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Thermal stability of *cis*-dithiocyanato(2,2′-bipyridyl4,4′dicarboxylate) ruthenium(II) photosensitizer in the free form and on nanocrystalline TiO_2 films

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Abstract

Thermal stability of ruthenium (II) complexes of the type $[Ru(H_2dcbpy)_2(NCS)_2]$ **1**, $(Bu_4N)_2[Ru(Hdcbpy)_2(NCS)_2]$ **2**, $(Bu_4N)_4[Ru(dcbpy)_2(NCS)_2]$ **3**, and $(Im)_4[Ru(dcbpy)_2(NCS)_2]$ **4**, where dcbpy=2,2′-bipyridyl-4,4′dicarboxylate, Bu_4N^+=tetrabutylammonium, and Im=dimethylethylimidazolium, has been studied using thermoanalytical techniques, IR, UV–VIS, and ^1H NMR spectroscopic methods. These complexes show remarkable stability in both nitrogen and air atmospheres at high temperatures, ranging from 180°C for **2** to 250°C for **1**. The only process that is observed at lower temperatures is the dehydration which occurs between 40 and 110°C. High temperature processes including deamination of the counterion as well as decarboxylation and decomposition of the complex occur between 200 and 400°C with different characteristics in air and in nitrogen. The decarboxylation reaction is an endothermic process in nitrogen atmosphere and overlaps with decomposition of the complexes. In air, on the other hand, it is an exothermic process distinctively separated from decomposition. Higher thermal stability is observed for **1** and **2** when anchored onto nanocrystaline TiO_2 films. The activation energy of decarboxylation is estimated for **1** in the free form (ca. 103 kJ mol^{-1}) and on TiO_2 (ca. 126 kJ mol^{-1}). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium dye; Charge transfer sensitizer; Thermal stability; TiO_2; Mesoporous solar cells

1. Introduction

Application of *cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) complex as the most efficient photosensitizer in dye sensitized solar cells is well established [1–17]. Long-term stability of the sensitizer under the operating conditions of the cell has also been investigated [18]. The sealing process of the cell is carried out at temperatures as high as 150°C. Therefore, it is important to scrutinize the thermal stability of the sensitizer at elevated temperatures. These effects can be determined by following the changes that are likely to occur during the heating. We have scrutinized the stability behavior of the title complex and its salts containing organic cations like tetrabutylammonium or dimethylethylimidazolium in the temperature range of 20–450°C.

Though there are several reports on the thermal behavior of compounds containing carboxylate [19–21], Bu_4N^+ [22–24] and Im^+ [25] groups, inorganic

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complexes containing functional groups have not been studied so far. In air, for organic cations containing carboxylate groups the major reactions are oxidative decarboxylation. Organic ammonium ions are converted into tertiary amines followed by further decomposition to gaseous products. Here we report the thermal behavior of the complexes **1–4** under dynamic nitrogen and air atmospheres using thermoanalytical techniques. The thermal stability of **1**and **2** when anchored onto TiO_2 relative to the free form is rationalized and the activation energy of decarboxylation of **1** on TiO_2 is estimated from kinetic studies.

2. Experimental

The ruthenium complexes were available from our previous studies [26]. UV–VIS absorption spectra were recorded on a HP 8450 diode-array spectrophotometer. Infrared spectra were recorded as KBr pellets with a Perkin–Elmer Paragon 1000 FTIR instrument. ^{1}H NMR spectra were obtained on a Bruker AC-P 200 MHz spectrometer. TGA and DSC were performed using Mettler TA 4000 and Rheometric Scientific STA 1000 thermal analyzers. TGA experiments were carried out in a dynamic atmosphere (20 ml/min) of air or nitrogen with a heating rate of 5°C/min. TG and DSC curves were recorded by heating the samples ca. 1–5 mg of the free dyes and 15–20 mg dye on TiO_2 up to about 450°C. Indium was used as reference to calibrate the temperature and heat flow.

3. Results and discussion

3.1. Thermal behavior of the free dyes

The thermoanalytical data for the free dyes **1–4** are summarized in Table 1. The combined TG, DTG, and DSC curves of **1** in dynamic atmosphere of air and nitrogen are presented in Figs. 1 and 2. In air, three well-defined steps can be observed in the TG and DTG curves (Fig. 1). The first, between 35–100°C, is associated with 8.14% mass loss which is attributed to the endothermic dehydration of the dye loosing 3.52 mol

Table 1
Thermoanalytical data for the thermal behavior of complexes **1**–**4** in dynamic nitrogen and air atmospheres at 5°C/min heating rate[a]

Complex	Step	Air; T_i (°C)	DSC	Δ*m* (%)		Attrib.	Nitrogen; T_i (°C)	DSC	Attrib.
				Exp.	Theor.				
1	1	35	endo	8.14	8.11	$-3.5H_2O$	35	endo	dhd
	2	250	exo	23.67	22.65	$-4CO_2$	290	endo	dcr+dcm
	3	335	exo	–	–	dcm	–	–	–
2	1	35	endo	2.23	2.23	$-1.5H_2O$	35	endo	dhd
	2	190	exo	33.63*	39.77	−2TBA	190	endo	dam
	3	295	exo	18.99*	14.52	$-4CO_2$	295	endo	dcr+dcm
	4, 5, 6	340	exo	–	–	dcm	–	–	–
3	1	40	endo	–	–	dhd	40	endo	dhd
	2	180	exo	50.61*	54.71	−4TBA	180	endo	dam
	3	220	exo	–	–	–	235	–	–
	4	280	exo	11.56*	9.99	$-4CO_2$	280	endo	dcr
	5, 6, 7	340	exo	–	–	dcm	345	endo	dcm
4	1	30	endo	5.50	5.33	$-4H_2O$	30	endo	dhd
	2	70	endo	2.55	2.66	$-2H_2O$	75	endo	–
	3	220	exo	48.80	53.92	−4Im	230	endo	dam
	4	–	–	–	–	–	283	endo	dcr
	5	310	exo	–	–	$-4CO_2$	310	endo	dcr+dcm
	6	355	exo	–	–	–	–	–	–
	7	380	exo	–	–	dcm	–	–	–

[a] Attrib.=attributed, Exp.=experimental, Theor.=theoretical, endo=Endothermic, exo=exothermic, dhd=dehydration, dam=deamination, dcr=decarboxylation, dcm=decomposition, TBA=tetrabutylammonium, Im=dimethylethylimidazolium.

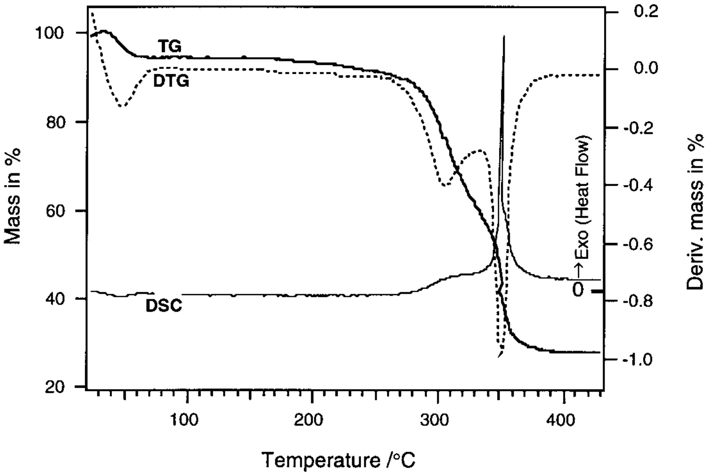


Fig. 1. TG, DTG, and DSC curves of **1** in a dynamic air atmosphere (20 ml/min).

of water ($-3.5H_2O=8.11\%$). The elemental analysis of the complex **1** shows the presence of 3.5 water molecules per ruthenium center, which is consistent with TGA analysis. The dye is stable up to about 250°C and does not undergo any changes detectable by TG and DSC (Fig. 1).

Further evidence for the stability of the dye comes from the IR and ^{1}H NMR studies. The IR and ^{1}H NMR spectra of the sample were essentially unchanged, when a sample of **1** was heated up to 150°C in air atmosphere and kept under these conditions for 1 h. The co-ordinated NCS ligand remains intact and shows an intense band at 2107 cm^{-1} due to thiocyanate ν(CN) in the IR spectrum and the ^{1}H NMR spectrum shows peaks at the positions identical to the unheated complex.

Decarboxylation of the complex **1** under N_2 takes place at a higher temperature (T_i=290°C) compared to air, and overlaps with decomposition, Fig. 2. These two processes occur concurrently as a single endothermic step. In air however, the decarboxylation reaction begins at 250°C and proceeds as a well-defined exothermic process which is clearly separated from the decomposition process. The mass loss in this step

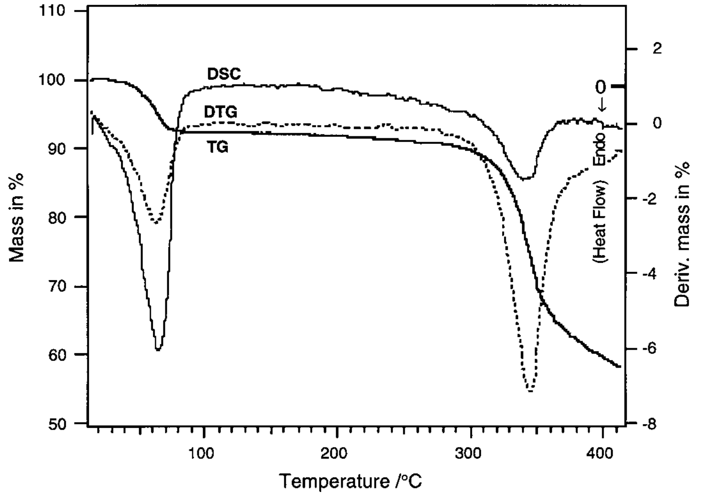


Fig. 2. TG, DTG, and DSC curves of **1** in a dynamic nitrogen atmosphere (20 ml/min).

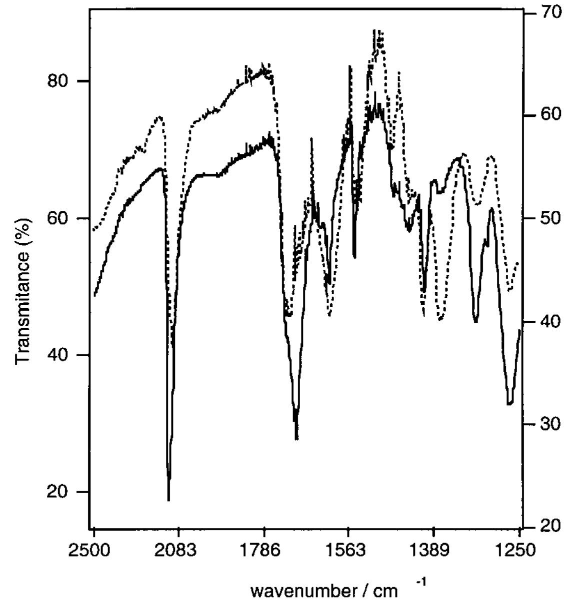


Fig. 3. Infrared spectra of **1** before ——, and after -------- heating up to 330°C in air.

is 23.67% ($-4CO_2$=22.65%) and during this process four carboxylate groups on the two bipyridine ligands are oxidized into carbon dioxide. Fig. 3 shows the IR spectrum of a sample of **1** which has been heated up to 330°C in air. The decrease in the relative intensity of the band at 1700 cm^{-1} proves unambiguously that the carboxylate functional groups are being removed in this process. The decomposition of the residue takes place rapidly above 335°C, and a sharp exothermic peak is observed in the DSC curve due to the oxidation of the organic ligands.

The TG, DTG, and DSC curves of **2** in dynamic air and nitrogen atmospheres are shown in Figs. 4 and 5. The major difference between thermal behavior of the dyes with organic cations (**2**–**4**), and **1** is the additional deamination process. Similar to **1**, the first step, between 35 to 90°C, is accompanied by 2.23% mass loss ($-1.5H_2O$=2.23%) which is attributed to the dehydration process. The dye is stable up to 190°C showing no changes detectable by TG and DSC. The IR and ^{1}H NMR spectra of a sample of **2** heated up to 150°C under nitrogen for 1 h were essentially unchanged. In the second step, between 190 and 295°C, tetrabutylammonium undergoes decomposition resulting in gaseous products. Thermal properties of tetraalkyl ammonium salts have been studied [22] and it is well established that tertiary amines are one of the thermal decomposition products formed at elevated temperatures according to the Eq. (1).

$$NR_3X \rightarrow R_3N + RX \quad (1)$$

An alternative reaction for the decomposition of R_4N^+ in the presence of a base B^- is a Hofmann elimination reaction shown in Eq. (2) [23,24].

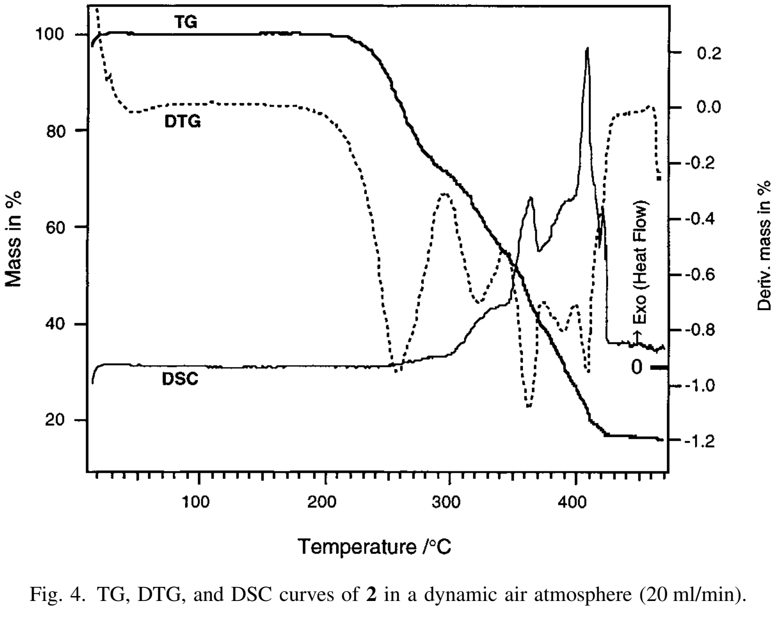


Fig. 4. TG, DTG, and DSC curves of **2** in a dynamic air atmosphere (20 ml/min).

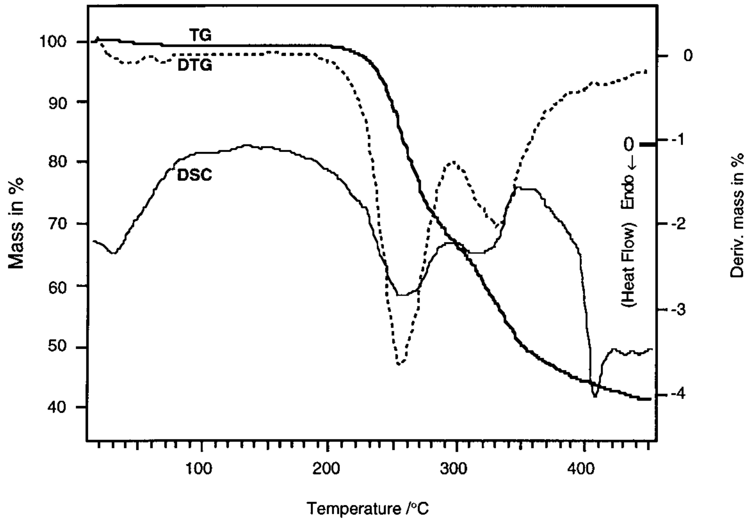
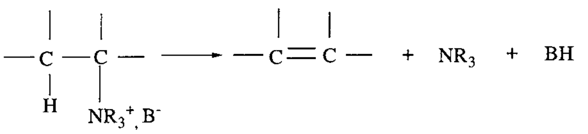


Fig. 5. TG, DTG, and DSC curves of **2** in a dynamic nitrogen atmosphere (20 ml/min).



$$-\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}-\underset{\displaystyle NR_3^+, B^-}{\overset{|}{\underset{|}{C}}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}- \;+\; NR_3 \;+\; BH \qquad (2)$$

R_3N undergoes further reactions at temperatures as high as 400°C. It is clear that in a dynamic atmosphere, most of the resulting amine escapes from the reaction chamber, however the possibility of secondary reactions for the trapped amine molecules cannot be ruled out. These reactions accompanied by the decomposition of the organic ligands in air atmosphere might well account for the three exothermic processes following the decarboxylation reaction which occurs in the third step between 295 and 345°C. The mass loss in the second step is 33.63% which correlates with the release of 1.69 mol of tetrabutylammonium ($-2Bu_4N^+ = 39.77\%$). This is a reasonable value considering the overlap between deamination and decarboxylation processes in steps 2 and 3. The mass loss in the third step is 18.99% which corresponds to the release of 5.2 CO_2 molecules ($-4CO_2=14.52\%$). A comparison between the theoretical and experimental values of the total mass loss for the release of 4 (CO_2+Bu_4N^+) in these two successive steps, which are 54.29 and 52.62%, respectively, indicates that a combination of these two processes can reasonably well account for the experimental results. In a nitrogen atmosphere, however, the decarboxylation and decomposition processes occur in a single endothermic step in a manner similar to **1**.

An interesting observation in the thermal behavior of **2** is that the decarboxylation and decomposition reactions take place at higher temperatures relative to **1**. While in a dynamic air atmosphere, decarboxylation begins at T_i=250°C for **1** (with the temperature for the maximum rate T_m=308°C) the corresponding temperatures for **2** are T_i=295°C and T_m=315°C. The decomposition process also takes place at higher temperature in **2**, T_i=340°C and T_m=360°C compared to **1**. This additional stability towards decarboxylation and decomposition, which is also observed in **3** and **4**, could be due to softer interaction between the bulky organic cations with carboxylate groups.

TG, DTG, and DSC of **3** in dynamic air and nitrogen atmospheres are shown in Figs. 6 and 7. The thermal processes are similar to those observed for **2** except for the higher water content of **3**, due to its more hygroscopic character relative to **2**, and a two step deamination process with a higher ratio, $4Bu_4N$ versus $2Bu_4N$. The interesting feature of the deamination of **3** is the

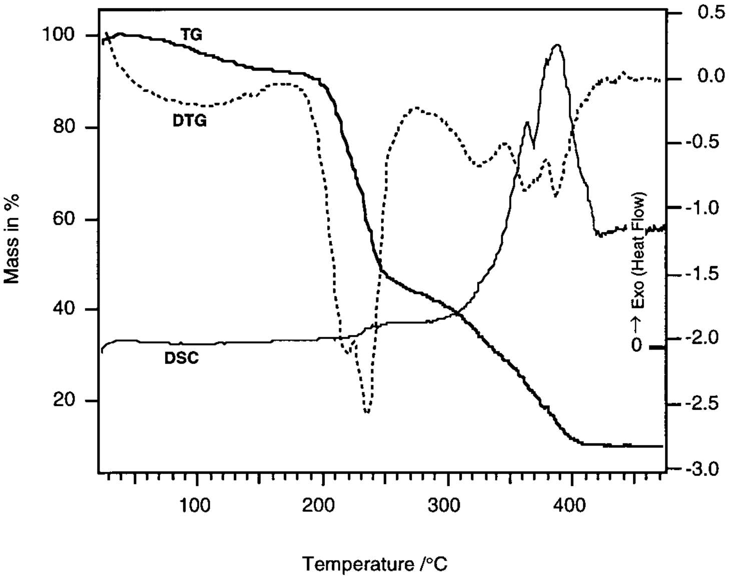


Fig. 6. TG, DTG, and DSC curves of **3** in a dynamic air atmosphere (20 ml/min).

decomposition of four Bu_4N groups in two successive steps with T_{m1}=210°C and T_{m2}=235°C. The pK_a of the carboxylate groups of **1** have been measured and it is clear that the two carboxylate groups located trans to NCS ligands are more basic than the ones trans to each other [26]. The observed two step deamination process for **3** can be rationalized on the basis of the difference in the extent of interaction between the two types of carboxylate anions with Bu_4N^+ cations.

Quantitative estimation of the mass loss in different steps is in accord with the expectation. In the dehydration step the mass loss is quite variable due to the

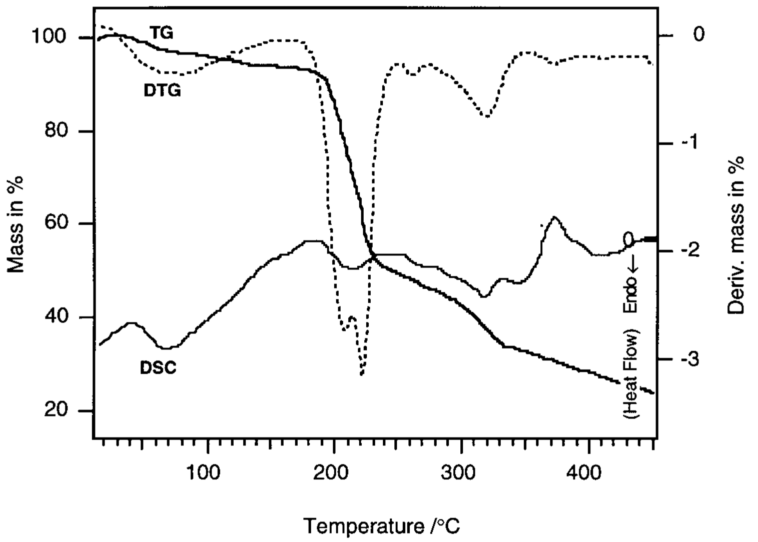


Fig. 7. TG, DTG, and DSC curves of **3** in a dynamic nitrogen atmosphere (20 ml/min).

hygroscopic nature of **3**, however, this is not very critical since no chemical changes are observed during the dehydration process. The ^{1}H NMR and IR spectra of a sample of **3** subjected to heating up to 150°C under nitrogen, did not show any changes comparing to the starting material. The mass loss in the deamination and decarboxylation steps are 50.61% ($-4Bu_4N^+$=54.71%) and 11.56% ($-4CO_2$=9.99%), respectively. The total experimental mass loss for combined deamination and decarboxylation is 62.17% as compared to the theoretical value of 64.70% for the release of 4 ($Bu_4N^+ + CO_2$). The agreement is good considering the overlap between these two processes and some overlap between the decarboxylation and decomposition reactions. Similar behavior is observed for **3** in nitrogen atmosphere, however the processes are endothermic and the decarboxylation and decomposition processes occur in a single step as in **2**.

The thermoanalytical data of **4** in dynamic air and nitrogen atmospheres are listed in Table 1. Thermal behavior of **4** in air atmosphere, is similar to that of **3**. However, the dehydration process consists of two very close steps associated with the successive release of the adsorbed and the crystallization water. In addition the deamination process begins at 220°C which is about 30°C higher than that for **3**, and the four Im^+ groups are released within a shorter temperature range with some overlap between the DTG peaks of the two types of Im^+. In nitrogen, the separation of the two peaks is more pronounced, however, the decarboxylation and decomposition processes occur in a single endothermic step. These observations are in accord with the higher thermal stability of Im^+ relative to Bu_4N^+. Quantitative estimation of the mass loss in different steps is satisfactory considering the extent of overlap between successive steps. The total experimental mass loss for combined deamination and decarboxylation is 48.80% as compared to the theoretical value of 53.92%. Since thermal decomposition of imidazolium is accompanied by the formation of some solid material, including urea [25] the estimated value is in accord with the expectation.

3.2. Thermal behavior of the dyes on TiO_2

One of the interesting features of the thermal behavior of the dyes is their additional thermal stability when anchored onto TiO_2 in comparison with their free form. The thermoanalytical data for the two sensitizers **1** and **2** in the free form and on TiO_2 are listed in Table 2. The TG and DTG curves of **1** anchored onto TiO_2 film and the blank are presented in Figs. 8 and 9, respectively. As in the free dye, the first step between 40 and about 100°C belongs to the dehydration process. In this step the water from the mesopores of TiO_2, which is mostly adsorbed from the environment, is released. Similar results are obtained in a blank experiment performed on pure TiO_2 film with no dye anchored onto it, Fig. 9. The decarboxylation process, however, begins at a higher temperature relative to the free dye. The initial temperatures (T_i) for decarboxylation and decomposition processes of **1** in the free form are 250 and 335°C, respectively. These two processes begin to occur at 320 and 370°C when **1** is anchored onto TiO_2.

A similar trend is observed for **2** on TiO_2 with T_i values of 340 and 378°C as compared to 295 and

Table 2
Thermoanalytical data for the thermal behavior of **1** and **2** in free form and on TiO_2 at 3°C/min heating rate in a dynamic air atmosphere[a]

Complex	Step	Free			on TiO_2		
		T_i (°C)	T_m (°C)	Attrib.	T_i (°C)	T_m (°C)	Attrib.
1	1	35	50	dhd	35	60	dhd
	2	250	308	dcr	320	360	dcr
	3	335	350	dcm	370	385	dcm
2	1	35	50	dhd	35	60	dhd
	2	190	255	dam	220	260	dam
	3	295	315	dcr	340	358	dcr
	4	340	360	dcm	378	386	dcm

[a] Attrib.=attributed, dhd=dehydration, dcr=decarboxylation, dcm=decomposition, dam=deamination.

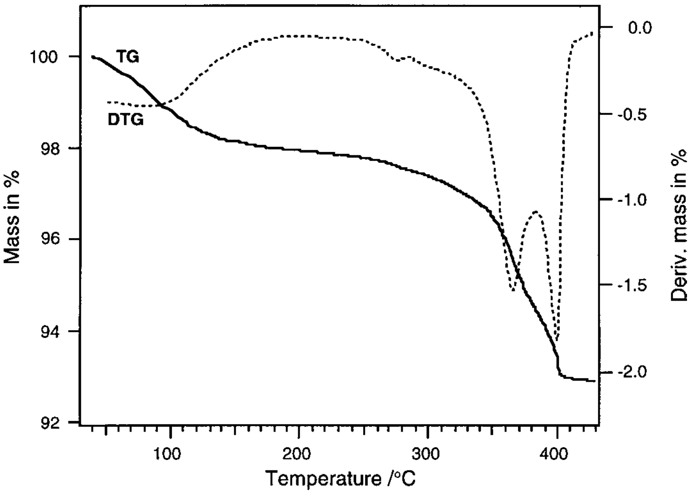


Fig. 8. TG and, DTG curves of **1**, anchored onto TiO_2, in a dynamic air atmosphere (20 ml/min).

340°C for decarboxylation and decomposition processes of the free dye. The remarkable increase of about 60°C in the thermal stability of the dyes against decarboxylation and about 40°C against decomposition can be rationalized in terms of the strong interaction between the carboxylate groups and TiO_2 [27]. A higher activation energy is also expected for the decarboxylation of the dye on TiO_2 relative to the free dye. In order to estimate the activation energy of the decarboxylation of **1**, the temperature (T_m) at maximum weight loss (TG) in the decarboxylation process was determined as a function of heating rate (θ) applied from the thermoanalytical curves. The activation energy was directly estimated from the slope of the graph log θ against $1/T_m$ (Fig. 10) according to the Eq. (3) [28]. The estimated value of E_a=126 kJ mol^{-1} for the decarboxylation of dye **1** on TiO_2 as compared to 103 kJ mol^{-1} for the free dye is consistent with the observed higher thermal stability of the dye anchored onto TiO_2. These results are in agreement with the recent theoretical calculations [29] indicating that the dye on TiO_2 is about 26 kJ mol^{-1} more stable than the free dye.

$$E_a = -2.19R\left[\frac{d(\log\theta)}{d(1/T_m)}\right] \quad (3)$$

It is evident from the thermoanalytical data obtained for **2** that the deamination process is slow and takes place within a large temperature range. In addition, the approximate weight loss in this process correlates well with the presence of about one Bu_4N^+ as a counterion with the dye on TiO_2. The ^1H NMR spectrum of the desorbed complex **2** from the TiO_2 surface gives an additional support for the presence of one Bu_4N^+. Therefore, it is most likely that the strong interaction between TiO_2 and the negatively charged carboxylate groups can account for the charge compensation by hydroxide loss from the TiO_2surface as well as for the additional stability of the dye toward decarboxylation [30].

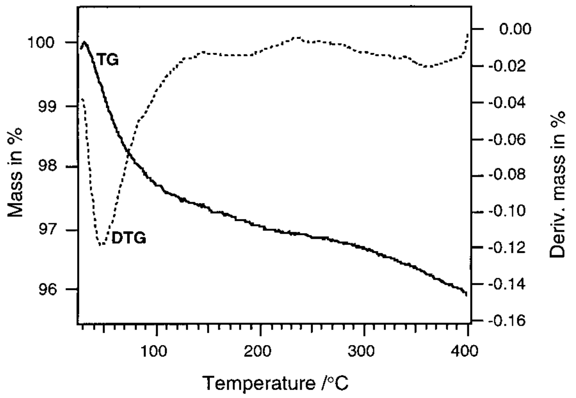


Fig. 9. TG and DTG of blank TiO_2 film in a dynamic air atmosphere (20 ml/min).

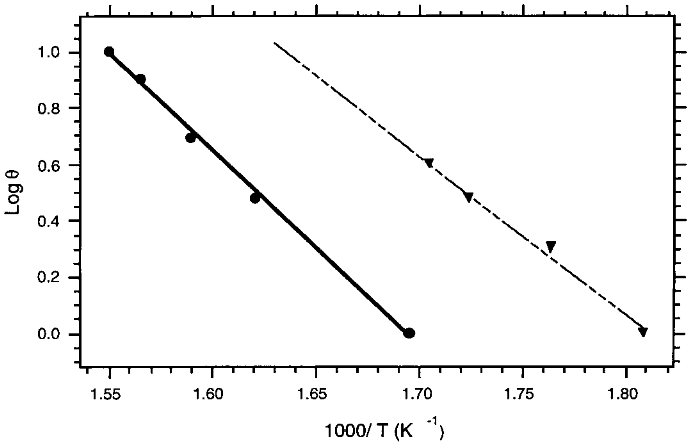


Fig. 10. log θ vs. $1/T$ plot for decarboxylation of **1** in the free form - - - - - and on TiO_2 ▬▬.

4. Conclusions

Ruthenium(II) complexes used as photosensitizers in dye sensitized solar cells show high thermal stability. Thermoanalytical results obtained in this study clearly demonstrate that dehydration is the only process that occurs below 180°C and, based on the spectral data, the dyes do not undergo any observable chemical change below 150°C. These complexes show different thermal behavior in air and nitrogen atmospheres. In air the decarboxylation reaction takes place as a well defined exothermic process prior to the decomposition of organic ligands while the decarboxylation and decomposition occur concurrently as a single endothermic step under nitrogen. The organic cations introduced to replace the protons have a noticeable effect on the thermal stability of the dyes increasing the decarboxylation temperature by about 40°C. In addition the deamination temperature increases by about 35°C when Bu_4N^+ cations are replaced by Im^+. An interesting observation is the two step deamination in dyes with four organic cations, which is due to the difference in the extent of interaction between these cations and the carboxylate groups.

Further intriguing results of this study are: (i) the higher thermal stability for the dyes anchored onto TiO_2, which leads to a higher decarboxylation temperature (330°C) as compared to the free dye (280°C). (ii) the coadsorption of only one cationic counterion along with the complex when the dye is anchored onto TiO_2. Further studies on the behavior of the different organic and inorganic cations co-adsorbed onto TiO_2 are under progress.

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