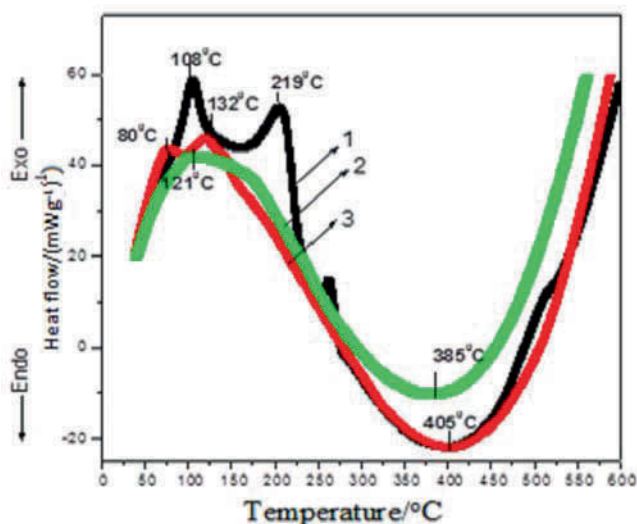


Fig. 7. DTA of gadolinium complex (1), pure PTP (2) and PTP composite (3).

interfacial interactions between PTP and the gadolinium(III) complex. The gadolinium(III) complex, when encapsulated in a large quantity in the PTP matrix, has a greater capacity for restricting the polythiophene chains, thereby enhancing the thermal stability to a greater extent. Also, the T_i of PTP composites increases with the increase in dopant concentration, which further confirms the enhancement of thermal stability.

DTA curves of the dopant, pure PTP and PTP composite are shown in Fig. 7. The DTA curve of the dopant shows three transitions, two exothermic and one endothermic. The first two exothermic transitions are attributed to the loss of the lattice water and chloride ion of the complex. The third endothermic transition is attributed to the main decomposition of the complex. The DTA of the pure PTP and PTP composites also show similar curves except that an addi-

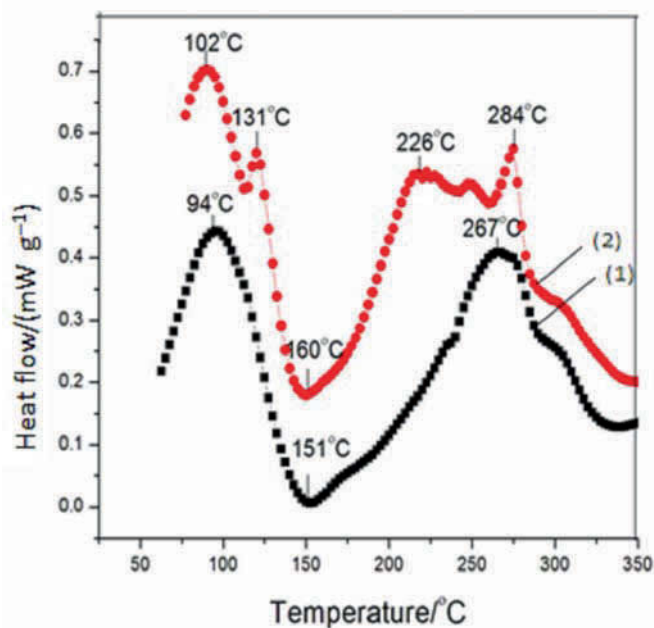


Fig. 8. DSC of pure PTP (1) and PTP composite (2).

tional small exothermic peak appears at 132°C in the PTP composite which could be due to the presence of dopant. The enthalpy change (ΔH) of endothermic transition is 6131 J g⁻¹ in the PTP composite whereas this value is 4245 J g⁻¹ in pure PTP. The endothermic transition is much wider in the PTP composite than in the pure PTP. Further, the shift in DTA temperature from 385°C in pure PTP to 405°C in PTP composite supports the higher thermal stability of the PTP composite.

The differential scanning calorimetry (DSC) of the pure PTP and PTP composites is shown in Fig. 8. The DSC of pure PTP shows three transitions: the first and third transitions are exothermic and the second is endothermic. The first transition, which occurs at a maximum temperature of 94°C, is attributed to the loss of lattice water. The second transition shows a broad endothermic dip at 151°C which represents the glass transition temperature (T_g) of polythiophene matrix. The third transition is exothermic, occurring in the temperature range of 200–325°C with a maximum at 267°C, corresponds to the crystallisation state of polythiophene. The molecules in the amorphous region sometimes acquire sufficient mobility and arrange themselves into an ordered crystal state, after which the melting occurs.

The DSC of the PTP composite shows five transitions, of which four are exothermic and one endothermic. The extra two transitions in the DSC of the PTP composite, as compared to the pure PTP, is the decomposition and phase change of the dopant gadolinium complex, thereby confirming its presence in the polymer matrix. These extra transitions occur at maximum temperatures of 131°C and 226°C. The T_g of

polythiophene in the PTP composite is 4°C higher than its T_g found in pure PTP. However, the temperature corresponding to the crystallisation state is increased by 17°C from 267°C to 284°C in the PTP composite. The increase in the glass transition temperature can be due to the more ordered arrangement and weak interaction between the dopant and PTP matrix.

The conductance of pure PTP, as detected by the four-probe conductivity meter, to be 3.1×10^{-7} S cm⁻¹, was significantly augmented to a value of 7.2×10^{-2} S cm⁻¹ in the case of the PTP composite. The conductance values of the pure PTP and PTP composite show the materials to be insulator and semiconductor, respectively. Therefore, the data show that the gadolinium(III) complex changed the electronic behaviour of polythiophene from being insulating to being semiconducting. This insulator-to-semiconductor transition from pure PTP to its composite is due to the enhancement in the flow of electrons by the insertion of the gadolinium(III) complex. The semiconducting nature of the PTP composite is attributed to the metallic nature of gadolinium and the delocalisation of π -electrons of 1,10-phenanthroline moieties into the conjugated polythiophene chains. The increase in conductivity can also be because of the movement of electrons from the oxygen of the oxalate ligand of the gadolinium(III) complex into the polaronic and bi-polaronic states of polythiophene.

Conclusions

The study revealed that, with the procedure mentioned, a successful synthesis of the composite occurred between the polythiophene and the gadolinium complex involving 1,10-phenanthroline and oxalate ion as ligands. The dopant changed the amorphous nature of the PTP and developed a good degree of crystallinity in its matrix. The reduction in particle size from dopant to PTP composite may be attributed to the microstrain in the composite and the stacking interaction between polythiophene chains. The surface morphology was studied using the SEM technique. The thermogravimetric analysis revealed a higher thermal stability of the gadolinium complex that then improved the thermal stability of the PTP composite. The DTA results also confirm the higher thermal stability of the PTP composite. The glass transition temperature of the PTP composite as compared to the pure PTP increased albeit to a smaller extent but the glass transition temperature corresponding to its crystallisation state increased by 17°C. Accordingly, like TG and DTA, DSC also confirms the higher thermal stability of the PTP composite. On the basis of the results of TG, DTA and DSC, the thermal stability decreases in order: gadolinium(III) complex, PTP composite, pure PTP. The gadolin-

ium(III) complex proved to be a successful dopant in improving the conductivity of the PTP composite.

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References

- Binnemans, K., & Gündogan, B. (2002). Synthesis and thermal behaviour of lanthanide complexes of cholesterylacetyl carbonyl benzo-15-crown-5. *Journal of Rare Earths*, 20, 249–255.
- Cohen, S. M., Xu, J., Radkov, E., & Raymond, K. N. (2000). Synthesis and relaxation properties of mixed gadolinium hydroxypyridonate MRI contrast agents. *Inorganic Chemistry*, 39, 5747–5756. DOI: 10.1021/ic000563b.
- Gallardo, H., Conte, G., Bortoluzzi, A. J., Bechtold, I. H., Pereira, A., Quirino, W. G., Legnani, C., & Cremona, M. (2011). Synthesis, structural characterization, and photo and electroluminescence of a novel terbium(III) complex: {Tris(acetylacetonate) [1,2,5]thiadiazolo[3,4-f][1,10]phenanthroline}terbium(III). *Inorganica Chimica Acta*, 365, 152–158. DOI: 10.1016/j.ica.2010.09.003.
- Gnanakan, S. R. P., Rajasekhar, M., & Subramania, A. (2009). Synthesis of polythiophene nanoparticles by surfactant-assisted dilute polymerization method for high performance redox supercapacitors. *International Journal of Electrochemical Science*, 4, 1289–1301.
- Jiang, H. J., Sun, W. L., & Zheng, R. H. (2006). Synthetic and magnetic properties of novel polymeric metal complexes with bis 1,10-phenanthroline ligands. *European Polymer Journal*, 42, 425–433. DOI: 10.1016/j.eurpolymj.2005.07.003.
- Khatamian, M., Fazayeli, M., & Divband, B. (2014). Preparation, characterization and photocatalytic properties of polythiophene-sensitized zinc oxide hybrid nanocomposites. *Materials Science in Semiconductor Processing*, 26, 540–547. DOI: 10.1016/j.mssp.2014.04.038.
- Leniec, G., Kaczmarek, S. M., Typek, J., Kołodziej, B., Grech, E., & Schilf, W. (2007). Magnetic and spectroscopic properties of gadolinium tripodal Schiff base complex. *Solid State Sciences*, 9, 267–273. DOI: 10.1016/j.solidstatesciences.2007.02.002.
- Majid, K., Tabassum, R., Ahmad, S., & Singla, M. L. (2009a). Synthesis, characterization and electric properties of polythiophene composites with various amphoteric oxides. *Materials Research Innovations*, 13, 87–91. DOI: 10.1179/143307509x435169.
- Majid, K., Tabassum, R., Shah, A. F., Ahmad, S., & Singla, M. L. (2009b). Comparative study of synthesis, characterization and electric properties of polypyrrole and polythiophene composites with tellurium oxide. *Journal of Materials Science: Materials in Electronics*, 20, 958–966. DOI: 10.1007/s10854-008-9817-8.
- Miéville, P., Jaccard, H., Reviriego, F., Tripier, R., & Helm, L. (2011). Synthesis, complexation and NMR relaxation properties of Gd³⁺ complexes of Mes(DO₃A)₃. *Dalton Transactions*, 2011, 4260–4267. DOI: 10.1039/c0dt01597k.
- Najar, M. H., & Majid, K. (2013). Synthesis, characterization, electrical and thermal properties of nanocomposite of polythiophene with nanophotoadduct: a potent composite for electronic use. *Journal of Materials Science: Materials in Electronics*, 24, 4332–4339. DOI: 10.1007/s10854-013-1407-8.
- Pusz, J., & Wolowiec, S. (2012). Solid compounds of Ce(III), Pr(III), Nd(III), and Sm(III) ions with chrysin. *Journal of Thermal Analysis and Calorimetry*, 110, 813–821. DOI: 10.1007/s10973-011-1989-4.
- Rafiqi, F. A., Rather, M. S., & Majid, K. (2013). Doping polyaniline with copper bis(glycinate)—Synthesis, characterization and thermal study. *Synthetic Metals*, 171, 32–38. DOI: 10.1016/j.synthmet.2013.03.009.
- Rafiqi, F. A., Rather, M. S., & Majid, K. (2014). Synthesis, characterization and thermal study of composite of polyaniline doped with multiligand urea complex of cobalt(II). *Materials Research Innovations*, 18, 307–313. DOI: 10.1179/1433075x13y.0000000149.
- Rafiqi, F. A., & Majid, K. (2015). Synthesis, characterization, luminescence properties and thermal studies of polyaniline and polythiophene composites with rare earth terbium(III) complex. *Synthetic Metals*, 202, 147–156. DOI: 10.1016/j.synthmet.2015.01.032.
- Rasool, R., & Majid, K. (2014). Synthesis, characterization, thermal and electrical properties of composite of polyaniline with cobalt monoethanolamine complex. *Bulletin of Material Sciences*, 37, 1181–1190.
- Rather, M. S., Majid, K., Wanchoo, R. K., & Singla, M. L. (2013). Nanocomposite of polyaniline with the photoadduct of potassium hexacyanoferrate and pyridine ligand: Structural, electrical, mechanical and thermal study. *Synthetic Metals*, 179, 60–66. DOI: 10.1016/j.synthmet.2013.07.010.
- Rather, M. S., Majid, K., Wanchoo, R. K., & Singla, M. L. (2014). Role of photoadduct of K₄Fe(CN)₆ and C₃H₄N₂ in improving thermal stability of polyaniline composite. *Journal of Thermal Analysis and Calorimetry*, 117, 611–619. DOI: 10.1007/s10973-014-3834-z.
- Riri, M., Hor, M., Kamal, O., Eljaddi, T., Benjjar, A., & Hlaibi, M. (2011). New gadolinium(III) complexes with simple organic acids (oxalic, glycolic and malic acid). *Journal of Material Environmental Science*, 2, 303–308.
- Salatelli, E., Angiolini, L., Brazzi, A., Lanzi, M., Scavetta, E., & Tonelli, D. (2010). Synthesis, characterization and electrochemical properties of new functional polythiophenes. *Synthetic Metals*, 160, 2681–2686. DOI: 10.1016/j.synthmet.2010.10.026.
- Taha, Z. A., Ajlouni, A. M., & Al-Mustafa, J. (2013). Thermal decomposition of lanthanum(III) complexes of bis-(salicylaldehyde)-1,3-propylenediimine schiff base ligand. *Chemical Papers*, 67, 194–201. DOI: 10.2478/s11696-012-0262-z.
- Wang, D. M., Zhang, J. H., Lin, Q., Fu, L. S., Zhang, H. J., & Yang, B. (2003). Lanthanide complex/polymer composite optical resin with intense narrow band emission, high transparency and good mechanical performance. *Journal of Materials Chemistry*, 13, 2279–2284. DOI: 10.1039/b305024f.
- Want, B., & Shah, M. D. (2014). Growth and characterization of terbium fumarate heptahydrate crystals. *Journal of Crystal Growth*, 389, 39–46. DOI: 10.1016/j.jcrysgro.2013.11.071.
- Zalas, M. (2014). Gadolinium-modified titanium oxide materials for photoenergy applications: a review. *Journal of Rare Earths*, 32, 487–495. DOI: 10.1016/s1002-0721(14)60097-1.
- Zalewicz, M., & Trzesowska, A. (2004). The coupled TG-MS investigations of lanthanide (III) nitrate complexes with hexamethylenetetramine. *Journal of Thermal Analysis and Calorimetry*, 78, 525–534. DOI: 10.1023/b:jtan.0000046116.43443.36.
- Zhong, C. F., Huang, H. L., He, A. H., & Zhang, H. L. (2008). Synthesis and luminescent properties of novel polymeric metal complexes with bis(1,10-phenanthroline) ligands. *Dyes*

- and Pigments*, 77, 578–583. DOI: 10.1016/j.dyepig.2007.08.008.
- Zhou, N., Ma, Y., Wang, C., Xu, G. F., Tang, J. K., Yan, S. P., & Liao, D. Z. (2010). Two tri-spin complexes based on gadolinium and nitrosyl notroxide radicals: Structure and ferromagnetic interactions. *Journal of Solid State Chemistry*, 183, 927–932. DOI: 10.1016/j.jssc.2010.02.012.
- Zhu, Y. F., Xu, S. B., Jiang, L., Pan, K. L., & Dan, Y. (2008). Synthesis and characterization of polythiophene/titanium dioxide composites. *Reactive and Functional Polymers*, 68, 1492–1498. DOI: 10.1016/j.reactfunctpolym.2008.07.008.