Synthesis of polymeric luminophores based on the carbazole derivative and terbium (III) complexes

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ABSTRACT

Key words: carbazole, salicylic acid, copolymer, ion, luminesce

This article focuses on the synthesis of a new polymeric phosphors containing Tb^{+3} ions as a potential material for next generation optoelectronic devices. Here we are presented the results of the synthesis and luminescence properties of copolymers containing: 2-(9-carbazolyl)ethyl methacrylate (CEM) and p-methacryloyloxybenzoic acid (pMBA) complexed with Tb(III). All copolymers have been characterized by HNMR, GPC, FTIR and UV-Vis. Solutions of the copolymers in THF or $CHCl_3$ have been examined for their photoluminescence properties. Finally, the possibility of using these materials in optoelectronics were compared to those already synthesized.

INTRODUCTION

The phenomenon of luminescence, occurring in organic complexes of rare earth elements (block f) is a common and popular subject of research, because of their unique luminescent properties. It is known, that the emission spectra of these compounds are characterized by long excited-state lifetime (10^{-3} s) while for the ordinary organic chromophores is of the order of 10^{-9} s. In addition, the rare earth complexes have a large Stokes shift and the emission spectra are very narrow and intense [1-4]. Most of the lanthanide ions (Ln (III)) surrounded by suitable organic ligand emit electromagnetic radiation with a wavelength between 312 nm and 1530 nm after excitation. However, both the intensity of the emitted light and quantum efficiency of conversion energy depend largely on the type of organic ligands. In consequence, their presence in the coordination complexes results in sensibilization of luminescence. Thus, due to the mechanism the key issue is so-called "antenna effect''. On the whole, it is the absorption of energy by the ligands and next its transfer as a result of intermolecular energy transfer to the lanthanide ion, which finally emits: UV, visible or infrared light. Furthermore, the behavior of systems upon excitation show a simplified Jablonski diagram. One of the examples is illustrated in Fig. 1. It shows the deactivation pathways of the excited states in the presented systems.

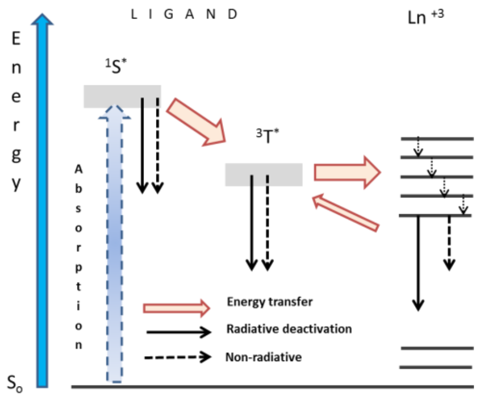

Fig. 1. A simplified Jablonski diagram

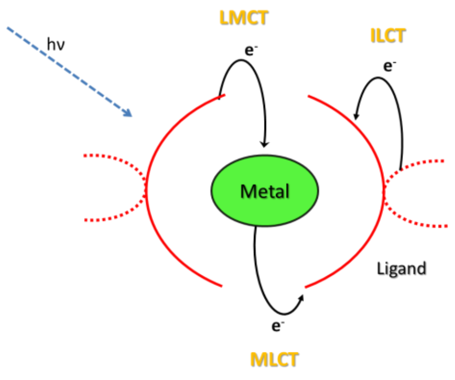

Fig. 2. Energy transfer paths

A wide range of the competing deactivation processes and energy transfer were reduced to a minimum for the clarity of figures. It is noteworthy, that in these complexes, the process of energy transfer to the central ion can be observed since the energy of the system is diversified by: excited singlet state (^1S *), excited triplet state (^3T *), Intra Ligand Charge Transfer (ILCT), Ligand to Metal Charge Transfer (LMCT), Metal to Ligand Charge Transfer (MLCT), 4f-5d transitions, and sometimes directly from the 4f orbitals [5]. Generally, it keep in mind that in the designing and implementation of the novel rare-earth metal complexes the best quantum efficiencies may be achieved when the energy of the excited triplet state ligands is less than the energy of the excited states of lanthanide ions. The literature suggests that in order to provide an effective sensitization of photoluminescence the size of energy gap should be in the range of 2500-3000 cm^{-1}. However, reduction of the non-radiative deactivation processes is possible when the energy difference between the leves: (^1S *) - (^3T *) is not greater than 5000 cm^{-1} [6]. Thus, the most common organic ligands used are derivatives of : 1,10-phenanthroline, salicylic acid, quinoline, pyridine, thiophene, β-diketones, etc. [7]. The class of these compounds has also been contributed to the development of time-resolved fluorescence spectroscopy because of the much longer lifetime of the excited states they have been applied as the immunoassay for protein biomarkers [9]. Another potential applications of lanthanide (III) coordination complexes are the light conversion molecular devices e.g. UV-VIS, UV-NIR [10]. Owing to their, good solubility properties it has been allowed to use them for the production of active layers in OLED devices [11]. In recent times, the electroluminescence from a polymer guest–host system has been described, what is more the organic lanthanide complexes can be incorporated into the transparent polymer matrixes such as: polymethyl methacrylate, polyvinyl alcohol, polyethylene, polystyrene, polyurethanes, polyesters, polycarbonates, polyimides and epoxy resins [12]. Further, more stable and efficient luminophores have been synthesized by covalent binding of the metal complexes with polymer chain [13]. Recently, Ling et. all obtained the copolymer by free radical copolymerization of N-vinylcarbazole, with Eu (III) complexes with acrylic acid that it has been used in the construction of OLED device. Moreover, they measured the photo and electroluminescent properties and as a result the highest luminance value has been obtained for the voltage about 29 V [14]. As for similar example it is worth noting the polymer composed of Eu (III) and 4-Vinylbenzoic acid. It has been applied to the construction of memory. This was possible because the material had two different stable conduction bands [15]. In short, the literature presents various examples of the lanthanide complexes. However, we payed attention mostly to Tb (III) complexes with ortho- and para- isomers of hydroxybenzoic acid because of the high luminescent efficiency (0.5-0.85). This fact inspired us to obtain and characterize the statistical copolymers containing methacrylic derivatives of carbazole, p-hydroxybenzoic acid and Tb (III) complexes. To recap, we would like to show the experimental results for the novel non-conjugated copolymers in the context of the potential applications in optoelectronic areas.

METHODS

The progress of synthesis of monomers was monitored through thin layer chromatography (TLC) (Silica gel on TLC; hexane:acetone:bromoform 10:1:2). Melting point was determined using BarnSteadt Electrothermal 9200. The structures of compound were verified by means of NMR and IR. NMR spectra were recorded on Varian Mercury-VX 300 MHz NMR spectrometer. IR spectra were measured using BioRad FTS 165 FTIR spectrophotometer. The molecular weights of the copolymers were calculated from chromatograms achieved from gel permeation chromatography (GPC) using Knauer chromatograph. Photoluminescence spectra datas were obtained using PG Instruments Ltd. T80+ UV/Vis spectrometer and Ocean Optics USB2000 spectrophotometer.

All of the reagents were purchased from Sigma Aldrich.

RESULTS AND DISCUSSION

Synthesis of CEM

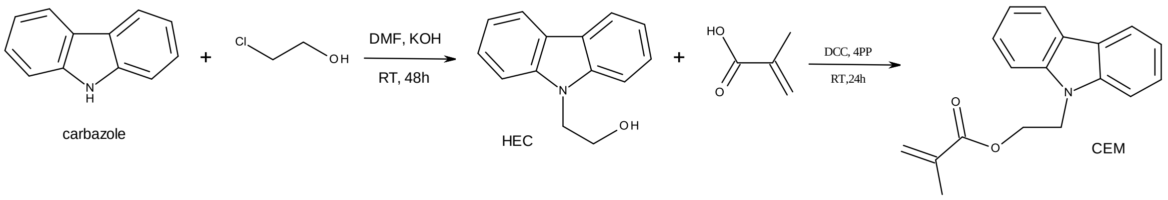

Fig. 3. General scheme of the preparation of CEM

Synthesis of CEM were carried out according to known procedures developed in our laboratory **[14]**. 9-(2-hydroxyethyl)carbazole (HEC) synthesized by a nucleophilic substitution reaction between carbazole and 2-chloroethanole in a presence of anhydrous DMF and KOH. The synthesis of 2-(9-carbazolyl)ethyl methacrylate (CEM) was carried out within 24 h at ambient temperature in round-bottom flask (500 ml), equipped with a reflux-condeser and magnetic stirrer. HEC (10 mmol), methacrylic acid (10.5 mmol) and 4– pyrrolidinopyridine (1.3 mmol) as a catalyst were mixed in ethylene dichloride (10 ml). Next an equimolar amount of N,N-dicyclohexylcarbodiimide (DCC) (10 mmol) in ethylene dichloride (5 ml) was added dropwise. At the end the by-product, N,N'-dicyclohexylurea (DCU), was filtered off from the solution. The filtrate was slowly concentrated under reduced pressure until a white needle crystals of the expected product precipitated. The product was purified by recrystallization from ethanol. The crude product was recrystallized twice from ethanol to effort 2.40 g of 2-(carbazol-9-yl)ethyl methacrylate. Yield: 86%; m.p. 81.5–82.5°C, lit. 77– 78°C, IR (KBr) ν= 3051(m), 1720(s), 2978(m), 1630(m), 1598(w), 1489(w), 1456(s),1318(s), 1172(s), 1157(m), 949(m), 816(m), 720 (s), 746 (s) cm^{-1}. ^{1}**HNMR** (300 MHz, $CDCl_3$): δ 1,79-1,82 (3H,s,$CH_2=C-CH_3$), 4,53-4,60 (4H, m, CH_2-CH_2), 5,45-5,49 (1H,m, trans $C=CH_2$) 7,13-7,50 (6H, m, arom.) 8,03-8,01 (2H, m, arom.).

Synthesis of pMBA

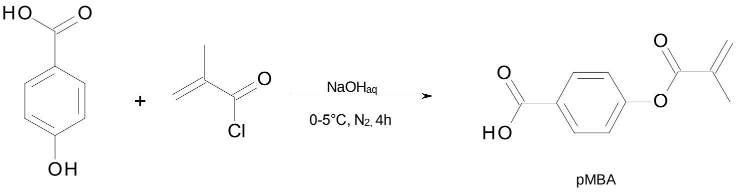

Fig. 4. General scheme of the preparation of pMBA

The second monomer was synthesized according to the literature procedure described by Van Ekenstein[17]. For this purpose, p-hydroxybenzoic acid (0.33 mol) was dissolved in 600 ml 5 wt% solution of NaOH (0.75) in H_2O. After complete dissolution the mixture was cooled to 0 ºC and methacryloylchloride (0.36 mol) was added dropwise in 1 h. The reaction was continued under Ar atmosphere for 2 h at room temperature. Next, dilute hydrochloric acid was then added dropwise until pH 5 was reached. Finally, p-methacryloyloxybenzoic acid was purified by crystallization from methanol twice.

Yield: 80%, m.p. 81–83°C, lit. 77– 78°C, FTIR (KBr, [cm-1]: 3500-2500 (O-H···O=C,), 2956 (C-H alif.), 1733(C=O), 1701 (C=O arom.) 1633 (C=C), 1606, 1508, 1124 (C=C), 945

^{1}HNMR - (300 MHz, $CDCl_3$) δ 8.23-8.09 (m, *2H arom.*), 7.31-7.18(m, 2H), 6.38 (t, 1H), 5.81 (p, 1H) $C=CH_2$, 2.08 (s, 3H)

^{12}CNMR – (75 MHz, $CDCl_3$) δ 171.04 (s1C), 165.17 (s1C), 155.32 (s1C), 135.50 (s1C), 131.85 (s1C), 127.93 (s1C), 126.66 (s1C), 121.80 (s1C), 18.31 (s1C)

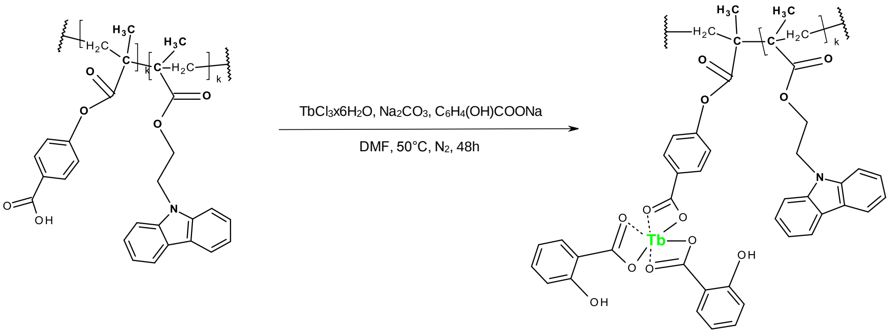

Fig. 5. Structure of copolymers after complexation

Synthesis of copolymers CEM-pMBA

In this stage, we carried out the free radical copolymerization of: 2-(9-carbazolyl)ethyl methacrylate (CEM) and p-methacryloyloxybenzoic acid (pMBA) in dried dioxane at 70 ° C . The initial solutions of monomers contained CEM and pMBA in specified molar ratio. Then, they were flushed with inert gas and azobisisobutyronitrile (AIBN) was used as initiator. Finally, the polymers were precipitated with methanol several times and dried. Each copolymer was obtained from the same polymerization conditions that it was presented in table 1.

Table 1. Reaction conditions of the polymerization

Acronym	CEM %mol	QM % mol	T[^{o}C]	t [h]	AIBN [%mol]	Solvent [ml]	Yield [%]
CEM-2MBA	98	2	80	72	1	5	80
CEM-4MBA	96	4	80	72	1	5	80
CEM-8MBA	92	8	80	72	1	5	80
CEM-12MBA	88	12	80	72	1	5	82
CEM-24MBA	76	24	70	72	1	5	94

Synthesis of complexed copolymers

The final stage of synthesis consisted of complexation reaction conducted on previously obtained copolymers. For the stoichiometric calculations it was assumed that the mole fraction of MBA units in the copolymer was the same as in the initial monomer mixture. Solutions of such copolymers in dried DMF (20 ml) were prepared then 0.5 eq. Na_2CO_3, 1 eq $TbCl_3x6H_2O$ and 2 eq of salicylic acid solution in 10 ml were dropped to these. Generally, syntheses were carried out for 48 h at 50 ° C under Ar atmosphere. After this time copolymers were precipitated in methanol. Products were additionaly purified by dissolving in CCl_3 and precipitated with methanol. Further, mixtures were centrifuged at 8000 rpm for 15 min and finally, analysis were performed after drying at 70 ºC.

DISCUSSION

Five different types of copolymers were synthesized and characterized by techniques such as GPC, IR, NMR, UV.

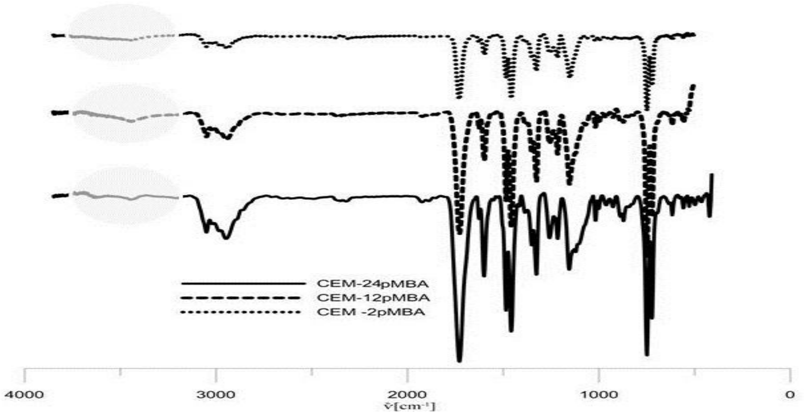

Fig. 6. FTIR spectra of the synthesized copolymers CEM-pMBA

Firstly, results of the FTIR analysis showed that products are macromolecular because of the band at 1650 cm^{-1} disappear from all spectra. It originates from the stretching vibrations of unsaturated C=C groups in monomers. Next, the broad and very intense absorption band in the 3300-3500 cm^{-1} region can be attributed to O-H stretching vibrations. This moiety is only presents in the carboxyl group and the polymer pMBA and may be evidence for the presence of pMBA units in copolymers.

Table 2. Number and weight average molecular weights of polymers

Acronym	Mn [g/mol]	Mw [g/mol]	Pd
CEM-2pMBA	12800	26890	2,09
CEM-4pMBA	13920	26960	1,93
CEM-8pMBA	15580	27240	1,74
CEM-12pMBA	16410	28200	1,71
CEM-24pMBA	15040	26080	1,73

The GPC analysis data are presented in table 2.It can be seen that the values of M_n and M_w are of the order of 10^4 and the degree of polydispersity in the range of 1,73-2,09.

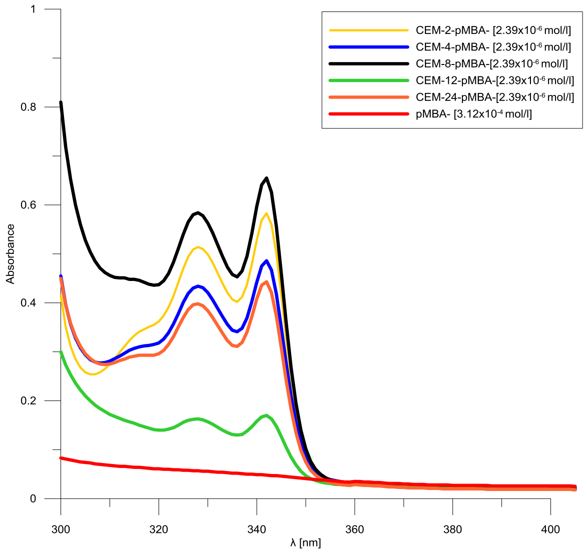

Fig 7. Absorption spectra of copolymers in dioxane.

UV-Vis spectra for copolymers was showed in figure 7. In this spectra characteristic absorption band from carbazole chromophore which has two maxima at 328nm and 341 nm can been seen. Nevertheless, aromatic rings derived from pMBA units can absorb to about 350 nm with maximum falls at 245 nm [16,17]. Generally speaking, with the increase of weight average molecular weights the absorption from both chromophores inrease. All the spectra were performed with the same concentration of copolymers (2,39 x10^{-5} mol/l) in 1,4-dioxane.

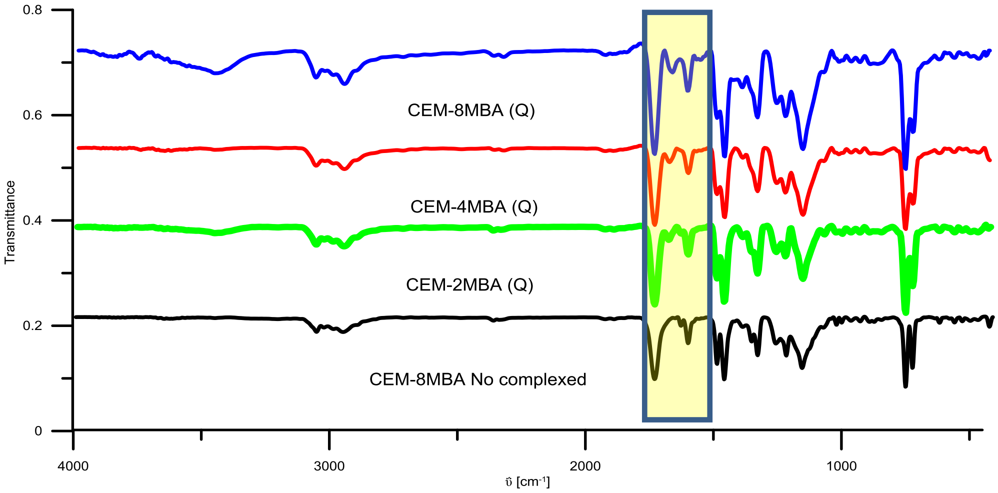

Fig. 8. The IR spectrum of the polymers before and after complexation:
CEM-8pMBA (Q) - complexed copolymer

The purified polymers as white powders under vacuum were dried to give an appropriate polymer complexes (CEM-pMBA Q). Further, we found that for CEM-pMBAQ copolymers containing an output (2,4,8)% mol of pMBA units the chelation in DMF proceeded efficiently without cross-linked polymer. On the other hand, we observed in the two other samples (12 and 24% mol o pMBA) the formation of insoluble cross-linked product in an amount 46% CEM-12-pMBA (Q) and 72% for CEM-24pMBA (Q). On the other hand, it was observed of the insoluble cross-linked copolymers which weren't soluble in DMF. We calculated this amount 46% CEM-12-pMBA (Q) and 72% for CEM-24pMBA (Q). Despite this fact, the copolymers CEM-xpMBAQ (where x= 2,4,8,12 % mol of pMBA) allowed to dissolve in CCl_3, CH_2Cl_2 etc. In figure 8, the graphical overview of the IR spectra for three complexed copolymers are presented. Only the spectrum of CEM-8pMBA showed the clearly and intense absorption band in the range of 3000-4000 cm^{-1}. It can be attributed to OH stretching vibration of water molecules. Bands occurred at 1660 cm-1 (υs C = O) and 1550 cm-1 (C = O υas) suggesting that copolymers were coordinated to the Tb (III) ions .

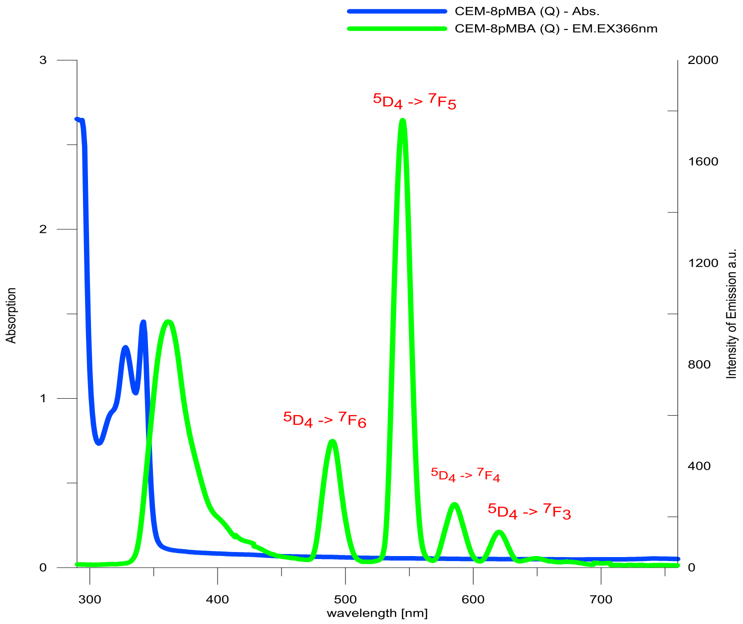

Fig. 9 Luminescence properties of copolymers,
conditions: 1,4-dioxane, RT

Finally, the luminescence properties of polymer complexes on the example of CEM-8pMBA(Q) in figure 9 was illustrated. As can be seen, the clearly absorption spectrum in the range of 290 to 900 nm shows that the polymer systems absorb strongly in UV which can be attributed to carbazole rings. Band with max. at 364 nm is associated with emission from carbazole rings. Analogously the range of emission from 450 to 680 nm with maxima at 452 nm corresponds to emission of Tb (III) organic complexes. Thus, the characteristic energy of a transition and hence the wavelength of visible energy transition in polymer complexes are shown as: : $^{5}D_{4}$ -> $^{7}F_{6}$ max.490nm, $^{5}D_{4}$ -> $^{7}F_{5}$ max. 544nm, $^{5}D_{4}$ -> $^{7}F_{4}$ max. 584nm , $^{5}D_{4}$ -> $^{7}F_{3}$ max. 584nm and the transition from $^{5}D_{4}$ -> $^{7}F_{4}$ is the strongest one.

CONLUSION

The monomers 2-(9-carbazolyl)ethyl methacrylate (CEM) and of p-methacryloyloxybenzoic acid (MBA) were synthesized and confirmed their chemical structure. As a result of free radical polymerization we managed to obtain polymers in different molar ratios of CEM-xMBA (x = 2,4,8,12,24 mol%). After the complexation reaction product was obtained as a white powder. For samples with a content of initial (2,4,8)% MBA found that the chelation was occurred effectively without cross-linked of polymers. Further discussion will be possible after a subsequent analysis.

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