

SILESIAAN UNIVERSITY OF TECHNOLOGY

Faculty of Chemistry

Department of Physical Chemistry and Technology of Polymers

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**DOCTORAL DISSERTATION:
EXTENDED SUMMARY**

*Characterisation of donor-acceptor systems as materials for organic
optoelectronics*

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Assistant promoter: dr hab. inż. Agata Blacha-Grzechnik

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1. Aim and scope of the work

The main aim of the presented work is a broad characterization of donor-acceptor (D-A) systems, commonly applied in organic optoelectronics, taking into account both radiative and non-radiative processes. In such an approach, attention is paid to the duality of D-A systems, i.e., their ability to act as an active layer in organic optoelectronic devices or as a singlet oxygen source. Thus, donor-acceptor systems commonly used in organic optoelectronics – either OLEDs (organic light-emitting diodes) or OPVs (organic photovoltaics), were selected. Furthermore, the heteroatom-containing D-A compounds based on dibenzo[a,j]phenazine acceptor, which has been designed for their applicability in OLED devices, were investigated. Finally, in the group of OPVs D-A systems, a novel fullerene dyad with bis-selenophene, and well-known phenyl-C61-butyric acid methyl ester with poly(3-hexylthiophene-2,5-diyl) (PCBM:P3HT), and porphyrin-phenothiazine systems were selected.

The main novelty of the presented work lies in the undertaken approach, in which the investigation of singlet oxygen photogeneration is added to a standard analysis conducted on D-A organic systems. Hence, the selected D-A systems were firstly subjected to electrochemical analysis and were, in the next step, deposited on solid support either via electrochemical polymerisation, spin-coating or chemical grafting. Finally, the photogeneration of singlet oxygen by the resulting layers was widely investigated, and the selected ones were tested in the industrial important oxidation process or as antimicrobial coatings.

2. Research subject

Nowadays, the most commonly developing fields of organic optoelectronics are organic light-emitting diodes (OLED), organic photovoltaics (OPV) and organic field-effect transistors (OFET). Thanks to the use of organic systems in those types of devices, it is possible to produce lightweight, flexible and easy to fast customization modules that perfectly match the electronics market¹⁻³. However, there is still much room for improvement, taking into account the stability and performance of organic optoelectronic devices. Due to the variety of types of optoelectronic devices, there are many different mechanisms involved in their organic backbone, but they all rely consistently on energy transfer. For example, in organic photovoltaic (OPV) devices, absorbed solar energy is transformed into electrical power. In OLED devices, the situation is quite the opposite – here, a current induces the photoluminescence process. Taking this into account, it might be stated that the basis of each of these systems lies in the Jabłoński diagram⁴⁻⁶. Considering the mechanisms occurring in all optoelectronic devices, it can be noted that the key feature that determines the processes occurring in photoactive compounds is the position of their energy levels. In OLED-type devices, the excess energy is emitted via luminescence⁷. In the first generation of organic devices – mainly phosphorescence occurs, while in the novel materials, so-called the third generation devices - a reverse InterSystem Crossing (rISC) process appear, which in turn leads to thermally activated delayed fluorescence (TADF)⁵. In the last type, the energy of the triplet state has to be high enough for reverse intersystem crossing to occur but not too high to avoid relaxation by non-radiative processes (Figure 1A). On the other hand, OPVs are designed to have a charge separation process as large as possible (Figure 1B).

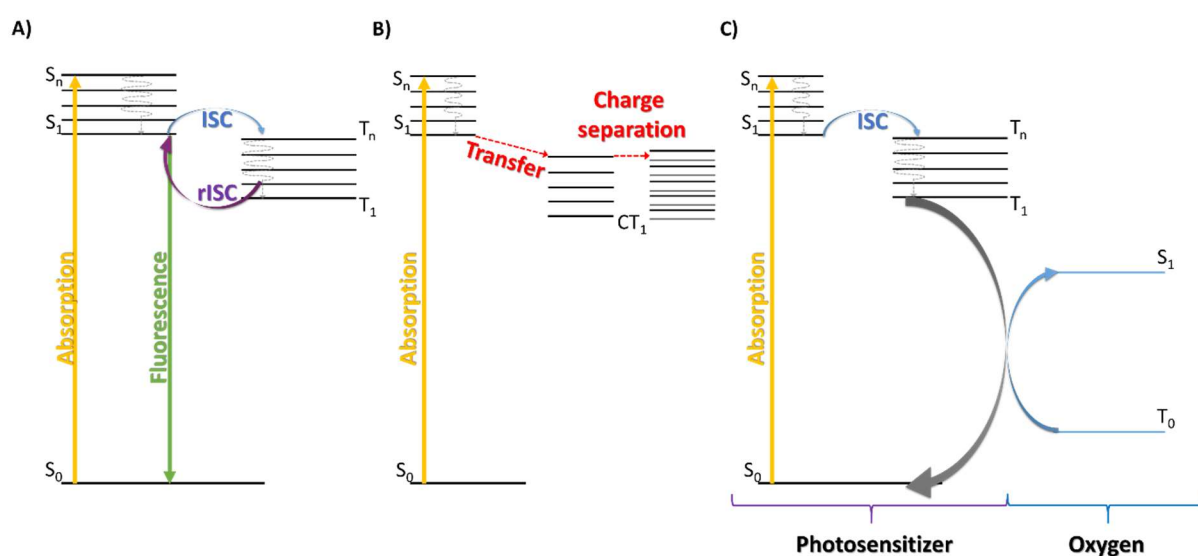


Figure 1. Energy transfer mechanisms occurring in A) TADF, B) OPV systems and C) Singlet oxygen photogeneration involving the photosensitizer as energy donor.

Thus, the triplet state has to be long-lived to increase the power conversion efficiency. Additionally, the energy of the triplet state has to be high enough to avoid relaxation without charge separation. Most of the currently developed optoelectronic technologies are based on further improvement of intermolecular interactions of organic units in photoactive compounds. These groups may have a donor (D) character when they are able to donate electrons, while in the case of groups hosting these electrons, we talk about acceptors (A). In such excited systems, the so called charge transfer (CT) state is created. At this point, electrons rearrange themselves moving toward the acceptor while the holes are formed in the donor unit. As a result of recombination and radiative relaxation, emission of a photon (OLED) or the so-called free charge carriers generation (OPV) may take place. D-A systems can have a single molecule structure, but in this group of materials we also have polymers composed of different D-A units. Another possibility is so-called blends, mixtures of active compounds interacting with each other. The characteristic structure and the possibility of combining different types of donor and acceptor groups allow to boost the properties and features of new photoactive systems.

Due to their specific structure, the energy transfer process occurring in OLEDs and OPV devices is very sensitive to several internal and external factors. The disruption of energy transfer often leads to worse performance of optoelectronic devices. This happens by increasing the efficiency of the so-called non-radiative transitions at the expense of the radiative ones. Generally, three types of relaxation which can cause energy losses^{8,9} can be named:

1. Radiative loss above bandgap/ energy gap
2. Radiative loss below bandgap/ energy gap
3. Non-radiative loss

While radiative losses (1) and (2) are traceable by suitable spectroscopic methods, investigating the non-radiative transition process isn't that straightforward. The non-radiative loss can be connected among all with a vibration-induced quenching, a concentration quenching, other energy transfers, and the most important from the topic point of view of this thesis - oxygen quenching¹⁰. Understanding the mechanisms behind the high contribution of non-radiative transitions in optoelectronic systems seems to be crucial in developing high-performance, state-of-the-art organic devices.

In the case of oxygen-caused non-radiative losses, the energy transfer from an excited organic moiety goes via Dexter Transfer. The energy from a conjugated domain is transferred to the oxygen molecule in the triplet ground state, $^3\text{O}_2$, which results in the formation of singlet

oxygen. Such process is so-called photosensitisation with organic compound acting as a so-called photosensitizer (Figure 1C)^{11,12}.

The vast majority of organic compounds used in optoelectronic devices are conjugated ones. Generally, increasing the number of π bonds leads to an increase in the stability of bulky molecules by lowering their total energy and also causes the shift of the absorption maximum toward higher wavelengths. However, as mentioned above, the formation of $^1\text{O}_2$ by photoactive molecules, being a competitive process, results in lower efficiency of the devices. Moreover, the π -conjugated systems themselves can be oxidized by this reactive form of oxygen that may lead to the degradation of the optoelectronic device. This can be avoided, for example, by encapsulation. When it comes to inhibiting the penetration of oxygen and water particles into devices, the type and quality of an encapsulation play a key role in the stability of optoelectronic devices^{13,14}. Another aspect that significantly affects the choice of protective coating is the elasticity of the devices, which is one of the most important advantages of optoelectronic technology. For rigid devices - a glass encapsulation may be proposed, but the encapsulation should not affect the flexibility of the elastic devices. Currently, the most promising is a thin-film encapsulation method, which involves applying nanocomposites, resins or nanolaminates as protective coatings¹⁵.

The chase for the best, the most effective, and the brightest photoactive molecules leaves no room for consideration of different possibilities of application of *less effective materials*. They may appear remarkably effective in another branch of industry, e.g. as photosensitizers. The oxidative properties of singlet oxygen imply its application in various fields of industry, starting from the “green” synthesis, through environmental technologies and wastewater treatment up to medical applications such as photodynamic anticancer (PDT) and antimicrobial (PACT) therapies^{12,16–21}. Thus, the ability of conjugated organic systems to photogenerate singlet oxygen can be considered an alternative application. Undoubtedly, this type of research allows us to understand the effect of molecule structure on the efficiency of singlet oxygen photogeneration. This, in turn, may lead to a more conscious design of photoactive organic systems taking into account their target application. For example, understanding how to avoid non-radiative transitions by optimizing chemical structure should lead to more efficient and stable organic electronic devices. Someday, it may also be possible to avoid production in an inert oxygen-free environment or the protection with dedicated coatings, which would strongly reduce the overall costs of such devices. On the other hand, such a broad approach can open doors to new opportunities in applying photoactive organic systems.

3. Results and discussion

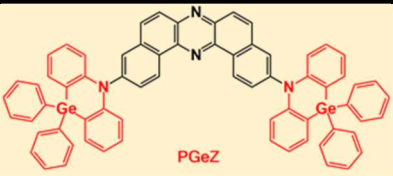
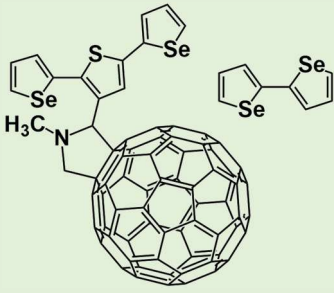
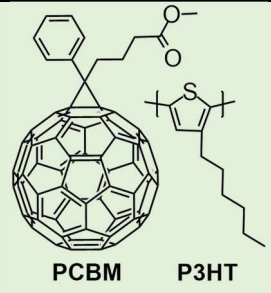

In the presented work, an extensive study of photoactive compounds commonly used in organic electronic devices has been carried out. Contrary to the classical approach, during the characterisation of photoactive systems, more attention was paid to investigating their ability to photosensitize singlet oxygen. The need for this research type is supported by a broad review (M1) of the topical literature that indicates the importance of non-radiative transitions affecting the performance of optoelectronic devices. The review mentioned above focuses on the photogeneration of singlet oxygen as one of the main causes of worsened performance of optoelectronic devices. Therefore, this work covers both the topic of non-radiative transitions in optoelectronic systems and also highlights the need for a broader perspective on the research on photoactive systems, their multi-purpose nature and potential versatile applications. Based on the literature review, it can be stated that only a limited number of works deal with the photoactive systems having a donor-acceptor structure which are applied in singlet oxygen photogeneration experiments. Thus, in order to fulfil this gap, the topic was undertaken in the presented work.

The selected systems studied in this work are summarized in Table 1. In the first part of the work (M2), a comprehensive electrochemical, spectroscopic and spectroelectrochemical analysis of the germanium derivative of dibenzo[a,j]phenazine was carried out, supplemented by studies conducted of respective heteroatomic silicon and phosphorus derivatives. Those compounds, with a donor-acceptor-donor structure, were designed as a potential TADF emitter for OLED devices. One of the investigated derivatives, which showed the highest tendency to undergo electropolymerisation, was in turn electrochemically deposited on a surface of an ITO electrode and further investigated in the form of a layer. Similarly, work M3 deals with the spectroscopic and electrochemical characterisation of novel compounds, in this case, fullerene dyads applicable in OPVs. Again, the investigated compounds were electrochemically deposited on an ITO surface. In this case, the donor-acceptor ratio was varied by conducting the electrochemical co-deposition of a bis-selenophene molecule - the donor form and a fullerene derivative, which acted as an acceptor.

Contrary to the above, works M4 and M5 present the results of the investigation of well-known systems that have been widely characterized for organic electronics applications. In the first case, the system of PCBM - a fullerene derivative that acted as an acceptor molecule – and a P3HT, which served as an energy donor was investigated. In this case, the photoactive

layer was formed by spin-coating of solutions on top of the glass substrates. All prepared active layers were then investigated as a potential source of singlet oxygen in an exemplary oxidation reaction. Finally, porphyrin and phenothiazine derivatives applicable in dye solar cells were covalently grafted to a glass surface and investigated as a potential photoactive antimicrobial layer.

Table 1. Overview of the examined molecules, their character and assignment.

		Title of work	Deposition technique	Investigated donor-acceptor systems
OLED	M2	Dual-photofunctional organogermanium compound based on Donor–Acceptor–Donor architecture	Electrochemical polymerisation	
	M3	Electrochemically deposited poly(selenophene)-fullerene photoactive layer: tuning of the spectroscopic properties towards visible light driven generation of singlet oxygen	Electrochemical polymerisation	
OPV	M4	Singlet oxygen formation from photoexcited P3HT:PCBM films applied in oxidation reactions	Spin coating	
	M5	Covalent immobilisation of organic photosensitizers on the glass surface: toward the formation of the light-activated antimicrobial nanocoating	Chemical grafting	

4. Conclusions

The presented work shows a broad approach to investigating conjugated organic systems, from classical spectroscopic/electrochemical studies of D-A type molecules, throughout a rather unconventional part dealing with the analysis of $^1\text{O}_2$ photogeneration by those systems, up to the preliminary investigation of their potential application as photocatalysts or antimicrobial coatings. Based on the conducted experiments, the following conclusions can be formulated:

- various approaches of formation of photoactive layers can be effectively applied, including electrochemical polymerisation, spin coating, or chemical grafting;
- duality of D-A systems, i.e., their ability to act as an active layer in organic optoelectronic devices or as a singlet oxygen source has been proved;
- it has been shown that between donor and acceptor units in presented photoactive layers, the efficient energy transfer takes place. Therefore, it is demonstrated that the appropriate combination of two photoactive compounds, and moreover the ratio of D to A units, can significantly boost the photoactive potential of the studied systems, leading to their better optimization for the planned application;
- optimization and skillful selection of co-existing photoactive systems might influence the ratio of radiative and non-radiative transition taking place in optoelectronic devices. Thus, understanding the processes occurring between the donor and acceptor in such systems is the key to improving known organic devices' efficiency;

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5. List of the main publications including contributions

M1. Multiapplicability of singlet oxygen – small molecule high impact in materials development.

Nyga A., Gusev I., Blacha-Grzechnik A., Data P.,

Applied Materials Today., (2022), Manuscript under revision (IF₂₀₂₂= 10.3; MNiSW= 140)

A.N. was responsible for conducting the literature review and writing the parts devoted to: (i) direct detection of singlet oxygen techniques, (ii) description of radiative and non-radiative transitions and (iii) discussion of photogeneration of singlet oxygen by organic systems applied in organic electronic devices. A.N. prepared figures: Figure 2, Figure 3, Figure 5, Figure 6, Figure 7, Figure 9 and was co-author of the graphical abstract.

M2. *Dual-Photofunctional Organogermanium Compound Based on Donor-Acceptor-Donor Architecture*

Nyga, A., Kaihara, T., Hosono, T., Sipala, M., Stachelek, P., Tonai, N., Minakata, S. de Sousa, L., de Silva, P., Data, P., Takeda, Y..

Chem. Commun., (2022), vol. **58**, s. 5889-5892 (IF₂₀₂₁= 6.22; MNiSW= 200)

A.N. was responsible for planning and conducting of the electrochemical analysis of compounds. Furthermore, A.N. conducted EPR as well as UV-Vis spectroelectrochemical characterization of a investigated compounds.

M3. *Electrochemically deposited poly(selenophene)-fullerene photoactive layer: tuning of the spectroscopic properties towards visible light-driven generation of singlet oxygen*

Nyga A., Motyka R., Bussetti G., Calloni A., Sangarashettyhalli Jagadeesh M., Fijak S., Pluczyk-Małek S., Data P., Blacha-Grzechnik A.

Appl. Surf. Sci. (2020) vol. **525** s. 1-9 (IF₂₀₂₀= 6.61; MNiSW= 140)

A.N. was responsible for planning and conducting the electrochemical analysis of C₆₀Se and BisSe. A.N. was responsible for the electrochemical deposition of photoactive layers and the optimization of the process parameters. the author was responsible for UV-Vis investigation of deposited films. Furthermore, A.N. examined the possibility of singlet oxygen photogeneration by the layers with α -terpinene trap. A.N. prepared figures: *Graphical abstract, Figure 1 and Figure S2.*

M4. *Singlet oxygen formation from photoexcited P3HT:PCBM films applied in oxidation reactions*

Nyga A., Blacha-Grzechnik A., Podsiadly P., Duda A., Kepska K., Krzywiecki M., Motyka R., Janssen R. A. J., Data P.

Mater. Adv. (2022) vol. **3**, nr 4, s.2063-2069 (IF₂₀₂₂= n/a; MNiSW= 20)

A.N. was responsible for conducting a broad literature review on the topic and preparing a draft version of the manuscript. Moreover, the author was working on formation of photoactive layers and their further investigation with UV-Vis spectroscopy in cooperation with P. Podsiadly. A.N. conducted *in-situ* singlet oxygen photogeneration studies with 1,5-dihydroxynaphtalene. A.N. took part in the analysis of the obtained results.

M5. *Covalent immobilization of organic photosensitizers on the glass surface: toward the formation of the light-activated antimicrobial nanocoating*

Nyga A., Czerwińska-Główka D., Krzywiecki M., Przysaś W., Zabłocka-Godlewska E., Student S., Kwoka M., Data P., Blacha-Grzechnik A..

Materials (2021) vol. **14** iss. 11 s. 1-15 (IF₂₀₂₁= 3.623; MNiSW= 140)

A.N. was responsible for the preparation of photoactive layers on glass substrate in a three-step procedure consisting in a covalent grafting and post-modifications. the author was also responsible for conducting UV-Vis characterization and the investigation of the process of photogeneration of reactive oxygen species (ROS). A.N. prepared figures: *Graphical abstract and Scheme 2, and the draft version of the Introduction part.*