

# Synthesis, spectroscopic characterization, thermal, and photostability studies of 2-(2'-hydroxy-5'-phenyl)-5-aminobenzotriazole complexes

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**Abstract** Three Mn(II), Co(II), and Cu(II) new transition metal complexes of the fluorescence dye: 2-(2'-hydroxy-5'-phenyl)-5-aminobenzotriazole/PBT derived from *o*-aminophenol and *m*-phenylenediamine have been synthesized. The structural interpretations were confirmed from elemental analyses, magnetic susceptibility and molar conductivity, as well as from mass, IR, UV–Vis spectral studies. From the analytical, spectroscopic, and thermal data, the stoichiometry of the mentioned complexes was found to be 1:2 (metal:ligand). The molar conductance data revealed that all the metal chelates are non-electrolytes and the chloride ions exist inside the coordination sphere. The thermal stabilities of these complexes were studied by thermogravimetric (TG/DTG) and the decomposition steps of these three complexes are investigated. The kinetic parameters such as the energy of activation ( $E^*$ ), pre-exponential factor ( $A$ ), activation entropy ( $\Delta S^*$ ), activation enthalpy ( $\Delta H^*$ ), and free energy of activation ( $\Delta G^*$ ) have been reported. Photostability of phenyl benzotriazole as fluorescence dye and their metal complexes doped in polymethyl methacrylate/PMMA were exposed to UV–Vis radiation and the change in the absorption spectra was achieved at different times during irradiation period.

**Keywords** Benzotriazole · Transition metals · Thermal analysis · Thermodynamic parameters

## Introduction

Metal–dye complexes play an important role in dyestuff technology [1–12]; chromium, cobalt, copper, nickel, ruthenium, and aluminum derivatives were used most frequently for these purposes [13–17].

The environment pollution has been a major concern of the present industrial societies. The protection from pollution, especially by chemical industries, has put the challenge to chemists and photophysicists in many countries. The determination of heavy and transition metal cations in the environment has been of great interest. Sensors for pollution by metal ions have been of particular actuality [18, 19].

Fluorescent dyes have found application in a number of areas including laser active media [20], potential photosensitive biological units [21], fluorescent markers in biology [22], analgesics in medicine [23], light emitting diodes [24], photo-induced electron sensors [25], fluorescence switchers [26], electroluminescent materials [27], liquid crystal displays [28], and ion probes [29].

For instance, azo compounds and their metal complexes and related features are much interested molecules as pigments and optical data storage [30, 31]. By comparison between azo dyes and their metal complexes is more light stable and have a good thermal stability [32, 33].

Photostability of the polymers is one of their most important properties. To solve the problem of polymer stabilization, a number of different stabilizers have successfully been applied [34]. Among them, 2-hydroxyphenylbenzotriazole UV absorbers are of a great interest due to their high photostabilizing efficiency. They are transparent to visible light and are supposed to dissipate the absorbed energy in a harmless manner, i.e., to convert the

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absorbed photon energy into heat without being chemically affected [35].

The essential target of the present paper is to synthesize, investigate thermal behavior, and detect the coordination power of PBT (Fig. 1) metal chelates, that this ligand contains several donar sites. The coordination behavior of PBT towards transition metal ions was investigated and the data are confirmed with their molar conductance and magnetic moment measurements. The thermal decomposition of the Mn(II), Co(II), and Cu(II) complexes was used to speculate the structures, also the thermal stabilities studies are essential feature in relation to their application as high-photostability materials.

## Experimental

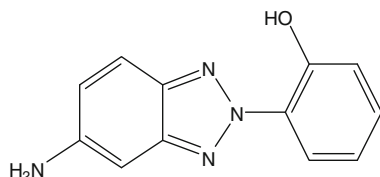
### Materials

All chemicals used were of the analytical reagent grade. They include *o*-aminophenol and *m*-phenylenediamine (Aldrich), methanol (Fluka), *N,N*-dimethylformamide (DMF), and dimethylsulphoxide (DMSO) (Fluka). MnCl<sub>2</sub>·4H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, and CuCl<sub>2</sub>·H<sub>2</sub>O (Fluka) were used as received. PMMA was purchased from (Aldrich).

### Synthesis of PBT and their metal complexes

The 2-(2'-hydroxy-5'-phenyl)-5-aminobenzotriazole (PBT) was synthesized as described in previous procedures [36] with melting point 212–215 °C.

All the Mn(II), Co(II), and Cu(II) of PBT complexes were synthesized by adding a respective metal(II) salts (0.1 mmol; in 10 mL 99% CH<sub>3</sub>OH) to a hot solution of PBT (0.2 mmol; in 20 mL 99% CH<sub>3</sub>OH). The mixtures were stirred and heated on a hot plate within 60–70 °C for 30 min. Before precipitation process, the Co(II) complex has a deep-brown color and in a solid form the color changed to black. The *m.p.* of Co(II)/PBT was >324 °C and the % yield (88%). While, the color of Cu(II) complex in solution manner before precipitation was faint-brown and after that turned to dark-brown precipitate complex with *m.p.* = 210 °C with % yield (87%). Concerning Mn(II)/PBT complex, the solution color before precipitation was



**Fig. 1** Structure of synthesized (PBT) fluorescent dye

brownish-yellow and then a brown precipitate complex was formed with *m.p.* = 205 °C and % yield (83%). All complexes are isolated in amorphous behavior.

Preparation of dyed polymer matrix: both PMMA grains and dye or its metal complexes were dissolved in chloroform and mixed using a magnetic stirrer. The homogenous mixture was poured into a glass container and allowed to dry.

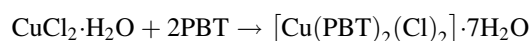
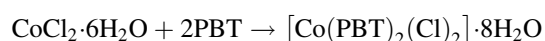
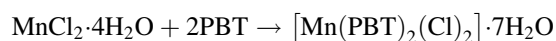
### Instrumentals

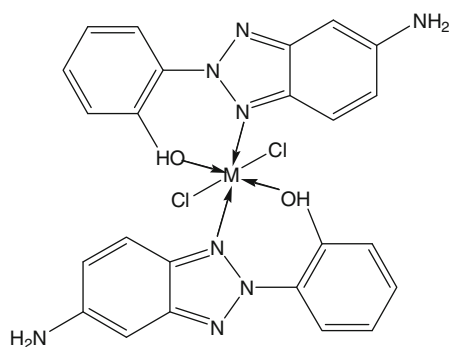
Carbon, hydrogen, and nitrogen contents were determined using a Perkin-Elmer CHN 2400. The manganese(II), cobalt (II), and copper(II) percentages were estimated gravimetrically by the direct ignition of these complexes at 800 °C for 3 h till constant mass. The residue was then weighed in the forms of metal oxides. IR spectra were recorded on Bruker FT-IR Spectrophotometer (4000–400 cm<sup>-1</sup>) in KBr pellets. The UV–Vis spectra were performed in the DMSO solvent with concentration (1.0 × 10<sup>-3</sup> M) for the free ligand PBT and their complexes using Jenway 6405 Spectrophotometer with 1 cm quartz cell in the range of 800–200 nm. The solid reflectance spectra were performed on a Shimadzu 3101pc spectrophotometer. The purity was checked from mass spectra at 70 eV using AEIMS 30 mass spectrometer with heating rate of 40 °C/min. Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method with Hg[Co(CNS)<sub>4</sub>] and [Ni(en)<sub>3</sub>](S<sub>2</sub>O<sub>3</sub>) as a calibrants. Molar conductivities of the freshly prepared solutions with concentration 1.0 × 10<sup>-3</sup> mol in DMSO were measured using Jenway 4010 conductivity meter. Thermogravimetric analyses (TG and DTG) were carried out in dynamic nitrogen atmosphere (30 mL/min) with a heating rate of 10 °C/min using a Shimadzu TGA-50H thermal analyzer.

Dye photostability: solar simulator xenon arc lamp “250 w” was used, which had the same spectrum as sun. The degradation of samples was studied by analyzing the UV–Vis absorption spectra. The dye photostability was calculated by dividing the absorbance after exposure to light by that before exposure.

## Results and discussion

The chemical reactions mechanisms concerning the interaction between MCl<sub>2</sub>·*n*H<sub>2</sub>O (M = Mn(II), Co(II), and Cu(II)) and PBT for the synthesis of PBT metal complexes are as follows:





**Fig. 2** Structure of PBT complexes (where, M = Mn<sup>II</sup>, Co<sup>II</sup> and Cu<sup>II</sup>)

The molar ratio for all isolated complexes in solid form is 1:2 (M<sup>II</sup>:PBT) with the general formula [M(PBT)<sub>2</sub>(Cl)<sub>2</sub>] $\cdot$ *n*H<sub>2</sub>O. The coordination structure of the PBT complexes is given in Fig. 2. The elemental analyses, molar conductance, and magnetic measurements data of the metal chelates of PBT are existed in (Table 1) and in good agreement with those suggested formulas.

#### Molar conductance measurements

The molar conductivity values ( $\Lambda_m/\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) of the free PBT ligand and their complexes soluble in DMF with 10<sup>-3</sup> M at 25 °C confirmed that the resultant complexes have non-electrolytic features [37, 38] by comparing the electrolytic nature for each complex with free PBT ligand. The values of the molar conductance data are listed in Table 1.

#### Infrared spectra and mode of chelation

Interpretation of infrared spectra of free PBT ligand and Mn(II), Co(II), and Cu(II) complexes (Fig. 3) gave an idea about the mode of chelation and follow-up of the effect of coordination of metal ions on the vibration motions of free

ligand. The IR spectra of the free ligand and its metal chelates were carried out within the mid-IR range 4000–400 cm<sup>-1</sup> (Table 2). The IR spectrum of the free ligand shows a very strong band at 3460 cm<sup>-1</sup>, which can be attributed to the aryl-OH group [39]. This band is shifted to lower wavenumbers at 3445 and 3405 cm<sup>-1</sup> in case of Mn(II) and Co(II) complexes, respectively, but this band was absent in case of Cu(II) complex which was assigned to the involvement of OH group in the chelating. The shared aryl-OH group in coordination is confirmed by the hypochromic effect (decrease in intensity) of the  $\nu(\text{C}-\text{O})$  stretching band observed at 1250 cm<sup>-1</sup> in the free ligand and the complexes due to substituents or interactions with the molecular environment [39]. The IR spectrum of the free ligand revealed a very strong-to-strong bands at 1633 and 1598 cm<sup>-1</sup> due to  $\nu(\text{C}=\text{N})$  of the benzotriazole moiety [40–42]. This band is shifted to lower frequencies (30–38 cm<sup>-1</sup>) in the complexes assigned that it has been affected upon complexation via metal ions. In the 500–400 cm<sup>-1</sup> region, the spectra of all complexes have a detected bands observed at  $\sim$ 550 and 468 cm<sup>-1</sup> [42], which can be assigned to the  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  stretching vibrations, respectively. Therefore, the IR spectra indicate that PBT behaves as a bidentate and the coordination sites being ArOH and C=N of the benzotriazole ring.

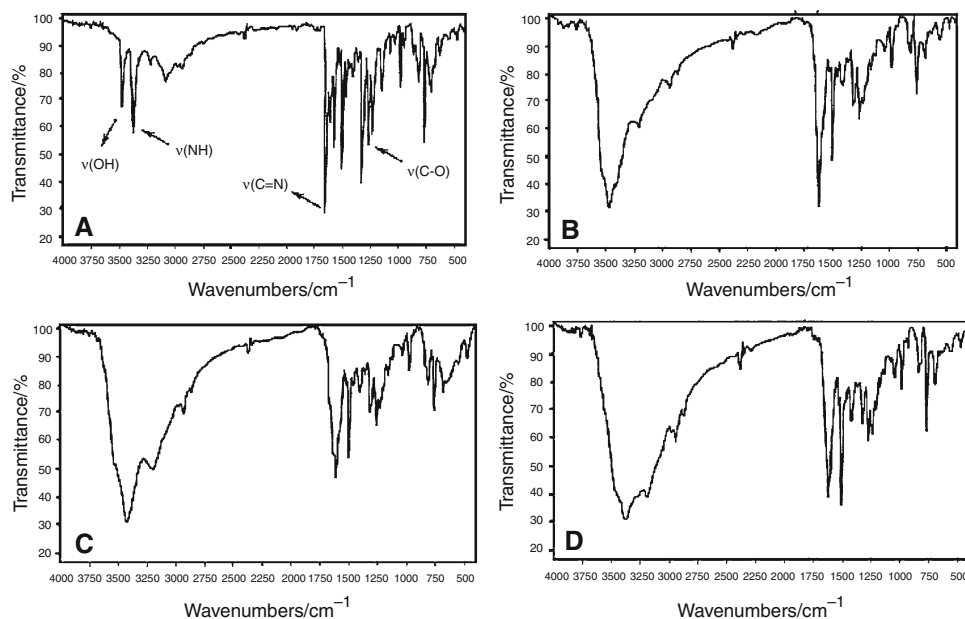
#### Electronic absorption spectra of the complexes

The electronic spectra for PBT and its complexes recorded in DMF solvent are given in Table 3. The electronic spectral data of the ligand exhibit more than one band in the UV region. The bands appearing in the range of  $\sim$ 230–335 nm are attributed to  $\pi-\pi^*$  transition of the ligands. The other bands observed in the region above 340 nm are assigned to  $n-\pi^*$  electronic transitions [42, 43]. In the three complexes of PBT, the absorption maxima has a bare close resemblance with the free ligand which indicates that no structural alteration of the ligand has occurred during complexation. However, the values shifted slightly to

**Table 1** Elemental analysis, molar conductance and magnetic measurements data of the PBT complexes

Complexes Empirical formula/Mwt	Found/calcd				Molar conductance/ $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	$\mu_{\text{eff}}$
	C/%	H/%	N/%	M/%		
PBT	63.71/63.66	4.46/4.39	24.76/24.65	–	63.30	–
C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> O/226.23						
[Mn(PBT) <sub>2</sub> (Cl) <sub>2</sub> ] $\cdot$ 7H <sub>2</sub> O	40.92/40.89	4.86/4.02	15.91/15.87	7.80/7.69	74.70	5.90
C <sub>24</sub> H <sub>34</sub> N <sub>8</sub> O <sub>9</sub> Cl <sub>2</sub> Mn/704.42						
[Co(PBT) <sub>2</sub> (Cl) <sub>2</sub> ] $\cdot$ 8H <sub>2</sub> O	39.68/39.57	5.00/4.78	15.43/15.33	8.11/8.05	81.10	5.12
C <sub>24</sub> H <sub>36</sub> N <sub>8</sub> O <sub>10</sub> Cl <sub>2</sub> Co/726.43						
[Cu(PBT) <sub>2</sub> (Cl) <sub>2</sub> ] $\cdot$ 7H <sub>2</sub> O	40.43/40.57	4.81/4.78	15.72/15.49	8.91/8.86	65.20	1.10
C <sub>24</sub> H <sub>34</sub> N <sub>8</sub> O <sub>9</sub> Cl <sub>2</sub> Cu/713.03						

**Fig. 3** IR spectra of: **a** free PBT, **b** Mn<sup>II</sup>/PBT, **c** Co<sup>II</sup>/PBT, and **d** Cu<sup>II</sup>/PBT complexes



**Table 2** Main IR peaks of PBT and its complexes

Compound	$\nu_{\text{OH}}$	$\nu_{\text{NH}}$ ; $\text{NH}_2$ $\nu_{\text{OH}}$ ; $\text{H}_2\text{O}$	$\nu_{\text{CH}}$ ; Ar	$\nu_{\text{C=N}} + \nu_{\text{C=C}}$ $\delta_{\text{H}_2\text{O}} + \delta_{\text{NH}_2}$	$\nu_{\text{C-O}}$ $\nu_{\text{C-N}}$ $\nu_{\text{C-C}}$	$\nu_{\text{M-O}}$ $\nu_{\text{M-N}}$
PBT	3460	3356, 3207	3071, 2968 2925, 2854	1633, 1598, 1561 1519, 1492, 1461 1426, 1403, 1356 1312	1254, 1223 1142, 1066 1032, 975 943, 812	–
Mn <sup>II</sup> /PBT	3445	3383, 3191	2924, 2853	1603, 1517, 1490 1452, 1400, 1353 1310	1253, 1222 1192, 1122 1033, 971 808, 753	550, 468
Co <sup>II</sup> /PBT	3405	3183	2925, 2853	1599, 1513, 1490 1455, 1400, 1353 1312	1253, 1222 1155, 1033 971, 809 754	551, 469
Cu <sup>II</sup> /PBT	–	3354, 3166	2960, 2853	1595, 1515, 1490 1405, 1353, 1311	1256, 1223 1190, 1156 1035, 977 828, 755	552, 468

lower or longer wavelength with absence of two bands at 545 and 575 nm in the free ligand due to the involvement of C=N and OH groups in metal complexation [44].

#### Magnetic susceptibility and electronic spectra

The diffuse reflectance spectrum of manganese(II) complex display the *d-d* transition bands in the region 625, 615, and 600 nm due to  ${}^4\text{T}_{1\text{g}} \rightarrow {}^6\text{A}_{1\text{g}}$ ,  ${}^4\text{T}_{2\text{g}}(\text{G}) \rightarrow {}^6\text{A}_{1\text{g}}$  and  ${}^4\text{T}_{1\text{g}}(\text{D}) \rightarrow {}^6\text{A}_{1\text{g}}$ , respectively [45, 46]. Manganese(II)

complex exhibits effective magnetic moments of 5.90 BM  $sp^3d^2$  which is present in the region of expected value 5.92–6.00 BM corresponding to five unpaired electrons. The transitions corresponds to the octahedral environment of the Mn(II) complex. The electronic spectrum of Co(II) complex show the *d-d* transition bands in the region, 770, 588, and 468  $\text{cm}^{-1}$ . These transitions are probably assigned to the  $\nu_1 = {}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{F})$ ,  $\nu_2 = {}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$  and  $\nu_3 = {}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{P})$ , respectively. Cobalt(II) complex has a magnetic moment of 5.12 BM indicating the presence

**Table 3** Electronic spectra of the PBT and its complexes

Compounds	$\lambda_{\max}/\text{nm}$	Assignments
PBT	240, 245, 250, 255, 260, 265	$\pi-\pi^*$
	270, 285, 295, 300, 325	
	340, 345, 390, 395, 545, 575	$n-\pi^*$
$\text{Mn}^{\text{II}}/\text{PBT}$	240, 250, 265, 295, 325	$\pi-\pi^*$
	340, 355, 390	$n-\pi^*$
$\text{Co}^{\text{II}}/\text{PBT}$	235, 240, 245, 260, 265, 300	$\pi-\pi^*$
	320, 325, 335	
	340, 345, 350, 360, 390, 395	$n-\pi^*$
$\text{Cu}^{\text{II}}/\text{PBT}$	240, 250, 255, 260, 270, 275	$\pi-\pi^*$
	285, 295, 300, 310, 325, 330	
	340, 345, 350, 355, 360, 390, 395	$n-\pi^*$

of three unpaired electrons and the transitions correspond to the octahedral geometrical structure [45, 46]. The spectrum of Cu(II) complex gives the band centered at 840 nm which may be assigned to  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition in an approximately octahedral environment ( $\mu_{\text{eff}} = 1.10 \text{ BM}$ ).

#### Mass spectra

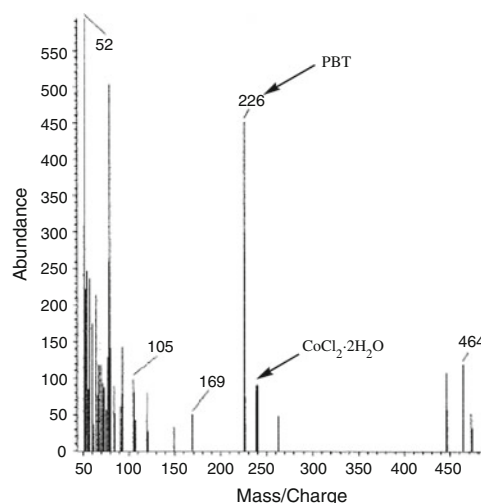
In the mass spectrum of  $[\text{Co}(\text{PBT})_2(\text{Cl})_2] \cdot 8\text{H}_2\text{O}$ , both peaks at  $m/z = 226$  and 238 refer to the molecular ion peak of PBT ligand and  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  (Fig. 4). The other fragments assigned to the fragmentation pattern of PBT ligand at 169, 105, and 52.

#### Thermal analysis and thermodynamic data

Thermal analysis curves (TG/DTG) of the PBT and their Mn(II), Co(II), and Cu(II) transition metal complexes were studied and interpreted in Table 4 and Fig. 5.

The PBT ligand melts at about  $\sim 212\text{--}215$  °C with simultaneous decomposition. The first mass loss was observed at 261 °C. From the TG curve, it appears that the sample decomposes in only one stage over the temperature range 30–800 °C. This step occurs at (150–300 °C) with a mass loss of (obs. = 98.50%, calc. = 100.00%) due to loss of  $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}$ , the difference between the calculated and observed data back to the residual carbon.

The thermal decomposition of Mn(II) complex occurs within five steps. The first degradation step takes place in the range of 30–75 °C and it corresponds to the elimination of  $\text{H}_2\text{O}$  molecules with a mass loss of (obs. = 2.10%, calc. = 2.55%). The second step falls in the range of 75–140 °C which is assigned to the loss of  $2\text{H}_2\text{O}$  molecule with a mass loss (obs. = 4.50%, calc. = 5.11%). Third decomposition step existed within the range 140–215 °C and was accompanied by mass loss of (obs. = 4.37%, calc. = 5.11%) which is assigned to loss of  $2\text{H}_2\text{O}$ . The fourth and final

**Fig. 4** Mass spectrum of  $[\text{Co}(\text{PBT})_2(\text{Cl})_2] \cdot 8\text{H}_2\text{O}$  complex

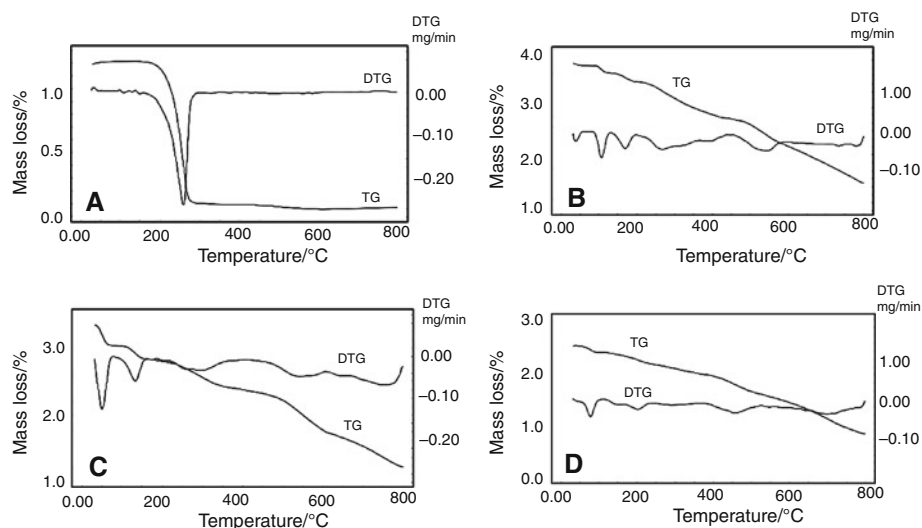
decomposition step exhibited within the range 215–800 °C and interpretive accordance the loss of  $2\text{H}_2\text{O}$ ,  $\text{Cl}_2$ , and  $\text{C}_9\text{H}_{20}\text{N}_8$  organic moiety with mass loss (obs. = 33.14%, calc. = 34.07%). The  $\text{MnO}_2$  and contaminated carbon atoms are the final products that remain stable till 800 °C.

The thermal decomposition of cobalt(II) complex occurs completely in five steps. The first step ranged at 30–100 °C corresponding to the loss of  $4\text{H}_2\text{O}$  molecules representing a mass loss of (obs. = 9.59%, calc. = 9.91%). The second and third steps occurring within 100–350 °C range corresponding to the loss of remaining  $4\text{H}_2\text{O}$  uncoordinated water molecules and chlorine atoms representing a mass loss of (obs. = 19.93%, calc. = 19.68%). The fourth and fifth steps occur within the temperature range 350–800 °C which refer to the decomposition of PBT moiety at  $\text{DTG}_{\max} = 538$  and 753 °C, respectively, the mass loss is (obs. = 33.49%, calc. = 34.41%). The CoO and the pollutant carbon atoms are the final products that remain stable till 800 °C.

The thermal degradation of the Cu(II) complex occurs in mainly five degradation stages. The first stage of decomposition occurs at a temperature maximum of 47 °C. The found mass loss associated with this step is (obs. = 5.41%, calc. = 5.05%) and may be attributed to the loss of  $2\text{H}_2\text{O}$  molecules. The second and third steps of decomposition occur at temperature maxima of 78 and 202 °C, respectively. The mass loss found at these steps equal to (obs. = 14.18%, calc. = 12.62%) corresponds to the loss of  $5\text{H}_2\text{O}$  uncoordinated. The fourth and fifth steps occurring at 250–800 °C ( $\text{DTG}_{\max} = 455$  and 698) correspond to the loss of chlorine molecule  $\text{Cl}_2$ ,  $2\text{NH}_2$ , and  $\text{C}_{10}\text{H}_{16}\text{N}_6\text{O}$  organic moiety representing a mass loss of (obs. = 47.62%, calc. = 47.54%). The final thermal product obtained at 800 °C is CuO with residual carbon atoms. The final residual products for all PBT complexes

**Table 4** Thermal data of the PBT and their Mn<sup>II</sup>, Co<sup>II</sup>, and Cu<sup>II</sup> complexes

Compounds	Steps	Temp. range/°C	DTG peak/°C	TG mass loss/%		Assignments
				Calc.	Found	
PBT	1st	30–800	261	100.00	98.50	C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> O/ligand moiety
Mn <sup>II</sup>	1st	30–75	37	2.55	2.10	H <sub>2</sub> O
	2nd	75–140	105	5.11	4.50	2H <sub>2</sub> O
	3rd	140–215	168	5.11	4.37	2H <sub>2</sub> O
	4th	215–435	266	15.19	16.20	2H <sub>2</sub> O + Cl <sub>2</sub>
	5th	435–800	540	34.07	33.14	C <sub>9</sub> H <sub>20</sub> N <sub>8</sub> MnO <sub>2</sub> + residual carbon
Co <sup>II</sup>	1st	30–100	49	9.91	9.56	4H <sub>2</sub> O
	2nd	100–165	131	7.43	6.89	3H <sub>2</sub> O
	3rd	165–350	288	12.25	13.04	H <sub>2</sub> O + Cl <sub>2</sub>
	4th	350–600	538	20.65	20.55	C <sub>7</sub> H <sub>10</sub> N <sub>4</sub>
	5th	600–800	753	13.76	12.94	CH <sub>10</sub> N <sub>4</sub> O CoO + residual carbon
Cu <sup>II</sup>	1st	30–50	47	5.05	5.41	2H <sub>2</sub> O
	2nd	50–100	78	7.57	8.18	3H <sub>2</sub> O
	3rd	100–250	202	5.05	6.00	2H <sub>2</sub> O
	4th	250–550	455	14.44	14.86	Cl <sub>2</sub> + 2NH <sub>2</sub>
	5th	550–800	698	33.10	32.76	C <sub>10</sub> H <sub>16</sub> N <sub>6</sub> O CuO + residual carbon

**Fig. 5** TG/DTG curves of: **a** free PBT, **b** Mn<sup>II</sup>/PBT, **c** Co<sup>II</sup>/PBT, and **d** Cu<sup>II</sup>/PBT complexes

were checked by infrared spectra and confirmed the formation of oxide feature as the end products.

The thermodynamic activation parameters (Table 5) of the first decomposition process of dehydration such as activation entropy ( $\Delta S^*$ ), pre-exponential factor ( $A$ ), activation enthalpy ( $\Delta H^*$ ), and Gibbs free energy ( $\Delta G^*$ ) were calculated using the Coats and Redfern and Horowitz-Metzger equations [47, 48]. The negative values of entropy ( $\Delta S^*$ ) for all complexes indicated that these are more ordered reactions [49–53]. The high values of the activation energy,  $E$ , of the PBT complexes reveal the high

stability of chelation due to their coordinated bond feature and also helpful to predict the bond strength of ligand towards the metal ions.  $\Delta G$  is positive while  $\Delta S$  is negative considered as unfavorable or non-spontaneous reactions. The thermodynamic data obtained with the two methods are in harmony with each other. The activation energy of Mn(II) complex is expected to increase in relation with decrease in their radii [49, 50]. The smaller size of the ions permits a closer approach of the ligand. Hence, the  $E$  value in of the Mn(II) complex is higher than that for the other Co(II) and Cu(II) complexes. The correlation coefficients

**Table 5** Thermodynamic parameters using the Coats–Redfern/CR and Horowitz–Metzger/HM operated for the PBT and their Cu<sup>II</sup>, Co<sup>II</sup>, and Mn<sup>II</sup> complexes

Compound	Stage	Method	Parameter					Correlation coefficient $r^2$
			$E^*/\text{kJ mol}^{-1}$	$A/\text{s}^{-1}$	$\Delta S^*/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta H^*/\text{kJ mol}^{-1}$	$\Delta G^*/\text{kJ mol}^{-1}$	
PBT	1st	CR	$1.26 \times 10^5$	$4.42 \times 10^{10}$	$-4.56 \times 10^1$	$1.22 \times 10^5$	$1.45 \times 10^5$	0.9936
		HM	$1.24 \times 10^5$	$6.21 \times 10^{10}$	$-4.28 \times 10^1$	$1.02 \times 10^5$	$1.42 \times 10^5$	0.9999
		Average	$1.25 \times 10^5$	$5.13 \times 10^{10}$	$-4.42 \times 10^2$	$1.12 \times 10^5$	$1.43 \times 10^5$	
Mn <sup>II</sup>	1st	CR	$1.65 \times 10^5$	$1.46 \times 10^{23}$	$-1.58 \times 10^2$	$1.62 \times 10^5$	$2.03 \times 10^5$	0.9889
		HM	$1.83 \times 10^5$	$1.61 \times 10^{24}$	$-2.17 \times 10^2$	$1.08 \times 10^5$	$2.01 \times 10^5$	0.9916
		Average	$1.74 \times 10^5$	$8.78 \times 10^{23}$	$-1.87 \times 10^2$	$1.35 \times 10^5$	$2.02 \times 10^5$	
Co <sup>II</sup>	1st	CR	$1.37 \times 10^5$	$4.19 \times 10^{21}$	$-1.49 \times 10^2$	$1.34 \times 10^5$	$8.67 \times 10^4$	0.9988
		HM	$1.44 \times 10^5$	$2.00 \times 10^{22}$	$-1.81 \times 10^2$	$1.42 \times 10^5$	$8.38 \times 10^4$	0.9994
		Average	$1.40 \times 10^5$	$1.20 \times 10^{21}$	$-1.65 \times 10^2$	$1.38 \times 10^5$	$8.52 \times 10^5$	
Cu <sup>II</sup>	1st	CR	$9.72 \times 10^4$	$5.96 \times 10^{12}$	$-1.63 \times 10^1$	$1.96 \times 10^5$	$9.49 \times 10^4$	0.9951
		HM	$1.04 \times 10^5$	$9.53 \times 10^{13}$	$-2.14 \times 10^1$	$2.81 \times 10^5$	$9.34 \times 10^4$	0.9934
		Average	$1.00 \times 10^5$	$5.06 \times 10^{12}$	$-1.88 \times 10^2$	$2.38 \times 10^5$	$9.41 \times 10^4$	

of the Arrhenius plots of the thermal decomposition steps were found to lie in the range from 0.9889 to 0.9999, showing a good fit with linear function.

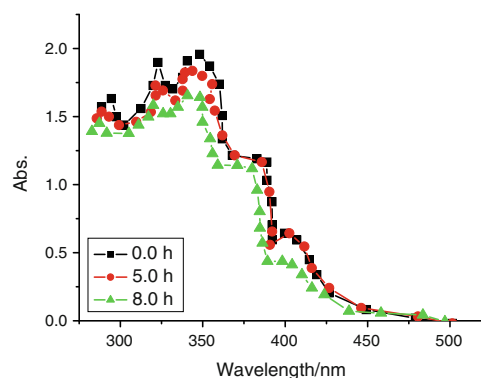
#### The photostability

Under the UV lamp, it is clear that  $[\text{Mn}(\text{PBT})_2(\text{Cl})_2] \cdot 7\text{H}_2\text{O}$  complex is more green fluorescent than both the other Cu(II) and Co(II) complexes and also the free ligand itself. Concluded that manganese(II) ions enhance the fluorescence properties of PBT rather than cobalt(II) and copper ions.

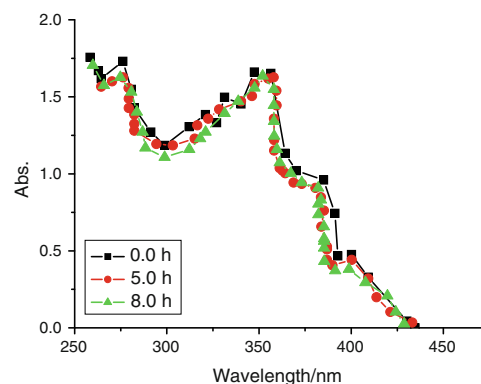
It is well known that all organic dyes undergo bleaching after prolonged exposure to sunlight. Dyes for fluorescent collectors have to fulfill particularly stringent conditions in this respect. A great many dyes deteriorate within hours or days in bright sunlight and that, on the other hand, solar collectors are expected to have a lifetime of between 10 and 20 years. A reasonable goal for dye lifetime in fluorescent collector is 5 years, because the most expensive part of the system, namely the solar cells, will not degrade and can stay in place, while the collector plates are exchanged at certain intervals. There are some parameters which have an influence on the photostability of dyes [54]: (i) manufacturing parameters such as additives in the plastic materials, method of polymerization, treatment after polymerization, and dye concentration; (ii) operating parameters such as temperature under illumination, periods without illumination, and temperature during these periods, spectrum of incident light and intensity of incident light.

The photochemical degradation of PBT doped in PMMA occurs only in the presence of suitable optical radiation (Xenon arc lamp power), which produces large local increases in temperature and thermal destruction of the dye molecules.

PBT and Mn(II)/PBT doped in PMMA were exposed indoors to UV–Vis radiation and the change in the absorption spectra was achieved at different times during irradiation period as shown in Figs. 6 and 7. After



**Fig. 6** Photostability of PBT doped in PMMA before and after exposure to UV–Vis light



**Fig. 7** Photostability of PBT/Mn<sup>2+</sup> complex doped in PMMA before and after exposure to UV–Vis light

**Table 6** Rate constants/*k* of photodegradation and half life times of doped PBT dye and manganese(II) complex in PMMA

Sample	<i>k</i> /min <sup>-1</sup>	<i>t</i> <sub>1/2</sub> /min
PBT/PMMA	385 nm	385 nm
	$9.31 \times 10^{-4}$	744
PBT/Mn <sup>II</sup> complex/PMMA	382 nm	382 nm
	$2.18 \times 10^{-4}$	3179

complexation, the Mn(II)/PBT enhance the photostability. The increase in photostability is referred to strong chelation between dye with metal ions. The rate constant of photodegradation of dyes was estimated according to the following equation [55, 56]:

$$k = \frac{2.303}{t} \log \frac{A_0}{A}$$

where *A*<sub>0</sub> and *A* are the absorptions before and after irradiation for time (*t*). The *k* value and half life times are listed in Table 6. It is clear from the degradation data that the complexations modify the photostability of dye.

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