



A Fluorescent Molecule Based on 1,8- Naphthalic Anhydride: Synthesis, Spectral Properties, And Studying The Conductance In Solution



Roza Al-Aqar*

Abstract

In this paper, the compound of (4-bromo-3-nitro-1,8 -naphthalic anhydride) and the dopant material (4-hydroxy-m-benzene-disulfonic acid) were synthesized. The UV- Vis absorption and emission spectra of the compound were recorded. 4-bromo-1,8- naphthalic anhydride was used as a starting material to prepare the compound (4-bromo-3-nitro-1,8 -naphthalic anhydride) in the presence of concentrated sulphuric acid and sodium nitrate. The dopant material (4-hydroxy-m-benzene-disulfonic acid) was prepared by using phenol in concentrated sulfuric acid. The absorption bands depend on the solvent polarity, which the compound shows significant red shift in DMSO solvent compared to in ethanol solvent.

The fluorescence spectra of this compound were sensitive to the solvent polarity, the calculated result indicates that the maximum peak is shifted to red in polar solvent, to the excited states of the polar ICT, which leads to decrease the energy of the excited states. The effect of the dopant material on the conductivities (ionic and specific) of the compound was studied, the ionic conductance was increased as the weight of the dopant material increases.

Keywords: Fluorescence; naphthalic anhydride; conductance; disulfonic acid; and charge transfer.

1. Introduction

There are many applications for organic fluorescent dyes, for example cosmetics, coatings and paint, food and textile industries, in addition to the applications in the technology industries, such as resonance energy transfer, solar cells and liquid crystal displays. There are many chemical compounds of organic fluorescent dyes, one group of these dyes are 1,8-naphthalimide derivatives which form a special class of compounds. Naphthalimide derivatives are used for solar energy collectors as fluorescent dyes and in liquid crystal displays as fluorescent dichroic dyes. 1,8-naphthalimide derivatives contain amino groups in the C- 4 position and display strong yellow- green fluorescence with a bright yellow color [1]. The presence of strong electron- donating groups, for example alkyl amine and alkoxy shows a good fluorescent properties of 1,8-naphthalimide compounds and 4- alkoxy-1,8-naphthalimides are used as fluorescent brightening agents [2].

1,8-naphthalimide derivatives are very sensitive to solvent effects and are able to bind to substrate, therefore the 1,8-naphthalimide properties (i.e., optical and photophysical properties) are very sensitive to the substituents in the aromatic ring in the chemical structure. In addition, the fluorescence spectra of these fluorophores are sensitive to the solvent environment [3]. The 1,8-naphthalimides are showed a high fluorescence quantum yields, which are used as laser dyes. The derivatives of the naphthalimide are used as fluorescent molecular probes [4]. The most kind of fluorescent chromophore which is used widely is naphthalic anhydrides, these compounds are high fluorescence efficiency and chemical stability. The presence of electron donating groups at the C-4 or C- 5 positions of the naphthalic ring leads to a “ push – pull ” molecule with an intramolecular charge-transfer (ICT) excited state and generate a dipole character [5]. 1,8 - naphthalimide is a conjugated fluorescent molecule with a rigid plane. The 1,8 - naphthalimides are showed good fluorescence

*Corresponding author e-mail: rozachemistry@yahoo.co.uk, Tel:- 07809758878

Receive Date: 20 October 2019, Revise Date: 27 December 2019, Accept Date: 21 March 2020

DOI: 10.21608/EJCHEM.2020.18464.2138

©2020 National Information and Documentation Center (NIDOC)

quantum yield and Stokes shift, therefore they have been used in laser dyes, DNA intercalators, fluorescent probes. In addition, they are widely used for the fluorescence probe, depend on the Schiff-base-type compounds with metal chelators [6]. The azo dyes are prepared by using 4-amino-N-substituted-naphthalimide which is characterized as a diazo component, and the

dual fluorescence is determined by the synthesis of some N-aryl-1,8-naphthalimides, and the twisted internal charge transfer (TICT) is studied by the dual fluorescence systems [7]. The 1,8-naphthalimide is shown to represent a visible emission wavelength and good photostability. The intramolecular charge transfer (ICT) is observed in the substituted naphthalimide, the ICT is arising by the combination of the electron-withdrawing of the imide core with the planar architecture of the naphthalimide [8]. The naphthalene compound with an amine substituent is sensitive to the solvent effects, therefore the fluorescence spectrum, quantum yield, and lifetime are changed with the solvent is changed because the binding to a substrate [9]. The optical molecular sensor is created by 1,8-naphthalimide, therefore the 1,8-naphthalimide derivatives are used as fluorescent markers in biology, anticancer drugs, electroluminescent compounds [10], and fluorescent brightening agents (FBA), energy sun collectors [11]. Recently, there are many researches depend on the synthesis of new photochromic devices, therefore new photochromic compounds are prepared by naphthalimide derivatives [12]. Naphthalene or pyrene has good fluorescent properties and is characterized as certain aromatic moieties, and naphthalene or pyrene is used as the fluorescent probe and hydrophilic moiety when transformed to hydrophilic groups [13].

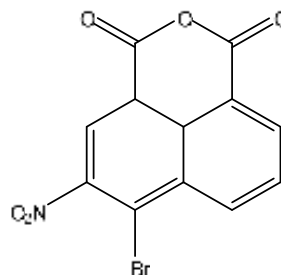
In the current work, we report on the synthesis of 4-bromo-3-nitro-1,8-naphthalic anhydride, the dye was prepared by a simple method. The UV-visible absorption and fluorescence spectral properties and ionic conductance were studied. Application in conductance by using dopant material (4-hydroxy-m-benzene-disulfonic acid) was investigated.

Experimental:

Preparation of 4-bromo-3-nitro-1,8-naphthalic anhydride

4-bromo-1,8-naphthalic anhydride (7.0 gm, 0.025 mole) in concentrated sulphuric acid (37.5 ml), then sodium nitrate (2.6 gm, 0.03 mole) was

added to the compound and the addition was completed within 1 hr. The solution was stirred for 2 hr in room temperature, and was poured into water (500 ml), the solution was filtered, washed with water. The yellow solid was obtained [14].



Scheme (1): The structure of 4-bromo-3-nitro-1,8-naphthalic anhydride

Preparation of dopant material, Preparation of 4-hydroxy-m-benzene disulfonic acid

In a flat-bottomed flask, phenol 31 gm (0.33 M) was added and then added 116 gm of concentrated sulfuric acid. The mixture was heated in a boiling water bath for 3 hr with mechanical stirrer on cooling to room temperature or below by immersing the flask in ice water, and the solution of sodium hydroxide (95 gm in 235 ml water) was added slowly, the solid salt was separated [15]. The FT-IR was measured by FTIR-8400S Shimadzu (JAPAN) instrument.

Measurement of the ionic conductance

The dye (0.022 gm) was dissolved in water (100 ml) as a solvent, and the ionic conductance was measured without the addition of the dopant material which was equal to 1×10^{-6} Siemens, then different weights of the dopant material (4-hydroxy-m-benzene-disulfonic acid) were added to the solution and the mixture was stirred for 2 mins., then the ionic conductance was measured at room temperature by the Konduktoskop E 365B instrument.

The photophysical properties (UV-Visible absorption)

The UV-Visible absorption of 4-bromo-3-nitro-1,8-naphthalic anhydride in ethanol, dimethyl sulfoxide DMSO, and butanol was recorded by the Spectroscan 80D (UK) instrument to study its spectral properties in different solvents of different

Table 1: Absorption and emission data for 4- bromo- 3- nitro -1,8-naphthalic anhydride in different solvents

Solvents	Absorption maxima (nm)	Fluorescence maxima (nm)
Ethanol	236, 318	361
Butanol	232, 306	370
DMSO	338, 402, 454	378

polarity Fig 1. The wavelengths corresponding to

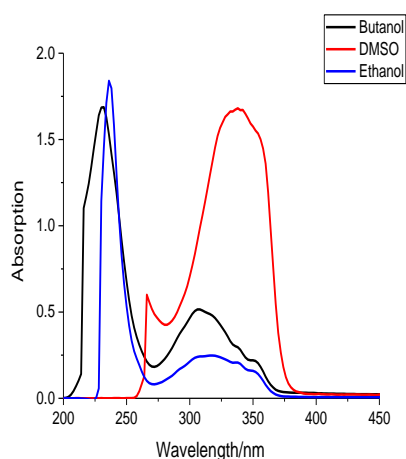


Figure (1): The absorption spectrum in different solvents

2. Results and Discussion

The compound has a common broad band at (300-320) nm in some solvents such as butanol and ethanol, on the other hand, bathochromic shifts in absorption due to solvent polarity was observed. For example, in ethanol, the compound had a λ_{max} value at 236.00 nm, and a red shift in absorption for the polar solvent, DMSO at 338 nm. It is important to study the effect of the substituents at C- 4 on the absorption spectrum, when the replacement the bromo group with strong electron-donating group, such as methoxy- ethoxy group [2]. The electron - donating leads to increase the intramolecular hydrogen bond strength [16]. In butanol, higher energy $\pi - \pi^*$ transitions were observed at wavelength ca. 232 nm. The compound exhibited a slight blue shift (ca. 4-5 nm) on moving from the less polar ethanol to highly polar 1-butanol. In DMSO solvent, the absorption spectrum for the compound

the spectral peaks are shown in Table 1.

displayed bands at 338, 402 , and 454 nm, there is a red shift ($\lambda_{max} = 338$ nm) compared to that of its compound ($\lambda_{max} = 236$ nm) in ethanol solvent. The band at ($\lambda_{max} = 338$ nm) was broad and was assigned to the internal charge transfer (ICT) absorption character of the 4- amino -1,8-naphthalimide which relates to the electron donating nature of the substituent [17]. The band in the UV region ($\lambda_{max} = 338$ nm), which could be attributed to the absorption of $\pi - \pi^*$ transition of naphthalic ring, and the two ICT bands in the visible region [18].

The fluorescence spectrum

The fluorescence spectra of 4- bromo- 3- nitro -1,8-naphthalic anhydride is displayed in Fig. 2.

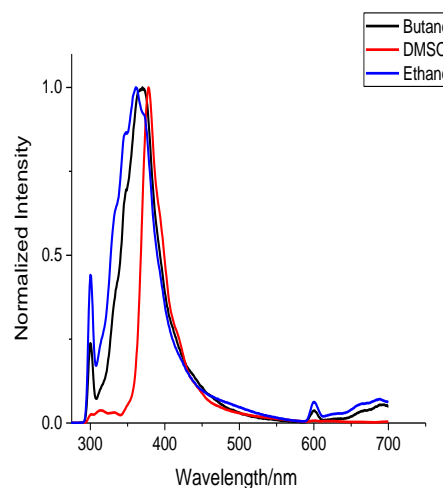


Figure (2): The fluorescence spectrum in different solvents

It can be observed from the figure that the fluorescence emission spectra of the compound were sensitive to solvent polarity. They move to lower energies with increasing the polarity of the solvent Table 1. The effect of the solvent polarity on the fluorescence maximum was more pronounced compared with the absorption maximum. In more

polar solvents, for example, DMSO, the long wavelength of fluorescence is undoubtedly due to an intramolecular charge transfer transition, this means

Table 2: The main functional groups and their frequencies in FT-IR of the compound (4-bromo-3-nitro-1,8-naphthalic anhydride)

C-H	C=O	C=C	C-Br	C-N
3082	1778,1732	1570	775	1134

that the S_1 excited state is highly polar nature. In DMSO, the fluorescence maximum is increased by approximately 17 nm compared with ethanol solvent. The fluorescence properties were found to strongly dependent on the solvent polarity, showing ca. 8 nm red shift on moving from butanol to DMSO, the excited states for the 4-amino-1,8-naphthalimides have ICT character [19]. Excitation of the compound at 300 nm gave a single emission band centred at 378 nm in DMSO, compared to the emission of 4-nitro-1,8-naphthalimides, which exhibit weak emission (ca. 450 nm) because of the electron withdrawing for a nitro group, the nitro-1,8-naphthalimide shows the absence of any fluorescence because of the constituent chromophores have a mixing of energy levels [17]. The fluorescence maximum of the compound gradually red shifted from 361 nm in ethanol, 370 nm in butanol, and 378 nm in DMSO, the polarity of the solvent triggered a significant bathochromic shift (17 nm) of the fluorescence wavelength of the compound with increasing the polarity of the solvent from ethanol to DMSO. The fluorescence position of the maximum peak is shifted to red in polar solvent, due to the solvation of the polar solvents to the excited states of the polar ICT, which has decrease the excited states energy, and lead to the remarkable red-shift of the emission peak (i.e. maximum of the emission peak) [18].

FT-IR characterization

The FT-IR was used for the characterization of the compound (4-bromo-3-nitro-1,8-naphthalic anhydride), Fig. 3, Table 2, and the dopant material (4-hydroxy-m-benzene-disulfonic acid). The FTIR data showed stretching band at 1570 cm^{-1} for C=C, and the band at 3066 cm^{-1} for C-H stretching [7], the band at 3082 cm^{-1} is due to C-H stretching for aromatic ring, the bands at 1778, 1732 cm^{-1} for C=O stretching carbonyl groups, the band at 1570 cm^{-1} for C=C stretching for aromatic ring, the bands at 1500, 1330 cm^{-1} are due to NO_2 stretching (asymmetry and

symmetry) [1]. The C-Br band was appeared at 775 cm^{-1} , the band at 1134 cm^{-1} for C-N band [3]. The aromatic C-H bending at about 1022 cm^{-1} [20]. The FTIR data for the dopant material showed the peak at 3456 cm^{-1} is assigned to O-H stretch, and S=O group (symmetry stretching) is appeared at 1126, the peaks at 1631, 1604 cm^{-1} for C=C cm^{-1} aromatic ring, the O-H (out of plane deformation) is appeared at 622 cm^{-1} .

The conductance

The conductance or conductivity means that the reciprocal of the resistivity normalized to a 1-cm cube of a liquid at a temperature according to the law.

$$\kappa = \frac{1}{\epsilon} = \frac{L}{RA} \text{ in } \text{ohm}^{-1} \cdot \text{cm}^{-1}$$

While the resistance is related to the length of a conductor (L) and inversely proportional to the area (A), $R = \frac{\epsilon L}{A}$, $\epsilon = \frac{RA}{L}$.

ϵ is the resistivity, which the units of ohm.cm [21].

The ionic conductance (G) of the compound was measured in water as a solvent. The influence of the dopant material (4-hydroxy-m-benzene-disulfonic acid) on the conductivities of the compound is shown in Fig. 4. It is apparent that the conductance increases as the weight of the dopant material increases, the conductance of the compound was 1×10^{-6} Siemens, while the conductance was 217×10^{-6} Siemens after adding the dopant material (0.096) gm, while was 8×10^{-6} Siemens in 0.002 gm, therefore the conductance depends on the free ions mobility and the concentration, the conductance is improved through the charge carriers and mobility of charge carrier and the conductance is increased by the difference in the doping efficiency and charge carrier mobility [22]. The low conductance ($8.00 \times 10^{-6} \text{ ohm}^{-1}$) is resulted from the dopant aggregation which is interrupt the charge transport of the compound [23]. Fig. 5, shows the relationship between the specific conductance and the weights of the dopant material, it can be seen the same behaviour of the ionic conductance. Table 3 shows the values of the conductance and specific conductance for the compound.

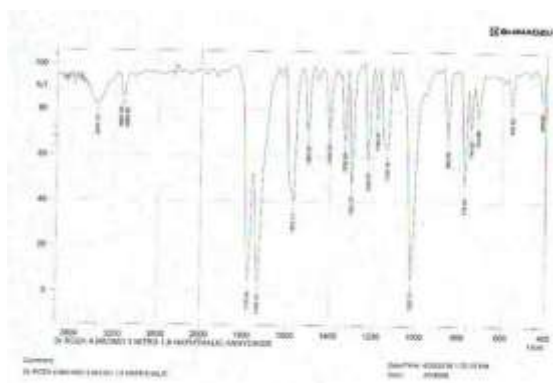


Figure (3): The FT-IR spectrum for the compound

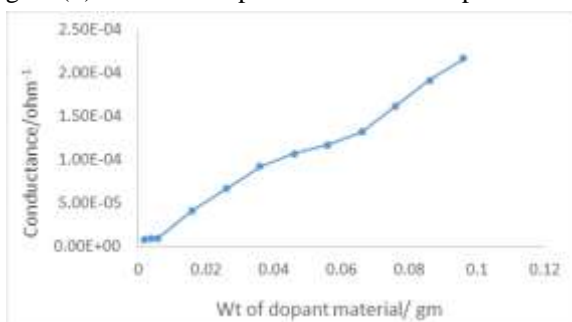


Figure (4): The conductance for the compound

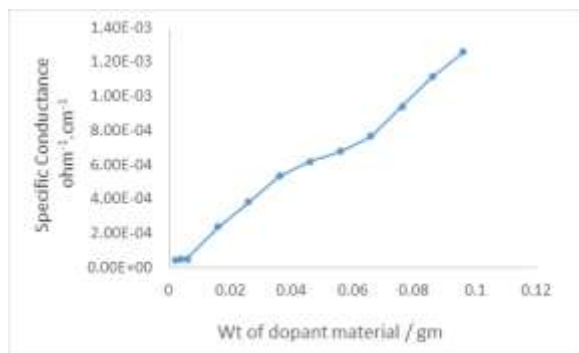


Figure (5): The specific conductance for the compound

3. Conclusions

In this paper, we have synthesized of naphthalic anhydride compound, UV – Vis absorption and emission spectra and ionic conductance were measured, the absorption spectra depend on the solvent polarity, which the compound shows significant red shift in some solvents, such as DMSO solvent.

The compound showed a specific fluorescence emission maximum at 378 nm in DMSO, 361 nm in ethanol, 370 nm in butanol, therefore the fluorescence spectra of this compound were sensitive to the solvent polarity, the calculated result indicates that the maximum peak is shifted to red in polar

Table 3: The values of conductance and specific conductance for the compound after doped with the dopant material

Weight /gm	Conductance /ohm ⁻¹	Specific Conductance/ ohm ⁻¹ .cm ⁻¹
0.002	8.00E-06	4.64E-05
0.004	9.00E-06	5.22E-05
0.006	9.00E-06	5.22E-05
0.016	4.10E-05	2.38E-04
0.026	6.60E-05	3.83E-04
0.036	9.20E-05	5.34E-04
0.046	1.07E-04	6.21E-04
0.056	1.17E-04	6.79E-04
0.066	1.32E-04	7.66E-04
0.076	1.62E-04	9.40E-04
0.086	1.92E-04	1.11E-03
0.096	2.17E-04	1.26E-03

solvent, which leads to decrease the energy of the excited states. The effect of the dopant material on the conductivities (ionic and specific) of the compound was studied, the ionic conductance was increased as the weight of the dopant material increases, the conductance of the compound was 1×10^{-6} Siemens, while the conductance was 217×10^{-6} Siemens after adding the dopant material (0.096) gm.

4. Conflicts of interest

“There are no conflicts to declare”.

5. Acknowledgments

This research was undertaken with the assistance of College of Science at the University of Basrah, Chemistry department.

6. References

- [1] Shaki H., Gharanjig K., Rouhani S., Khosravi A., Synthesis and photophysical properties of some novel fluorescent dyes based on naphthalimide derivatives, *J. Photochem. Photobiol. A: Chem.*, 216, 44 (2010).
- [2] Xiao H., Chen M., Shi G., Wang L., Yin H., Mei C., A novel fluorescent molecule based on 1,8-naphthalimide: synthesis, spectral properties, and application in cell imaging, *Res Chem Intermed.*, 36, 1021 (2010).
- [3] Saito G., Velluto D., Resmini M., Synthesis of 1,8-naphthalimide-based probes with

- fluorescent switch triggered by flufenamic acid, *R. Soc. Open sci.*, 5, 172137 (2018).
- [4] Bekere L., Gachet D., Lokshin V., Marine W., Khodorkovsky V., Synthesis and spectroscopic properties of 4-amino-1,8-naphthalimide derivatives involving the carboxylic group: a new molecular probe for ZnO nanoparticles with unusual fluorescence features, *Beilstein J. Org. Chem.*, 9, 1311 (2013).
- [5] Chen S., Li X., Song L., A fluorescent photochromic diarylethene based on naphthalic anhydride with strong solvatochromism, *RSC Adv.*, 7, 29854 (2017).
- [6] He G., Liu C., Liu X., Wang Q., Fan A., Wang S., Qian, X., Design and synthesis of a fluorescent probe based on naphthalene anhydride and its detection of copper ions, *PLoS ONE.*, 12(10), e0186994 (2017).
- [7] Panah H. S., Khosravi A., Gharanjig K., Khorassani M., Zadeh M. K., Taromi F. A., Synthesis and Characterization of New Fluorescent Polymerizable Dyes Based on Naphthalimide, *Iran. Polym. J.*, 19(7), 491 (2010).
- [8] Choi S.-A., Park C. S., Kwon O. S., Giong H.- K., Lee J.-S., Ha T. H., Lee C.-S., Structural effects of naphthalimide- based fluorescent sensor for hydrogen sulfide and imaging in live zebrafish, *Sci. Rep.*, 6, 26203 (2016).
- [9] Alexiou M. S., Tychopoulos V., Ghorbanian S., Tyman J. H. P., Brown R. G., Brittain P. I., The UV-Visible Absorption and Fluorescence of some Substituted 1,8-Naphthalimides and Naphthalic Anhydrides, *J. Chem. Soc. Perkin Trans.*, 2, 837 (1990).
- [10] Arkhipova A. N., Panchenko P. A., Schepel N. E., Fedorov Y. V., Rummyantseva M. N., Marikutsa A. V., Gaskov A. M., Fedorova O. A., Synthesis, Optical Characteristics and Complex Formation of Molecular Receptors Based on 1,8-Naphthalimide Derivatives in Solution and in Composition of Hybrid Tin Dioxide Nanoparticles, *Macrocyclics.*, 10(1), 84 (2017).
- [11] Grabtchev I., Philipova T., Synthesis of 1,8-Naphthalic Anhydride Derivatives for Use as Fluorescent Brightening Agents for Polymeric Materials, *Dyes Pigment.*, 27(4), 321 (1995).
- [12] Orhan E., Synthesis of Novel Diarylethenes Bearing Naphthalimide Moiety and Photochromic Fluorescence Behaviors, *JOTCSA.*, 4(2), 501 (2017).
- [13] Srivastava A., Singh P., Srivastava A., Kumar R., Amphiphilic Fluorescent Well- Defined Living Polymer from Indole-3-Carboxaldehyde and 4-Bromo-1,8-Naphthalic Anhydride: Synthesis and Characterization, *J. Polym.*, 2014, 1 (2014).
- [14] Tan S., Yin H., Chen Z., Qian X., Xu Y., Oxo-heterocyclic fused naphthalimides as antitumor agents: Synthesis and biological evaluation, *Eur. J. Med. Chem.*, 62, 130 (2013).
- [15] Kahol P. K., Satheesh Kumar K. K., Geetha S., Trivedi D. C., Effect of dopants on electron localization length in polyaniline, *Synth. Met.*, 139(2), 191 (2003).
- [16] Bojinov V., Panova I., Synthesis of novel fluorophores-combination of hindered amine and UV absorber in the molecule of benzo[de]isoquinoline-1,3-dione, *J. Univ. Chem. Technol. Metallurgy.*, 41(3), 277 (2006).
- [17] Ryan G. J., Elmes R. B. P., Quinn S. J., Gunnlaugsson T., Synthesis and photophysical evaluations of fluorescent quaternary bipyridyl-1,8-naphthalimide conjugates as nucleic acid targeting agents, *Supramol Chem.*, 24(3), 175 (2012).
- [18] Wang L., Shi Y., Zhao Y., Liu H., Li X., Bai M., "Push-pull" 1,8-naphthalic anhydride with multiple triphenylamine groups as electron donor, *J. Mole. Struc.*, 1056-1057, 339 (2014).
- [19] Banerjee S., Kitchen J. A., Gunnlaugsson T., Kelly J. M., Synthesis and photophysical evaluation of a pyridinium 4-amino-1,8-naphthalimide derivative that upon intercalation displays preference for AT-rich double-stranded DNA, *Org. Biomol. Chem.*, 10, 3033 (2012).
- [20] Ventura B., Bertocco A., Braga D., Catalano L., d'Agostino S., Grepioni F., Taddei P., Luminescence Properties of 1,8-Naphthalimide Derivatives in Solution, in Their Crystals, and in Co-crystals: Toward Room- Temperature Phosphorescence from Organic Materials, *J. Phys. Chem. C.*, 118, 18646 (2014).
- [21] Miller R L., Bradford W L., Peters N E., Specific Conductance: Theoretical Considerations and Application to Analytical Quality Control, United States Government Printing Office,(1988).
- [22] Liang Z., Zhang Y., Soury M., Luod X., Boehm A M., Lie R., Zhanga Y., Wangf T., Kima D.-Y., Meid J., Marderb S R., Graham K R., Influence of dopant size and electron affinity on the electrical conductivity and thermoelectric properties of a series of conjugated polymers, *J. Mater. Chem. A.*, 6, 16495 (2018).
- [23] Li H., DeCoster M E., Ming C., Wang M., Chen Y., Hopkins P E., Chen L., Katz H E., Enhanced Molecular Doping for High Conductivity in Polymers with Volume Freed

for Dopants, *Macromolecules.*, 52, 9804
(2019).