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Optoelectronic characterization of organic photovoltaic devices with emerging architectures

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Optoelectronic characterization of organic photovoltaic devices with emerging architectures

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Prof. Dr. Paulo Barbeitas Miranda

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ABSTRACT

LIMA FILHO, J. B. **Optoelectronic characterization of organic photovoltaic devices with emerging architectures**. 2020. 121 p. Thesis (Doctor in Science) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2020.

Following the worldwide interest in organic electronics (OE) devices, the first part of this work aimed at setting up an experimental apparatus for continuous-wave photoinduced absorption (cw-PA) spectroscopy with potential application to the characterization of organic photovoltaic (OPV) devices. This technique is part of a group known as pump-probe spectroscopy, which requires two light sources: one for pumping and the other one for probing the sample under investigation. The cw-PA spectroscopy allows the characterization of long-lasting photogenerated species in OPVs. The optical spectra of such species yield relative changes in transmission of the probe beam that are typically in the order of 10^{-4} . To obtain these spectra, the setup was assembled with advanced detection techniques based on a lock-in amplifier (LIA), with pump light modulation at frequencies ranging from Hz to MHz. This feature makes cw-PA an important tool for the investigation of both dynamics and kinetics of photogenerated species. The setup was automated using LabView[®] and subjected to several tests to establish its reliability. After passing all the tests, the setup was applied to characterize devices with emerging architectures. One of them was the surface metal-organic frameworks (SURMOFs), which can form organized crystalline structure achieved with application of organic materials. After having preliminary photoconductivity results with SURMOFs based on *buckminsterfullerene* (C60) and *5,15-bis-(3,4,5-trimethoxyphenyl)-10,20-bis(4-carboxyphenyl) porphyrinato zinc-II* (ZnTPP) fabricated at Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), in Germany, professor Wöll sent some samples to our laboratory to be further characterized. Measurements with cw-PA and current-voltage (JV) showed that the devices present poor charge photogeneration, with low short circuit current, open circuit voltage, and fill factor. The poor photogeneration may be caused by the low ratio acceptor/donor, while the low short circuit current, open circuit voltage, and fill factor may be caused by the assembling of C60 in a cage on ZnTPP, in which case C60 molecules are not electronically connected with each other and may be working as a sink (or trap) of electrons. Another emerging architecture named the light harvesting capacitor (LHC) differs from the usual OPVs because it drives an output current without charge collection. The photogenerated charges are stored in nanodipoles within the dielectric layer when the device is illuminated and the LHC outputs peaked current upon illumination by modulated light, differently from the usual photovoltaic devices. The second part of this work aimed at developing a mathematical model for LHCs as well as fabricating and characterizing an LHC. For the fabrication, the polymer *poly(3-*

potassium-6-hexanoate thiophene) (P3KHT) was used as electron donor and two organic molecules, namely the *N,N'*-bis(6-aminohexyl)-3,4,9,10-perilenediimide (P6N) and the *perylenediimide-polyethyleneimine* (PDI-PEI) as electron acceptors. The layer-by-layer (LbL) assemblies led to very thin films with average thickness of ~ 1.5 nm. Results obtained from multi layer LHCs built with up to 30 active bilayers sandwiched by insulating bilayers are presented. Results from ultraviolet and visible (UV-Vis) spectroscopy show that the LbL technique leads to linear growth of self assembled films. Characterizations with cw-PA reveal that there is charge photogeneration with good efficiency for both types of LHCs. The photogenerated charges present average lifetime in the range 100-200 μ s with predominantly bimolecular recombination. Regarding to charge photogeneration, LHCs based on PDI-PEI:P3KHT are found to be less efficient than those based on P6N:P3KHT. However, results from photocurrent (PC) measurements reveal that the photogenerated charges in LHCs based on PDI-PEI:P3KHT are more efficiently organized in aligned dipole configuration than those in LHCs based on P6N:P3KHT, indicating that PDI-PEI diffuses less into the macromolecules of P3KHT than P6N. These results for the LHCs and SURMOFs show that cw-PA is a powerful characterization technique for organic electronic devices, in combination with other electric characterization tools.

Keywords: Organic electronics. Light harvesting capacitor. Surface metal-organic frameworks. Continuous-wave photoinduced absorption spectroscopy. Impedance spectroscopy. Photocurrent.

RESUMO

LIMA FILHO, J. B. **Caracterização optoeletrônica de dispositivos fotovoltaicos orgânicos com arquiteturas emergentes**. 2020. 121 p. Tese (Doutorado em Ciências) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2020.

Seguindo o interesse mundial em eletrônica orgânica, a primeira parte deste trabalho teve como objetivo a montagem do aparato experimental para espectroscopia de fotoabsorção induzida de onda contínua (**cw-PA**, do inglês continuous-wave photoinduced absorption) com potencial aplicação à caracterização de dispositivos fotovoltaicos orgânicos (**OPV**, do inglês organic photovoltaic). Esta técnica é parte de um grupo denominado espectroscopia de bombeio-e-prova que requer duas fontes de luz: uma para o bombeio e a outra para a prova de amostras em investigação. A espectroscopia **cw-PA** permite a caracterização de espécies fotogeradas de longa duração em **OPVs**. O espectro ótico dessas espécies geram mudanças relativas à transmissão do feixe de prova que são tipicamente da ordem de 10^{-4} . Para obter estes espectros, o aparato foi montado com técnicas de detecção avançadas em um amplificador lock-in (**LIA**, do inglês lock-in amplifier), com modulação da luz de bombeio a frequências que vão desde o Hz ao MHz. Esta característica faz do **cw-PA** uma ferramenta importante para a investigação tanto da dinâmica quanto da cinética das espécies fotogeradas. O aparato foi automatizado utilizando-se LabView® e submetido a vários testes para estabelecer confiabilidade. Depois de passado nos testes, o aparato foi utilizado para caracterizar dispositivos com arquiteturas emergentes. Uma delas foi a arquitetura chamada de **SURMOFs** (do inglês *surface metal-organic frameworks*), que pode formar estrutura cristalina organizada obtida com o emprego de materiais orgânicos. Após obter resultados preliminares de fotocondutividade com **SURMOFs** baseados em *fulereno* (**C60**) e (**ZnTPP**, do inglês *5,15-bis-(3,4,5-trimethoxyphenyl)-10,20-bis(4-carboxyphenyl) porphyrinato zinc-II*) fabricados no Institute of Functional Interfaces (**IFG**), Karlsruhe Institute of Technology (**KIT**), na Alemanha, professor Wöll enviou algumas amostras ao nosso laboratório para caracterizações adicionais. Medidas com **cw-PA** e Corrente-Voltagem (**JV**) mostram que esses dispositivos apresentam fraca fotogeração de cargas, com corrente de curto circuito, voltagem de circuito aberto e fator de preenchimento muito baixos. A fraca fotogeração de cargas pode ser causada pela baixa razão aceitador/doador, enquanto que os baixos valores de curto circuito, voltagem de circuito aberto e fator de preenchimento podem ser causados pela montagem de **C60** em uma gaiola de **ZnTPP**, em que as moléculas de **C60** não têm conexão eletrônica entre si e podem estar agindo como sumidouras de elétrons. Outra arquitetura emergente denominada **LHC** (do inglês *light harvesting capacitor*), difere dos **OPVs** usuais porque gera corrente elétrica sem coleção de cargas. As cargas fotogeradas são armazenadas em nanodipolos limitados pelas camadas dielétricas quando o dispositivo é iluminado e o **LHC** gera uma corrente em

forma de picos devida à iluminação por luz modulada, diferentemente dos fotovoltaicos usuais. A segunda parte deste trabalho teve como objetivo o desenvolvimento de um modelo matemático para os LHCs, bem como a fabricação e a caracterização de um LHC. Para a fabricação, o polímero P3KHT (do inglês *poly(3-potassium-6-hexanoate thiophene)*) foi usado para automontar as camadas doadoras de elétrons e duas moléculas orgânicas, a saber P6N (do inglês *N,N'-bis(6-aminoheptil)-3,4,9,10-perilenediimide*) e PDI-PEI (do inglês *perylenediimide-polyethyleneimine*) foram utilizadas para automontar camadas aceitadoras de elétrons. A técnica LbL proporcionou automontagem de filmes muito finos com espessura média de ~ 1,5 nm. São apresentados resultados obtidos para LHCs com até 30 camadas ativas, cada uma sanduichada a bicamadas isolantes. Resultados obtidos por espectroscopia de absorção UV-Vis (do inglês *ultraviolet and visible*) mostra que a técnica LbL proporciona crescimento linear das camadas automontadas. Caracterizações com cw-PA revelam que há fotogeração de cargas com boa eficiência para ambos os tipos de LHCs. As cargas fotogeradas apresentam tempo médio de vida entre 100 e 200 μs com recombinação predominantemente bimolecular. Em relação à fotogeração de cargas, verificou-se que LHCs baseados em PDI-PEI:P3KHT são menos eficientes quando comparados àqueles baseados em P6N:P3KHT. No entanto, resultados das medidas de fotocorrente (PC, do inglês *photocurrent*) revelam que as cargas fotogeradas nos LHCs baseados em PDI-PEI:P3KHT são mais eficientemente organizadas em configuração de dipolos alinhados do que naqueles baseados em P6N:P3KHT, indicando que PDI-PEI se difunde menos entre as macromoléculas de P3KHT do que o P6N. Estes resultados para os LHCs e SURMOFs mostram que a cw-PA é uma técnica poderosa para caracterização de dispositivos eletrônicos orgânicos, em combinação com outras ferramentas de caracterização elétrica.

Palavras-chave: Eletrônica orgânica. Capacitor coletor de luz. Redes metálicas montadas em superfície. Espectroscopia de absorção fotoinduzida por onda contínua. Espectroscopia de impedância. Fotocorrente.

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