

KAUNAS UNIVERSITY OF TECHNOLOGY

RITA BUTKUTĖ

SYNTHESIS OF BLUE FLUORESCENCE
PHENANTHROIMIDAZOLE DERIVATIVES AND INVESTIGATION
OF PROPERTIES AND POLYMERIZATION KINETICS

Summary of Doctoral Dissertation
Technological Sciences, Chemical Engineering (05T)

2018, Kaunas

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

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DARINIŲ SINTEZĖ, SAVYBIŲ BEI POLIMERIZACIJOS PROCESŲ
TYRIMAS

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INTRODUCTION

Motivation of the research. The development of energy efficient technologies intensified the studies of organic light emitting diode (OLED), solar cells, and organic transistors. These devices are formed using organic materials that must satisfy several requirements. The investigation of thermal, optical, photophysical, and photoelectrical properties can create structure-properties relationship and selected materials with a complex of optimum properties. The materials, from which is formed, for example, the carrier carrying a layer by casting process, must have film-forming properties, morphological stability and a certain high ionization potential, and carrier mobility. The most important characteristics of the emissive layer of LED are quantum efficiency of luminescence, luminescence color, and color purity. The charge transport materials for paints sensitized solar cells must have low ionization potential and high mobility. With the help of various synthesis methods, there can be selected variously modified molecular fragments, i.e., to connect different substituents to different positions, and only a comprehensive study of the characteristics can get structure-properties relationship. Then, it is possible to select suitable materials with the complex of the required properties.

Organic electronic devices are generally fabricated by vapor deposition. The main deficiency of this method is the high cost of production, which covers huge investments in fabrication techniques. In order to reduce the production costs, the layers can be fabricated by solution-based techniques. Such method is less expensive compared to the vapor deposition method as well as large area devices that could be produced easily. A potential disadvantage of using this method is that layers that are already coated could be partially dissolved by the following spin-coating steps. In order to make the spin-coating method suitable for the preparation of multilayer devices, the solubility of the layers must be reduced after their deposition. One possibility solving this problem is to use soluble compounds with reactive functional groups, which can be transformed into polymers with lower solubility or even into insoluble networks.

Phenanthroimidazole-based derivatives attracted a lot of attention of the scientific community due to their simple and cheap synthesis, attractive bipolar properties and excellent luminescence efficiency, etc. Mainly, phenanthroimidazole-based materials were exploited in two application areas related to the OLED's relying on their emitting or bipolar properties.

Aim of the work

The investigation of structure-properties relationship of blue solid state emissive phenanthroimidazole-based derivatives and the investigation of thermal polymerization processes of derivatives with reactive functional groups.

In order to achieve the aim of the thesis, the following tasks were formulated:

1. To synthesize phenanthroimidazole-based derivatives with different aliphatic and heterocyclic substituents at different positions in the phenanthroimidazole unit;
2. To investigate thermal, optical, photophysical, electrochemical, and photoelectrical properties of synthesized compounds and investigate the structure-properties relationship;
3. To synthesize phenanthroimidazole-based derivatives with reactive functional groups and investigate the kinetics of thermal polymerization processes;
4. To propose a technological scheme for the production of one of the intermediate compounds.

Scientific novelty of the work. New phenanthroimidazole-based compounds were synthesized. Thermal, optical, photophysical, electrochemical, photoelectrical properties of synthesized compounds, and the structure-properties relationship were investigated.

The influence of temperature and compound structure on the polymerization reaction rate of vinyl benzyl-containing phenanthroimidazole compounds was determined.

The practical value of the work. It has been shown that the compounds containing phenanthroimidazole fragments can be used to obtain active layers for the organic light-emitting diodes. The compounds with heterocyclic substituents have been used in the production of emission layers for the electroluminescence devices.

The optimal conditions for the formation of polymeric electroactive layers by casting have been found.

The technological scheme of production of 3,6-dibromophenanthrene-9,10-dione is proposed.

Dissertation statements to be defended. Carbazolyl- and diphenylamine fragment-functionalized phenanthroimidazole-based derivatives with a balanced ambipolar carrier transition and effective blue solid state emission are suitable for the formation of emissive layers for the light emitting diodes.

Thermal polymerization of phenanthroimidazole derivatives with reactive functional groups can form insoluble layers that are potentially suitable for the organic electronics technologies.

Approval and publications of the results of the study. The results of the research have been published in 2 scientific articles in the journals indexed in *Clarivate Analytics Web of Science* database, and 8 papers have been presented in the proceedings of scientific conferences.

Structure and content of the dissertation. The dissertation consists of an introduction, three chapters, conclusions, a list of references, and a list of publications relevant to the subject of the dissertation. The dissertation text covers 107 pages, it features 15 tables and 28 figures, and the list of references includes 207 bibliographic sources.

1. RESULTS AND DISCUSSION

1.1. Phenanthroimidazole derivatives with aromatic groups in 5,10- and 6,9- positions

Synthetic routes for the donor-substituted phenanthroimidazole derivatives **9-16** are outlined in **Figure 1.1.** and **Figure 1.2.**

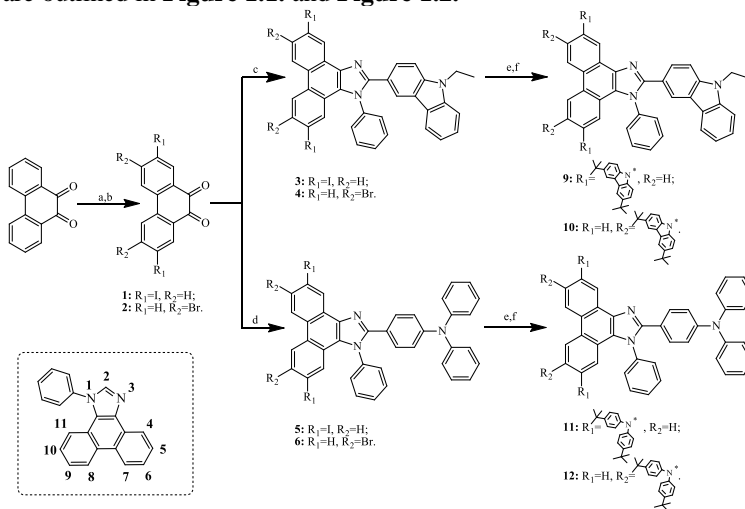


Figure 1.1. Synthetic routes for the phenanthroimidazole derivatives **9-12**

The starting compounds **1** and **2** were prepared according to the procedures reported in the literature earlier [1,2]. The key intermediate phenanthroimidazole derivatives **3-8** were obtained by the reactions of compounds **1** or **2** with the corresponding aldehydes. The target compounds **9**, **11**, **13**, and **14** were prepared by Ullmann coupling reactions [3]. Derivatives **10**, **12**, **15**, and **16** were synthesized using Buchwald-Hartwig conditions [4].

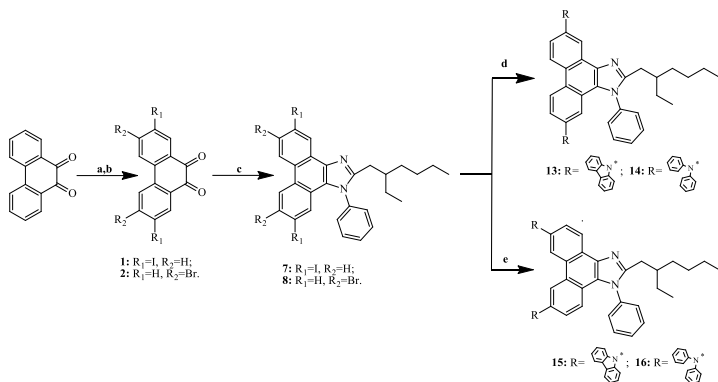


Figure 1.2. Synthetic routes for the phenanthroimidazole derivatives **13-16**

All the synthesized compounds were purified by column chromatography and characterized by IR, NMR spectroscopies, and mass spectrometry.

1.1.1. Thermal properties

The thermal properties of phenanthroimidazole-based derivatives **9-16** were investigated by TGA and DSC under a nitrogen atmosphere. Their thermal characteristics are summarized in **Table 1.1**.

Table 1.1. Thermal properties of compounds **9-16**

Derivative	9	10	11	12	13	14	15	16
T_g (°C) ^a	206	239	192	183	146	81	115	87
T_m (°C) ^b	-	-	394	-	313	-	-	-
T_{ID} (°C) ^c	524	511	491	503	399	392	327	321

^a Determined by DSC 2nd heating, scan rate 20 °C/min, N₂ atmosphere. ^b Determined by DSC 1st heating, scan rate 20 °C/min, N₂ atmosphere ^c T_d is 5% weight loss temperature; scan rate 20 °C/min, N₂ atmosphere.

Their 5% weight-loss temperatures (T_{ID}) range from 321 to 524 °C. The DSC curves of the second heating of the compounds **9-16** demonstrate that these compounds can exist in the glassy state (**Fig. 1.3**).

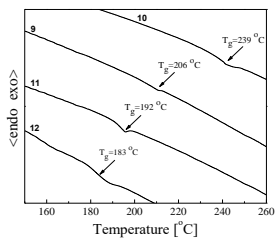


Figure 1.3. DSC curves (2nd heating) of the phenanthroimidazole derivatives **9-12**

The glass-transition temperatures (T_g) of **9-16** were observed in the region of 81-239 °C. Compounds **9-12** having aromatic moieties in the 2nd position of the imidazole ring exhibited considerably higher T_g than phenanthroimidazole derivatives **13-16** with aliphatic substituents. Such high T_g and T_{ID} values of compounds **9-12** indicate that the amorphous layers of these compounds can be fabricated by the vapor deposition. In addition, they are expected to exhibit high morphological stability, which is desirable for the materials used in OLEDs [5].

1.1.2. Optical and photophysical properties

Optical and photophysical properties of the dilute solutions in THF and films of **9-16** are presented in **Table 1.2**.

Table 1.2. Optical and photophysical properties of phenanthroimidazoles **9-16**

Derivative	λ_{Abs}^a (nm)		λ_{PL}^a (nm)		Φ_f (sol/film) ^b		CIE ^c (x;y)
	solution	film	solution	film	solution	film	
9	349	353	414	421	0.35	0.55	(0.16;0.03)
10	348	350	417;434	424;444	0.09	0.49	(0.15;0.03)
11	365	374	435	443	0.22	0.51	(0.15;0.09)
12	364	364	444;467	443;468	0.26	0.27	(0.14;0.07)
13	343	348	378;395	378;413	0.11	0.24	(0.16;0.02)
14	373	375	406;416	406;417	0.25	0.28	(0.16;0.06)
15	339	344	399;417	404;427	0.12/	0.34	(0.16;0.02)
16	359	359	435;456	434;456	0.09/	0.11	(0.15;0.05)

^a Maxima bands of absorption and fluorescence recorded at room temperature. ^b The fluorescence quantum yield of the solution using a 0.5 M H₂SO₄ solution of quinine as reference (0.51); the solid state quantum yield estimated using an integrating sphere. ^c Estimated from the fluorescence spectra of the solutions in THF.

The solutions of the compounds exhibit the emission peaks in the range from 399 to 467 nm. In the solid state, the emission of these materials shows negligible red shift, which is coherent with the similar red-shifts of the corresponding absorption spectra. The fluorescence spectra presented in **Figure 1.4b** clearly show that emission color depends on the donor chromophore.

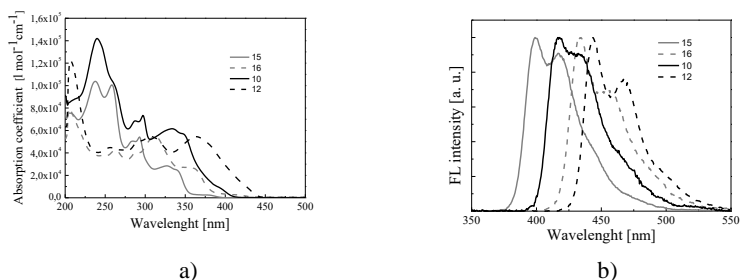


Figure 1.4. Normalized absorption (a) and fluorescence (b) spectra of compounds **10**, **12**, **15**, **16**

In the case of carbazolyl substituted compounds (**10**, **15**), the emission maxima are blue-shifted compared to the spectra of the derivatives containing diphenylamine moieties (**12**, **16**), which is coherent with the same trend observed for the low energy absorption bands. However, the emission is blue-shifted in the case of phenanthroimidazole moiety substituted at 5th and 10th positions (**9**, **11**, **13**, **14**), compared to the spectra of the derivatives where the substitution is realized at 6th and 9th positions (**10**, **12**, **15**, **16**). Both the nature of the substituent and the linking position are important for tuning the emission color.

Fluorescence quantum yields (Φ_f) of the solid films of compounds **9-16** were found to be considerably higher than those of dilute THF solutions and reaches 0.55 (**Table 1.2.**).

1.1.3. Photoelectrical properties

Charge-drift mobilities of the compounds **9-16** were measured by the ToF technique (**Table 1.3.**, **Fig. 1.5.**).

Table 1.3. Charge-drift mobilities of compounds **9-16**

Derivative	d (μm)	μ_h ($\text{cm}^2/\text{V}\cdot\text{s}$) ^a	μ_e ($\text{cm}^2/\text{V}\cdot\text{s}$) ^a
9	3.1	3.14×10^{-4}	5.69×10^{-4}
10	3.9	1.91×10^{-4}	2.14×10^{-4}
11	1.8	3.02×10^{-5}	8.52×10^{-5}
12	7.1	1.60×10^{-4}	1.91×10^{-4}
13	5.1	3.07×10^{-4}	2.74×10^{-4}
14	2.2	1.28×10^{-4}	7.68×10^{-4}
15	3.5	1.62×10^{-4}	5.90×10^{-4}
16	1.7	3.20×10^{-4}	1.90×10^{-4}

^a Hole- and electron-drift mobilities at the electric field of $3.6 \cdot 10^5$ cm^2/Vs .

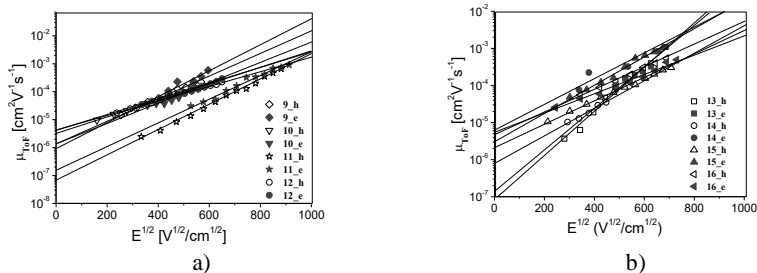


Figure 1.5. Hole-drift and electron-drift mobilities for the layers of compounds **9-12** (a) and **13-16** (b) at room temperature

Well balanced hole and electron transport was observed for the layers **9-16** and exhibit in the range of 3.02×10^{-5} – 3.20×10^{-3} $\text{cm}^2/(\text{V}\cdot\text{s})$ (holes), 8.52×10^{-5} – 7.68×10^{-4} $\text{cm}^2/(\text{V}\cdot\text{s})$ (electrons) at the electric fields of 3.6×10^5 V/cm .

1.1.4. Electrochemical properties

In order to evaluate the applicability of the materials in the optoelectronic devices, the electrochemical properties of compounds **9-16** were further studied by CV measurements (using their in 10^{-5} M solutions) and by electron photoemission in the air method. The results of the measurements are shown in **Table 1.4**.

Table 1.4. Electrochemical characteristics of compounds **9-16**

Derivative	E_{ox}^{a} (V)	$\text{IP}_{\text{CV}}^{\text{b}}$ (eV)	$E_{\text{opt}}^{\text{g}}$ (eV)	$\text{EA}_{\text{CV}}^{\text{d}}$ (eV)	$\text{IP}_{\text{EP}}^{\text{e}}$ (eV)
9	1.02	5.52	3.14	2.38	5.29
10	0.85	5.38	3.04	2.34	5.31
11	0.51	5.03	3.02	2.01	5.27
12	0.42	4.96	2.81	2.15	5.15
13	0.73	5.31	3.19	2.12	5.41
14	0.64	5.22	2.87	2.35	5.11
15	0.52	5.10	3.11	1.99	5.39
16	0.48	5.06	2.54	2.52	5.17

^a Onset oxidation potential vs Ag/Ag^+ . ^b $\text{IP}_{\text{CV}} = (E_{\text{ox}} - E_{\text{Fc}/\text{Fc}^+}) + 4.8$ (eV). ^c Estimated from the onset wavelength of optical absorption according to the empirical formula: $E_{\text{opt}}^{\text{g}} = 1240/\lambda_{\text{edge}}$, in which the edge is the onset value of the absorption spectrum in the long wave direction. ^d $\text{EA}_{\text{CV}} = \text{IP}_{\text{CV}} - E_{\text{opt}}^{\text{g}}$. ^e Established from the electron photoemission in the air spectra.

The ionization potential (IP_{CV}) and electron affinity (EA_{CV}) values of the compounds were calculated from their onset potentials of oxidation and their $E_{\text{opt}}^{\text{g}}$. IP_{CV} values of the compounds varied in the range from 4.96 to 5.52 eV, and EA_{CV} values ranged from 1.99 to 2.52 eV. The difference between ionization potential values estimated by electron photoemission in the air method (IP_{EP}) and

IP_{CV} is due to the different environments in solutions and solid layers of compounds.

1.1.5. Devices

Electroluminescent devices based on the non-doped light-emitting layers **9-12** with the following architectures were fabricated: ITO/MoO₃(3 nm)/m-MTDATA (30 nm)/**9,10,11,12**(20 nm)/PBD(10 nm)/TPBi(25 nm)/Ca(10 nm)/Al(60 nm) (marked as devices A, B, C, and D, respectively). The electroluminescence characteristics of the non-doped electroluminescent devices are summarized in **Table 1.5**.

Table 1.5. EL characteristics of the fabricated devices

Device	V _{on} (V) ^a	Brightness (cd/m ²)	Current efficiency (cd/A)	Power efficiency (lm/W)	External quantum efficiency (%)	CIE 1931 UCS coordinates (x,y)
A	5.5	750	1.30	0.80	0.95	(0.183; 0.162)
B	4.5	270	0.06	0.03	0.03	(0.265; 0.250)
C	4.0	140	1.15	0.80	0.75	(0.190; 0.184)
D	4.0	130	0.97	0.64	0.70	(0.166; 0.133)
AI	4.8	1970	4.00	1.50	1.75	(0.275; 0.467) ^b
AII	5.1	6130	5.30	1.70	2.90	(0.468; 0.381) ^b
DI	2.6	870	0.58	0.53	0.24	(0.324; 0.289) ^b
DII	2.5	1300	0.56	0.53	0.24	(0.207; 0.268) ^b

a – the values were taken at the applied voltage of 8 V.

The turn-on voltages (V_{on}) of the devices were found to be in the range from 4.0 to 5.5 V at the brightness of 1 cd/m², while the maximum brightness was recorded in the range from 130 to 750 cd/m² at the driving voltage of 10 V. These parameters are comparable with those of the fluorescent deep blue OLEDs [6,7]; however, the efficiencies of the devices were rather low (the maximal current, power, and external quantum efficiencies were lower than 1.3 cd/A, 0.8 lm/W, 0.95%, respectively). Commission Internationale de l’Eclairage (CIE) chromaticity coordinates (x, y) for the devices based on the non-doped emitting layers **9, 10, 11, and 12** correspond to the blue color.

In order to increase the efficiencies of devices, doped light-emitting layers were used with the most promising emitters (**9** and **12**), while m-MTDATA and 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) were additionally utilized as the hosts. Electroluminescent devices based on the doped light-emitting layers with the following architectures were fabricated: ITO/MoO₃(3 nm)/m-MTDATA(30 nm)/ TAPC:**9**, m-MTDATA:**9**, TAPC:**12**, or

m-MTDATA:12 (20 nm)/PBD(10 nm)/TPBi(25 nm)/Ca(10 nm)/Al(60 nm) (marked as devices AI, AII, DI, and DII).

Low-energy bands with the maxima at 585 nm for the devices AI and DI and at 540 nm for the devices AII and DII were additionally observed in the electroluminescence spectra of the doped OLEDs as compared to the spectra of the non-doped OLEDs. The appearance of the additional band can apparently be explained by the formation of electroplexes between TAPC and **9** (**12**), which only occurs under the electric fields. The similar electroplex emission between TAPC and a bipolar transporting material 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine was observed previously [8].

CIE chromaticity coordinates (x;y) of the TAPC:12 based device at voltages from 8 V to 9 V were found to be very close to the white point (0.33; 0.33) due to the mixed blue monomer emission and orange electroplex emission in the TAPC:12 emitting layer. The improved maximal current of 4 and 5.3 cd/A, power of 1.5 and 1.7 lm/W, and external quantum of 1.75 and 2.9% efficiencies were achieved for the devices AI and DI (**Table 1.5**).

1.2. Phenanthroimidazole derivatives with amphiphilic chains

Synthetic routes for the phenanthroimidazole derivatives with amphiphilic chains **20-24** are outlined in **Figure 1.6**.

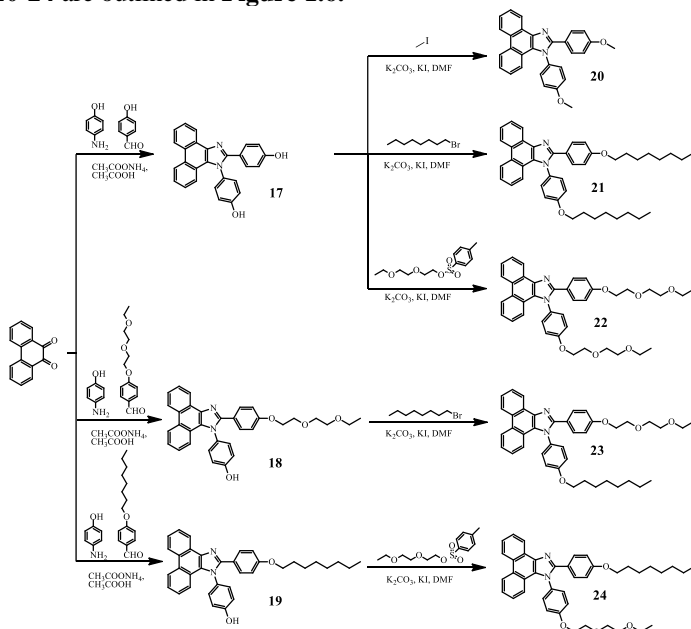


Figure 1.6. Synthesis of phenanthroimidazole derivatives **20-24**

The starting compounds **17-19** were prepared by the reactions of 9,10-phenanthroquinone with the corresponding aldehydes. The target phenanthroimidazole derivatives **20-24** were prepared by alkylation of phenanthroimidazole with different alkylation agents.

All the synthesized compounds were purified by the column chromatography and characterized by IR, NMR spectroscopies, and mass spectrometry.

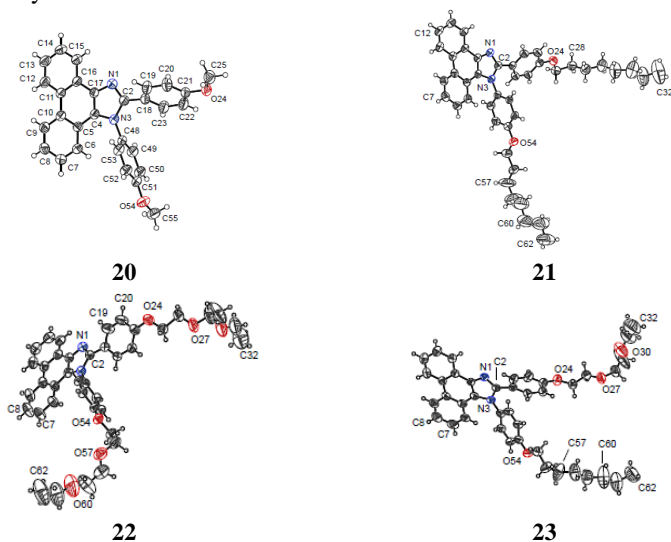


Figure 1.7. ORTEP projections of compounds **20-23**

The structures additionally were proved by analyzing single-crystal x-ray diffraction results. ORTEP projections of the molecules are shown in **Fig. 1.7**.

1.2.1. Thermal properties

The thermal properties of phenanthroimidazole derivatives **20-24** were investigated by TGA and DSC under a nitrogen atmosphere. Their thermal characteristics are summarized in **Table 1.6**.

Table 1.6. Thermal properties of compounds **20-24**

Derivative	20	21	22	23	24
T_m (°C) ^a	205	110	114	122	119
T_{cr} (°C) ^b	167	79	-	-	86
T_R (°C) ^b	77	-	-	-	-
T_{10} (°C) ^c	334	382	407	362	394

a - determined by DSC 1st heating, scan rate 20 °C/min, N₂ atmosphere; b - determined by DSC 2nd heating, scan rate 20 °C/min, N₂ atmosphere; c - T₁₀ is 5% weight loss temperature, scan rate 20 °C/min, N₂ atmosphere.

All synthesized compounds exhibit high thermal stability; 5% weight-loss and sublimation temperatures (T_{ID}) of compounds **20-24** range from 334 to 407 °C (**Fig. 1.8b**)

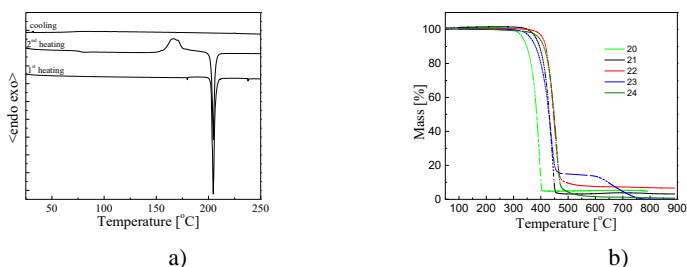


Figure 1.8. DSC curves of compound **20** (a) and TGA curves of the phenanthroimidazole derivatives **20-24** (b)

The DSC curves of the second heating of the compounds **20-24** demonstrate that these compounds are crystalline materials and cannot be transformed into a glassy state (**Fig. 1.8a**).

1.2.2. Optical and photophysical properties

UV-Vis absorption and fluorescence spectra of the diluted solutions in THF and thin films are recorded. Optical and photophysical properties of the compounds **20-24** are presented in **Table 1.7**.

Table 1.7. Optical and photophysical properties of compounds **20-24**

Derivative	λ_{Abs}^a (nm)		λ_{PL}^a (nm)		Φ_f^b		λ_{phos} (nm)	E_T^c (eV)	CIE ^d (x;y)
	solution	film	solution	film	solution	film			
20	364	366	378;393	384;398	0.50	0.02	478	2.59	(0.17;0.03)
21	366	368	379;395	379;402	0.56	0.18	473	2.62	(0.17;0.03)
22	365	369	378;394	398	0.53	0.06	491	2.53	(0.17;0.03)
23	365	367	372;390	400	0.51	0.15	470	2.64	(0.17;0.03)
24	365	368	378;395	383;398	0.52	0.15	466	2.66	(0.17;0.04)

a - maxima bands of absorption and fluorescence recorded at room temperature; b - the fluorescence quantum yield of the solution and solid state estimated using an integrating sphere; c - triplet energy estimated from the onset of phosphorescence spectra; d - estimated from the fluorescence spectra of the solutions in THF.

The solutions of the compounds exhibit emission peaks in the UV range from 378 to 395 nm. In the solid state, the emission of these molecules shows red shift, which is coherent with the similar red -shifts of the corresponding absorption spectra.

Fluorescence quantum yields (Φ_f) of the dilute THF solutions of the compounds **20-24** were found to be considerably higher than those of the solid

films and reach 0.56 (Table 1.7.). The analyses of photophysical data of the phenanthroimidazole-polystyrene mixtures show that the values of quantum yields decrease with the increase of phenanthroimidazole concentration in the mixture due to self-quenching.

1.2.3. Electrochemical properties

Electrochemical properties of the compounds **20-24** were studied by CV (using their in 10^{-5} M solutions) and by electron photoemission in air method. The results of the measurements are shown in Table 1.8.

Table 1.8. Electrochemical characteristics of phenanthroimidazoles **20-24**

Derivative	E_{ox}^a (V)	IP_{CV}^b (eV)	$E_r^{opt\ c}$ (eV)	EA_{CV}^d (eV)	IP_{EP}^e (eV)
20	0.629	5.48	3.30	2.18	5.70
21	0.616	5.46	3.30	2.16	5.59
22	0.638	5.49	3.30	2.19	5.51
23	0.629	5.48	3.28	2.20	5.55
24	0.611	5.45	3.28	2.17	5.60

a - onset oxidation potential vs Ag/Ag⁺; b - $IP_{CV} = (E_{ox} - E_{Fc/Fc^+}) + 4.8$ (eV); c - estimated from the onset wavelength of optical absorption according to the empirical formula: $E_{opt}^g = 1240/\lambda_{edge}$, in which the λ_{edge} is the onset value of the absorption spectrum in the long wave direction; d - $EA_{CV} = IP_{CV} - E_{opt}^g$; e - established from the electron photoemission in air spectra.

The ionization potential (IP_{CV}) values of the compounds were calculated from their onset potentials of oxidation and their E_{opt}^g . IP_{CV} values of the compounds are very similar and varied in the range from 5.45 to 5.49 eV. The ionization potential (IP_{EP}) values of the compounds established from electron photoemission in the air spectra varied in the range from 5.51 to 5.70 eV.

1.3. Phenanthroimidazole derivatives with reactive functional groups

Structures of synthesized phenanthroimidazole derivatives with reactive functional groups **33-38** are outlined in Fig. 1.9.

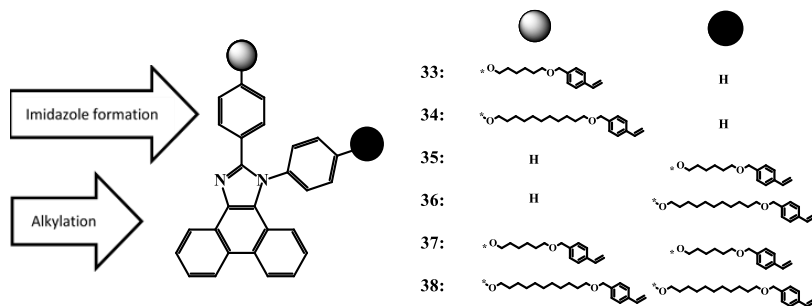


Figure 1.9. Structures of monomers **33-38**

The starting compounds were prepared by the reactions of 9,10-phenanthraquinone with the corresponding aldehydes. The key intermediate phenanthroimidazole derivatives were prepared by the alkylation of phenanthroimidazole with 11-bromo-1-undecanol or 6-bromo-1-hexanol. The target compounds were prepared by the reaction with 4-vinylbenzyl chloride.

All the synthesized compounds were purified by the column chromatography and characterized by the IR, NMR spectroscopies, and mass spectrometry.

1.3.1. Thermal properties

The thermal properties of phenanthroimidazole-based monomers **33-38** were investigated by the TGA and DSC methods under a nitrogen atmosphere. Their thermal characteristics are summarized in **Table 1.9**.

Table 1.9. Thermal properties of monomers and GPC data of polymerization products

Derivative	33	34	35	36	37	38
T_g (°C) ^a	19	22	38	-2	1	-16
T_m (°C) ^b	76	100	131	72	59	66
T_{ID} (°C) ^c	386	378	402	400	315	409
M_n	18500	8030	17900	19000	-	-
M_w	213000	100100	235000	196000	-	-
PDI ^d	11	12	13	10	-	-
p, %	84	90	91	94	-	-

a - estimated from DSC 2nd heating; b - estimated from DSC 1st heating; c - estimated from TGA data; d - PDI= M_w/M_n ; e - polymerization conversion calculated from the GPC data.

All the synthesized compounds exhibit high thermal stability and can exhibit in the glassy state. Their 5% weight-loss temperatures (T_{ID}) range from 315 to 409 °C. The DSC heating scans of compounds **33-38** show endothermic melting signals (59-131 °C). Glass transition temperatures are fixed in the range from -16 to 38 °C in the 2nd heating curve after cooling. Compounds **33-35** having one substituent of the imidazole ring exhibited considerably higher T_g .

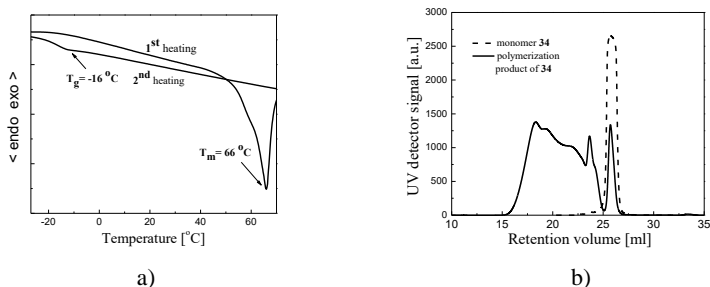


Figure 1.10. DSC curves of monomer **38** (a) and GPC chromatograms of **34** and polymerization product of **34** (b)

In order to identify that the polymerization reactions take place, the GPC analyses were performed of the layers of compounds **33-36** which were heated up to 300 °C (**Table 1.9**). After heating the layers up to 300 °C, the monomer conversion was observed (decrease of monomer peak (**Fig. 1.10b**)), but the polymerisation reaction products have been showing quite broad distribution of the molecular weights. The weight average molecular weight of polymerization products of monomers **33-36** are in the range from 100100 to 235000 Da; the polydispersity indexes are in the range from 10 to 13. Polymerization conversion calculated from the GPC data is in the range from 84 to 94%.

1.3.2. Optical and photophysical properties

The optical and photophysical properties of phenanthroimidazole based monomers **33-38** were investigated. UV-Vis absorption and fluorescence spectra of the diluted solutions in THF and thin films are recorded; the characteristics are presented in **Table 1.10**.

Table 1.10. Optical and photophysical characteristics of compounds **33-38**

Derivative	$\lambda_{\text{Abs}}^{\text{a}}$ (nm)		$\lambda_{\text{PL}}^{\text{a}}$ (nm)		$\Phi_{\text{f}}^{\text{b}}$		λ_{phos} (nm)	E_{T}^{c} eV	CIE ^d (x;y)
	solution	film	solution	film	solution	film			
33	364	368	395	381;398	0.48	0.02	468	2.65	(0.16;0.03)
34	364	370	397	379;398	0.50	0.03	474	2.62	(0.16;0.04)
35	362	365	392	375;397	0.49	0.06	476	2.61	(0.16;0.02)
36	362	366	388	372;391	0.49	0.13	476	2.61	(0.16;0.02)
37	365	367	398	381;398	0.46	0.02	469	2.64	(0.16;0.02)
38	365	367	398	379;398	0.46/	0.01	472	2.63	(0.16;0.03)

a - Maxima bands of absorption and fluorescence recorded at room temperature; b - the fluorescence quantum yield of the solution and solid state estimated using an integrating sphere, c - triplet energy estimated from the onset of phosphorescence spectra; d - estimated from the fluorescence spectra of the solutions in THF.

The solutions of compounds exhibit emission peaks in the range from 388 to 398 nm. In the solid state, the emission of these molecules shows red shift, which is coherent with the similar red-shifts of the corresponding absorption spectra. The absorption spectra presented in **Figure 1.11**. show that the substitutions at the N1- or C2-positions have influence on the properties.

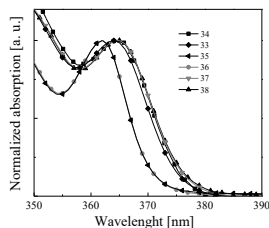


Figure 1.11. Normalized absorption spectra of compounds **33-38**

In the case of substitution at N1-position (**35**, **36**), the absorption maxima are blue-shifted compared to the spectra of the derivatives containing substitution at C2- and both positions.

Fluorescence quantum yields (Φ_f) of the dilute THF solutions of compounds **33-38** were found to be considerably higher than those of solid films and reaches 0.50 (**Table 1.10**).

1.3.3. Electrochemical properties

Electrochemical properties of compounds **33-38** were studied by CV measurements (using their in 10^{-5} M solutions) and the electron photoemission in the air method. The results of measurements are shown in **Table 1.11**.

Table 1.11. Electrochemical characteristics of phenanthroimidazoles **33-38**

Derivative	E_{ox}^a (V)	IP_{CV}^b (eV)	E_{opt}^g (eV)	EA_{CV}^d (eV)	IP_{EP}^e (eV)
33	0.639	5.49	3.30	2.19	5.56
34	0.637	5.49	3.29	2.20	5.54
35	0.749	5.65	3.34	2.31	5.62
36	0.734	5.63	3.34	2.29	6.16
37	0.621	5.47	3.29	2.18	5.62
38	0.598	5.44	3.28	2.16	5.60

a - onset oxidation potential vs Ag/Ag⁺; b - $IP_{CV} = (E_{ox} - E_{Fc/Fc^+}) + 4.8$ (eV); c - estimated from the onset wavelength of optical absorption according to the empirical formula: $E_{opt}^g = 1240/\lambda_{edge}$, in which the λ_{edge} is the onset value of the absorption spectrum in the long wave direction; d - $EA_{CV} = IP_{CV} - E_{opt}^g$; e - established from the electron photoemission in the air spectra.

The ionization potential (IP_{CV}) values of the compounds were calculated from their onset potentials of oxidation and their E_{opt}^g . IP_{CV} values of the compounds are very similar and varied in the range from 5.44 to 5.65 eV. The ionization potential (IP_{EP}) values of the compounds established from the electron photoemission in the air spectra varied in the range from 5.54 to 5.60 eV.

1.4. The investigation of polymerization kinetics

The thermal polymerization kinetics of the monomers were investigated by DSC technique and activation energies calculated by the isothermal [9] and dynamic methods (Ozawa [10] and Kissinger [11] methods).

1.4.1. The investigation of polymerization kinetics by the isothermal method

The kinetic parameters of the polymerization process investigated by the isothermal method are presented in **Table 1.12**.

Table 1.12. Result of the polymerization kinetics investigated by the isothermal method

Monomer	Temperatures of curing, °C	E_a , kJ/mol	$\ln A$	R^2
33	85/100/110/120	108.0	28.2	0.9880
34	110/120/130/140	132.1	33.5	0.9996
36	170/190/210/230	88.2	15.8	0.9997
37	135/150/165/180	118.7	25.3	0.9588
38	80/90/100/115	122.9	33.3	0.9771

The values of the activation energy of monomers **33-34** and **36-38** varied in the range from 88.2 to 132.1 kJ/mol. Monomer **34** having one substituent of the imidazole ring at C2- position of the imidazole ring exhibited considerably higher E_a . Monomer **36** having one substituent of the imidazole ring at N1- position of the imidazole ring exhibited lowest value of E_a . The values of the activation energy of compounds **37** and **38**, containing substitution at both, C2- and N1-, positions of imidazole ring, are 118.7 and 122.9 kJ/mol.

1.4.2. The investigation of polymerization kinetics by the dynamic method

Thermal polymerization kinetics was investigated by the dynamic method at heating rates (β) of 5, 10, 15, and 20 °C/min (**Fig. 1.12.**).

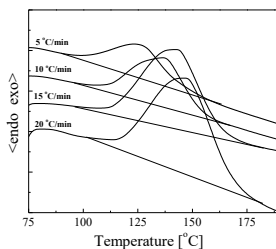


Figure 1.12. DSC curves of **38**

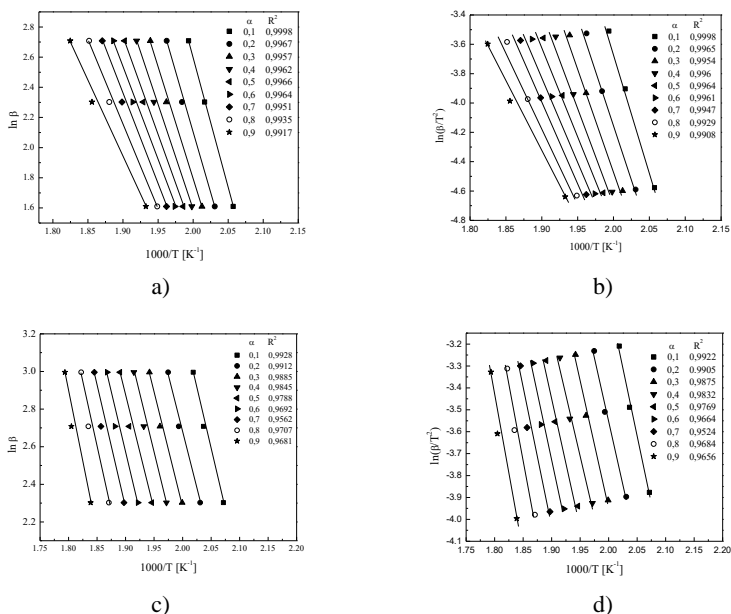
By performing the DSC scans at different heating rates, integrating exothermic peaks, and measuring the temperature at different conversion degrees, the activation energy of the process was estimated using Ozawa and Kissinger methods by the following equations (Ozawa – 1, Kissinger – 2):

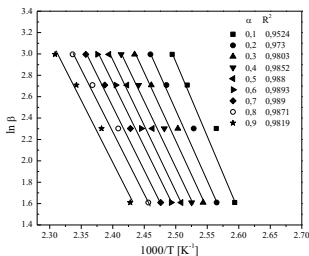
$$\ln(\beta) = \ln A - 1.052 \cdot \frac{E_a}{RT} \quad (1)$$

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT} \quad (2)$$

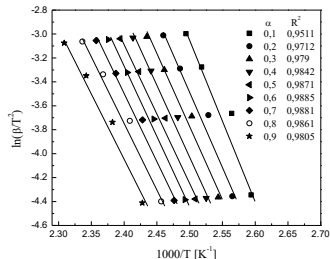
where, β - heating rate ($^{\circ}\text{C}/\text{min}$); E_a - activation energy (kJ/mol); R - gas constant (8.314 J/K·mol); T_i – temperature at the selected percent conversion (K), A - pre-exponential factor.

Figure 1.13. shows typical isoconversional plots based on the Ozawa and Kissinger methods for compounds **34**, **36**, and **38**, which show a general trend of activation energy. The slope of line of the natural logarithm of β or β/T^2 vs $1/T$ gives E_a/R values, and the intercept gives natural logarithm of pre-exponential factor A . It is shown that there exists a fairly good linear relationship between the heating rate and the reversal of exothermic peak temperature ($R^2 > 0.95$).





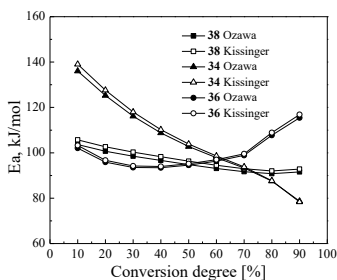
e)



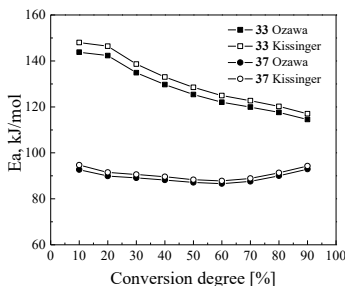
f)

Figure 1.13. Polymerization conversion vs \ln of the heating rate calculated from the DSC scan by the Ozawa method (**34-a**, **36-c**, **38-e**) and the Kissinger method (**34-b**, **36-d**, **38-f**)

Figure 1.14. shows the dependence of E_a and $\ln A$ on conversion degrees based on the Ozawa and Kissinger methods.



a)



b)

Figure 1.14. Conversion degree vs activation energy: monomers with C11 chain bridge (a) and monomers with C6 chain bridge (b)

The values of the activation energy of the polymerization reaction of monomers **37** and **38** with two functional groups are similar for all the conversion degrees in the range of 0.1-0.9 (**Fig. 1.14a, b**). This observation shows that for the polymerization reactions in which the network is formed, neither the length of the aliphatic chains, nor the temperature has an effect on the rate of reaction.

Polymerization reactions in which the linear polymers are formed, the structure of the monomers, and the temperature have an effect on the rate of reaction, what can be seen from the nature of the curves **33**, **34**, and **36** (**Fig. 1.14a, b**). The values of the E_a of the polymerization reaction of monomer **34** containing vinylbenzyl group in the C2 position decrease with the increasing conversion degree. This dependence shows that the influence of temperature on

the rate of polymerization reaction is higher at the beginning of the process. The values of E_a of the polymerization reaction of the monomer **36** containing vinylbenzyl group at the N1 position are very slight when $\alpha < 70\%$. When the degree of the polymerization conversion is equal to 70%, the values of E_a begin to increase. A decrease in the mobility of macromolecules in a solid state may cause an increase in the values of E_a , which means that the temperature has a higher effect on the reaction rate at the end of the reaction. The obtained results show that the polymerization reactions in which the linear polymers are formed, a compound having a vinylbenzyl groups in the C2 position is more appropriate. The values of E_a of the polymerization reaction of the monomer **33** containing vinylbenzyl group in the C2 position connected to the phenanthroimidazole fragment via the hexyl bridge decrease with the increasing conversion degree. However, the change in the values of E_a is less than that of monomer **34**. This observation shows that the temperature has a higher effect on the rate of reaction for the polymerization of monomers with shorter alkyl chains in its structure.

To sum up, it can be stated that the thermal polymerization of crystalline monomers by isothermal and dynamic methods has been investigated. The kinetic parameters determined by both methods are similar. Using the results of the study, optimal thermal polymerization conditions are selected, which will form the basis for the formation of electroactive polymeric layers of the organic electronic devices in the future.

1.5. Technological scheme for the synthesis of 3,6-dibromophenanthrene-9,10-dione

Phenanthroimidazole compounds containing heterocyclic substituents at the 5th, 10th and 6th, 9th positions were used for the formation of electroluminescence devices. 3,6-dibromo-9,10-phenanthracinone is the starting compound for the synthesis of 2-(4-(diphenylamino)phenyl)-N⁵, N⁵, N¹⁰, N¹⁰-tetrakis(4-*tert*-butylphenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole-5,10-diamine (**12**).

A technological scheme for the production of 3,6-dibromo-9,10-phenanthracinone was proposed (**Fig. 1.15.**) The production of 3,6-dibromophenanthrene-9,10-dione consists of two steps: synthesis and purification.

9,10-phenanthracinone from the dosing tank (1) is supplied to the mixing tank (2), where nitrobenzene is supplied as well. The solution is pumped from the mixing tank (2) to the reactor (3), where small amounts of bromine are injected. When the required amount of bromine enters the reactor, the temperature is raised to 120 °C, and the reaction takes place for 22 hours. The released HBr acid is collected and neutralized in a neutralization tank (4), which provides 10% NaOH solution to a neutral medium. After neutralization, the aqueous mixture is supplied for cleaning.

After 22 hours, the reaction mixture from the reactor (3) is supplied to the cooler (5). The reaction mixture is cooled to room temperature and pumped to a mixing tank (2) containing 3% aqueous NaHSO₃ solution to neutralize the unreacted bromine. The well-blended mixture is pumped to the extractor (6), where the organic phase is extracted with dichloromethane. Water is combined with nitrobenzene residues and is supplied for cleaning. The dichloromethane solution is self-titrated to the evaporator (7), where the mixture is concentrated, filtered with a filter (9), and crystallized in a crystallizer (10), where the crystals are washed with cold methanol. The dichloromethane vapors are condensed (8), and the solvent is returned to the extractor (6).

The obtained crystals of 3,6-dibromophenanthrene-9,10-dione are dried in a dryer (11) and stored in a product storage (12).

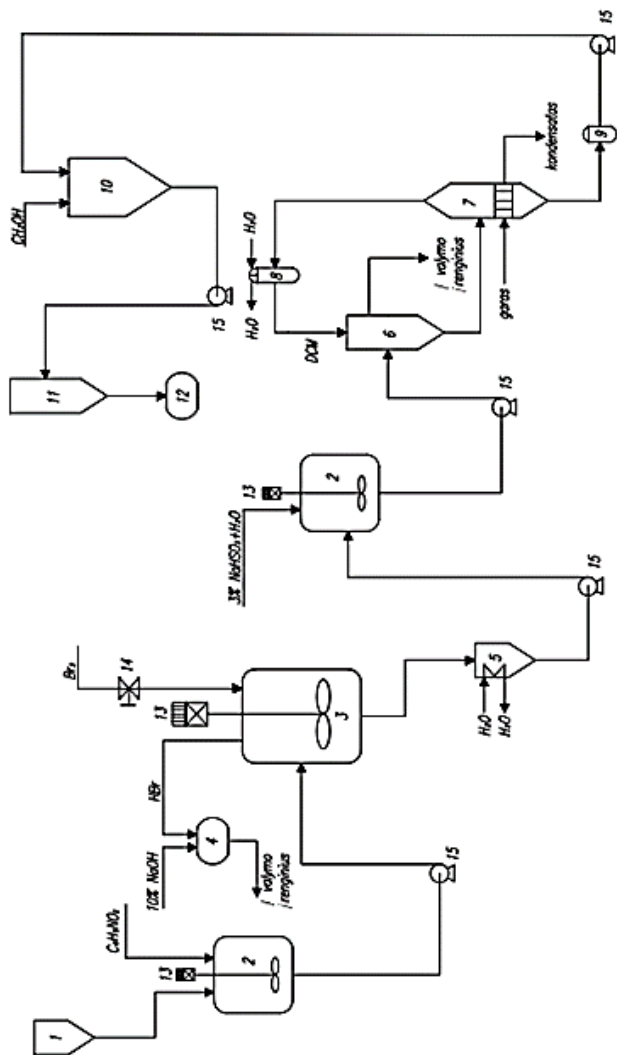


Figure 1.15. A technological scheme for the synthesis of 3,6-dibromophenan-threne-9,10-dione: 1- dosing tank; 2 – mixing tank; 3 – reactor; 4 – neutralization tank; 5 – cooler; 6 – extractor; 7 – evaporator; 8 – condenser; 9 – filter; 10 – crystallizer; 11 – dryer; 12 – product storage; 13 – mixers; 14 – valve; 15 – transporters.

CONCLUSIONS

1. The properties of the synthesized phenanthroimidazole derivatives depend on the nature of the substituents and the position of the attachment. The substitution of heterocyclic substituents has the greatest influence on the thermal and photophysical properties. The larger glass transition temperatures are characterized by the compounds containing carbazolyl moieties. The modification of the C5 and C10 atoms of phenanthroimidazole has the greatest influence on the values of the fluorescence quantum yields. The compounds containing heterocyclic substituents show a balanced charge mobility. Using the matrices (4,4',4''-Tris[phenyl(m-tolyl)amino]triphenylamine (m-MTDATA) and 4,4'-Cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC)) for the immobilization of emitters (5,10-bis(3,6-di-*tert*-butyl-9H-carbazol-9-yl)-2-(9-ethyl-9H-carbazol-3-yl)-1-phenyl-1*H*-phenanthro [9,10-d]imidazole and 2-(4-(diphenylamino)-phenyl)-6,9-(4-*tert*-butylphenyl)-1-phenyl-1*H*-phenanthro[9,10-d]imidazol-6,9-diamine) received diodes with an external quantum efficiency of 68% higher compared to the devices based on the non-doped emitting layers.

2. The values of quantum yield of amorphous layers of the compounds with amphiphilic substituents in the N1 and C2 positions of the imidazole ring are lower than the values found in the solutions due to the aggregation-caused quenching effect. The distribution of molecules in the crystal lattice is determined by the nature of the substituents. The molecules containing alkoxy groups are more compact in a crystal lattice.

3. After analysis of the kinetics of thermal polymerization processes of phenanthroimidazole derivatives with reactive functional groups by isothermal method, it has been found that the values of the activation energy of monomers with reactive substituents in the N1-position of the imidazole ring are lower comparing with the values of the compounds with substituents in the C2-position of the imidazole ring. The results obtained from the polymerization kinetics study by the dynamic method showed that for the polymerization reactions in which the network is formed, neither the length of the aliphatic chains, nor the temperature has an effect on the rate of reaction. In the polymerization reactions in which the linear polymers are formed, temperature has a higher effect on the rate of reaction for the polymerization of monomers with shorter alkyl chains in its structure and vinyl benzyl groups in the C2 position.

4. The technological scheme of production of 3,6-dibromo-9,10-phenanthraquinone is proposed.

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1. **Butkutė, Rita**; Lygaitis, Ramūnas; Mimaitė, Viktorija; Gudeika, Dalius; Volyniuk, Dmytro; Sini, Gjergji; Gražulevičius, Juozas Vidas. Bipolar highly solid-state luminescent phenanthroimidazole derivatives as materials for blue and white organic light emitting diodes exploiting either monomer, exciplex or electroplex emission. *Dyes and Pigments*. Oxford: Elsevier, 2017, vol. 146, pp. 425-437. ISSN 0143-7208. doi: 10.1016/j.dyepig.2017.07.029
2. **Butkutė, Rita**; Pečiulytė, Laura; Lygaitis, Ramūnas; Gudeika, Dalius; Buika, Gintaras; Gražulevičius, Juozas Vidas. Phenanthroimidazole-based monomers: synthesis, properties, and self-polymerization. *Polymer Bulletin*. doi: 10.1007/s00289-018-2373-3

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REZIUMĖ

Temos aktualumas

Besivystant energiją tausojančioms technologijoms, labai suintensyvėjo organinių šviesos diodų (OŠD), saulės elementų ir organinių tranzistorių tyrinėjimai. Minėti įrenginiai yra formuojami iš organinių medžiagų, kurios turi tenkinti keletą reikalavimų. Ištyrus termines, optines, fotofizikines ir fotoelektrines savybes, galima sudaryti savybių priklausomybę nuo struktūros ir atrinkti optimaliu savybių kompleksu pasižyminčias medžiagas. Medžiagos, iš kurių yra formuojamas (pvz., liejimo būdu) krūvininkus pernešantis sluoksnis, turi pasižymėti plėvėdaros savybėmis, morfologiniu stabilumu, tam tikru jonizacijos potencialu bei dideliu krūvininkų judriu. Jeigu tai būtų emisinis šviesos diodo sluoksnis, tuomet svarbios charakteristikos yra kvantinis liuminescencijos našumas, liuminescencijos spalva ir spalvos grynumas. Krūvio pernašos medžiagos, skirtos dažikliais sensibilizuotiems saulės elementams, turi pasižymėti mažu jonizacijos potencialu bei dideliu krūvininkų judriu. Pasitelkus įvairius sintezės metodus, galima įvairiai modifikuoti pasirinktą molekulinį fragmentą, t. y. skirtingose padėtyse prijungti skirtingus pakaitus. Kompleksiškai ištyrus savybes, galima gauti savybių priklausomybę nuo struktūros ir tada parinkti konkrečiai pritaikymo sričiai tinkamas medžiagas su reikiamu savybių kompleksu.

Organinės elektronikos prietaisai dažniausiai gaminami naudojant vakuuminio sluoksnių užgarinimo techniką. Pagrindinis šio metodo trūkumas – didelė pagaminto prietaiso kaina, kuri priklauso nuo brangios naudojamos įrangos. Norint sumažinti gamybos kaštus, galimas sluoksnių formavimas naudojant medžiagų tirpalus. Tokie metodai pigesni, palyginti su vakuuminio garinimo metodu, taip pat galima gaminti didesnio paviršiaus ploto prietaisus. Pagrindinis sluoksnių formavimo, naudojant medžiagų tirpalus, trūkumas – dalinis padengto sluoksnio tirpinimas liejant kitą sluoksnį. Norint pritaikyti šiuos metodus gaminant daugiasluoksnius prietaisus, reikia sumažinti sluoksnių tirpumą. Šiai problemai spręsti gali būti naudojami tirpūs organiniai junginiai su reaktyviomis funkcinėmis grupėmis, kurie būtų paverčiami netirpiais juos polimerizuojant.

Fenantroimidazolo fragmentą turintys junginiai sulaukė didelio mokslininkų susidomėjimo dėl paprastos ir pigios sintezės, subalansuoto krūvininkų transporto, efektyvios emisijos bei kitų savybių. Daugiausia fenantroimidazolo dariniai buvo panaudojami srityse, susijusiose su organiniais šviesos diodais, remiantis jų emisijos arba bipolinio krūvininkų pernešimo savybėmis.

Šio **darbo tikslas** – naujų mėlynos spalvos spindulių emisija pasižyminčių fenantroimidazolo darinių struktūros ir savybių tarpusavio priklausomybės bei reaktyvias funkcines grupes turinčių darinių terminės polimerizacijos proceso kinetinių parametru nustatymas.

Darbo tikslui pasiekti suformuluoti šie **uždaviniai**:

1. Susintetinti fenantroimidazolo darinius su skirtingais alifatiniais ir heterocikliniais pakaitais skirtingose fenantroimidazolo žiedo padėtyse;
2. Ištirti susintetintų junginių terminės, optinės, fotofizikinės, elektrocheminės ir fotoelektrinės savybes bei nustatyti savybių priklausomybę nuo struktūros;
3. Susintetinti reaktyvias funkcines grupes turinčius fenantroimidazolo darinius, ištirti jų savybes bei terminės polimerizacijos proceso kinetiką.
4. Pasiūlyti vieno iš sintezei naudojamų tarpinių junginių technologinę gamybos schemą.

Mokslinis darbo naujumas

Susintetintos nauji fenantroimidazolo fragmentus turintys junginiai. Ištirtos susintetintų junginių terminės, optinės, fotofizikinės, elektrocheminės ir fotoelektrinės savybės bei nustatyta struktūros ir savybių tarpusavio priklausomybė.

Nustatyta temperatūros ir junginio struktūros įtaka vinilbenzilo grupių turinčių fenantroimidazolo junginių terminės polimerizacijos reakcijos greičiui.

Praktinė darbo vertė

Įrodyta, kad susintetinti fenantroimidazolo fragmentus turintys junginiai gali būti naudojami aktyviems organinių šviesos diodų sluoksniams gauti. Junginiai su heterocikliniais pakaitais panaudoti gaminant elektroliuminescuojančių prietaisų emisinius sluoksnius.

Rastos optimalios sąlygos netirpiems polimeriniams elektroaktyviems sluoksniams formuoti terminus polimerizacijos būdu.

Pasiūlyta 3,6-dibrom-9,10-fenantrachinono technologinė gamybos schema.

Ginamieji disertacijos teiginiai

Karbazolilo bei difenilamino fragmentais funkcionalizuoti fenantroimidazolo dariniai, pasižymintys subalansuota ambipoline krūvininkų pernaša bei efektyvia kietos būsenos mėlynos spalvos spindulių emisija, yra tinkami šviesos diodų emisiniams sluoksniams formuoti.

Iš fenantroimidazolo darinių su reaktyviomis funkcinėmis grupėmis termiškai polimerizuojant galima suformuoti netirpius sluoksnius, potencialiai tinkamus organinės elektronikos technologijoms.

Darbo rezultatų apibavimas

Doktorantūros studijų metu 2 publikacijos disertacijos tema paskelbtos „*Clarivate Analytics Web of Science*“ duomenų bazės žurnaluose, turinčiuose citavimo indeksą, 8 straipsniai paskelbti mokslinių konferencijų pranešimų medžiagoje.

Darbo apimtis

Daktaro disertaciją sudaro įvadas, 3 skyriai, išvados, literatūros sąrašas, publikacijų disertacijos tema sąrašas ir padėka. Bendra apimtis – 112 puslapių. Darbe pateikti 28 paveiksai, 15 lentelių. Literatūros sąrašą sudaro 207 šaltinių.

IŠVADOS

1. Susintetintų fenantroimidazolo darinių savybės priklauso nuo pakaitų prigimties ir prijungimo padėties. Didžiausią įtaką terminėms ir fotofizikinėms savybėms turi heterociklinių pakaitų prijungimas. Didesnėmis stiklėjimo temperatūrų vertėmis pasižymi junginiai, turintys karbazolilo pakaitus. Didžiausią įtaką fluorescencijos kvantinių išeių vertėms turi pakaitų prijungimas prie C5 ir C10 fenantroimidazolo atomų. Junginiai, turintys heterociklinius pakaitus, pasižymi subalansuota krūvininkų pernaša. Panaudojant matricas (4,4', 4''-tris[3-metilfenil(fenil)amino]trifenilaminas ir 4,4'-cikloheksilidenbis[N, N-bis(4-metilfenil)benzenaminas) emiterių (5,10-bis(3,6-di-*tert*-butil-9H-karbazol-9-il)-2-(9-etil-9H-karbazol-3-il)-1-fenil-1H-fenantro-[9,10-d]imidazolo ir 2-(4-(difenilamino)-fenil)-6,9-(4-*tert*-butilfenil)-1-fenil-1H-fenantro[9,10-d]imidazol-6,9-diamino) imobilizavumui, gauti diodai, kurių išorinis kvantinis efektyvumas padidėjo 68 proc., palyginti su prietaisais, kuriuose kaip emiteriai panaudoti gryni junginių sluoksniai.

2. Fenantroimidazolo junginių, turinčių amfifilinius pakaitus imidazolo žiedo N1- ir C2- padėtyse, amorfinių sluoksnių emisijos kvantinių išeių vertės mažesnės už tirpaluose nustatytas vertes dėl agregacijos sukkelto emisijos gesinimo efekto. Molekulių išsidėstymą kristalų gardelėje lemia pakaitų pobūdis. Molekulės, turinčios alkolsipakaitus, yra kompaktiškesnės ir kristalinėje gardelėje išsidėsto tvarkingiau.

3. Ištyrus reaktyvias funkcines grupes turinčių fenantroimidazolo darinių terminės polimerizacijos procesų kinetiką izoterminiu metodu, nustatyta, kad monomerų, turinčių reaktyvius pakaitus imidazolo žiedo N1-padėtyje, polimerizacijos proceso aktyvacijos energijų vertės mažesnės, palyginti su

junginiais, turinčiais pakaitus imidazolo žiedo C2- padėtyje. Iš polimerizacijos kinetikos tyrimo dinaminio metodu gauti rezultatai parodė, kad polimerizacijos reakcijų, kurių metu susidaro tinklas, greičiui nei alifatinių grandinių ilgis, nei temperatūra įtakos neturi. Polimerizacijos reakcijoms, kurių metu susidaro linijiniai polimerai, temperatūra didesnę poveikį greičio konstantai turi polimerizuojant monomerus, turinčius trumpesnes alkilines grandinėles bei vinilbenzilo pakaitus C2-padėtyje.

4. Pasiūlyta 3,6-dibrom-9,10-fenantrachinono technologinė gamybos schema.

PADEKA

Dėkoju prof. Juozui Vidui Gražulevičiui už suteiktą galimybę pradėti mokslininko kelią jo mokslinėje grupėje. Dr. Laurai Pečiulytei – už pagalbą atliekant terminės polimerizacijos kinetikos tyrimus bei junginių terminių savybių nustatymą. Marytei Krenevičienei ir dr. Gretai Ragaitei – už branduolių magnetinio rezonanso spektroskopijos matavimus. Dr. D. Volyniukui – už junginių jonizacijos potencialų nustatymą, šviesos diodų gamybą bei charakterizavimą.

Nuoširdžiai dėkoju Polimerų chemijos ir technologijos katedros kolegoms už konsultacijas bei draugišką atmosferą. Dr. Daliui Gudeikai ir dr. Viktorijai Andrulevičienei už pagalbą ir naudingus patarimus rengiant publikacijas. Dr. Rasai Keruckienei nuoširdžiai dėkoju už motyvaciją ir palaikymą.

Taip pat dėkoju šeimai ir artimiesiems už begalinę kantrybę ir palaikymą. Mokytojai Virginijai Mačiulaitienei padėjusiai pamatus šiai kelionei.

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