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The influence of experimental conditions and intermolecular interaction on the band gap determination. Case study of perylene diimide and carbazole-fluorene derivatives.

Michał Filapek*, Marek Matussek, Agata Szlapa, Slawomir Kula, Michał Pająk

Institute of Chemistry, Faculty of Mathematics, Physics and Chemistry, University of Silesia, Szkolna 9, 40-007 Katowice, Poland

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ABSTRACT

The perylene diimide and carbazole-fluorene derivatives are intensively investigated in organic electronic and photovoltaic applications. However, they intermolecular interactions vary considerably. Herein, we present a systematic UV–vis spectroscopy and electrochemical study of intermolecular interaction influence on determination of HOMO, LUMO and band gap. The influence of this type of interactions on photophysical properties with the aid of NMR spectroscopy and DFT calculations was examined. Effect of the electrode type was investigated as well. The cyclic voltammetry results obtained at different species concentrations (including solid state measurements) were compared. We have found that when interactions are strong differences in determined bang gap are significant. Contrary to half wave potential, peak onset was found to be concentration independent. Finally, we have observed that comparison of values from solid state measurement and carried out for diluted species can introduce high inconsistencies in determination of structure/property relationships.

1. INTRODUCTION

Organic electronic and photovoltaic are being developed extremely fast. Progress in this field is possible thanks to structure ↔ properties feedback – in each step it is better known how the structure affects physical and chemical characteristics of the molecule and by that device performance. With that knowledge it is easier to design and synthesize compounds which have exaggerated most desired properties. However, sometimes it is difficult to compare results from different sources, especially properties related to energy levels in the molecule (HOMO and LUMO energies). This is due to the inability to measure their absolute value experimentally. On the other hand, energy values calculated by quantum chemistry methods depends on the base and functional which were used (and also by HF/DFT ratio in hybrid functional [1]). That makes those values very often only estimated. Differences between calculated and experimental values of LUMO energy are predominately especially different [2]. In contrast to HOMO, LUMO is unreal (it is empty in the real molecule which is in ground state). Furthermore, by definition of MO, that is an orbital energy which has paired electrons (formally it would entail adding two electrons to the neutral molecule). This does not reflect the experience – electrochemical reduction the most often is a single-electron process [3], photoexcitation processes involved one electron as well. That is why sometimes radicals are analyzed using *unrestricted* DFT approach [4,5] The ionization energy (IE) and electron affinity (EA) can be directly determined by UV-photo electron spectroscopy (UPS) and inverse photo electron spectroscopy (IPES). On the other hand, the most convenient (the fastest, the cheapest and very small amount of sample is needed) methods of the EA and IE determining are the electrochemical methods. Generally speaking, UPS/IPES values are larger than the values derived from CV. The offset is about 0.5–0.8 eV in case of EA and 0.4–1.0 eV for IE [6,7]. Moreover, when comparing values determined on the physical (eV) and electrode potential scales (V vs. reference electrode) in solution the potential drop across an electrical double layer (the Helmholtz layer) needs to be considered. Usually zeta potential is used for estimating the degree of this surface – solution interactions (a typical value is approximately 25–100 mV). But still there is the problem of reference calculation results to the experimental values which has been described in detail by Jean-Luc Bredas [8], P. Bujak [9], or A. Pron [10]. As mentioned before the inability to measure the absolute value of MO is the biggest problem. Because of that those

* Corresponding author at: Institute of Chemistry, University of Silesia, 9 Szkolna Str 40-006 Katowice, Poland.
E-mail address: michal.filapek@us.edu.pl (M. Filapek).

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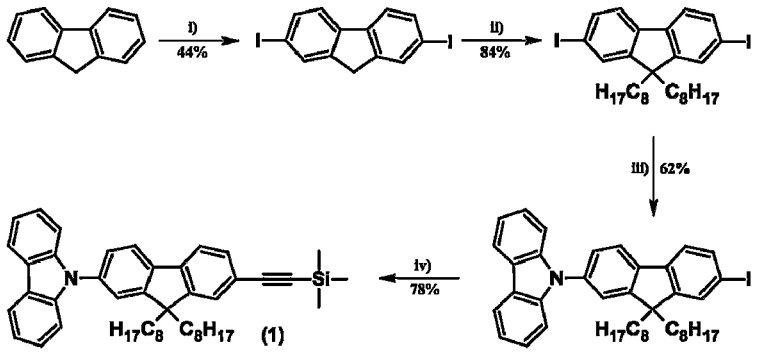


(i) I_2, H_5IO_6, $AcOH/H_2O/H_2SO_4$ (100:20:3 v/v), 65 °C, 4h; (ii) *n*-$C_8H_{17}Br$, TBAB, 50% $NaOH_{(aq)}$, DMSO, 40 °C, 6h; (iii) CuI, 1,10-phenantroline, carbazole, K_2CO_3, DMF, reflux, 24h; (iv) TMSA, $Pd(PPh_3)_4$, CuI, TEA/THF, 40 °C, 24h.

Fig. 1. Synthetic pathway for 1. (i) 2-ethylhexylamine, DMF, reflux, 8 h.

values have to be showed in relation to a standard, for example SCE, NHE or ferrocene [11]. It is worth to be mentioned that in literature there are different values of ionization energy of ferrocene (-4.8 eV [12], −4.88 eV [13], − 5.1 eV [9]). Taking into consideration fact that this value is directly use to calculate HOMO and LUMO levels this inconsistency may hinder comparison of data from different sources.

Moreover, intermolecular interaction can also affect determination of values connected with energetic levels. Thus, we have choose compounds differing greatly in intermolecular interactions i.e. perylene diimide (exhibiting strong π − interaction between the flat aromatic sections [6]) and carbazole-fluorene (which is an amorphous substance). This paper is an attempt to systematize measurement techniques and the compare electrochemistry in solution and in the solid state with results of theoretical calculations and obtained by NMR and UV–vis spectroscopy. In addition, we examined the electrode type, scan rate and whether the sample (whether the sample is in form of solid or solution) on the obtained empirical value.

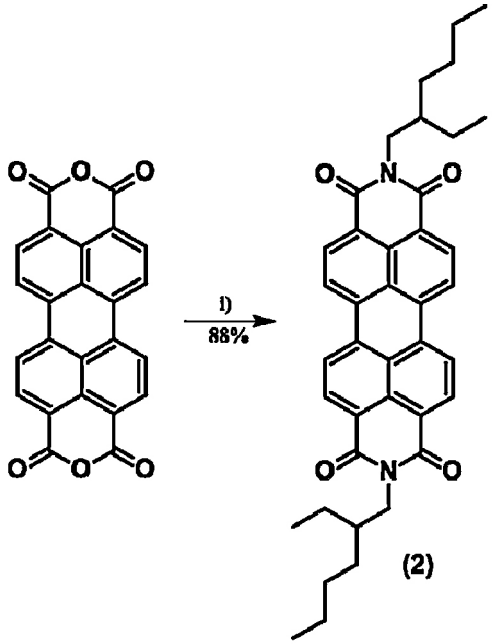
2. EXPERIMENTAL

2.1. General Methods

All chemicals and starting materials were commercially available and were used without further purification. Solvents were distilled as per the standard methods and purged with nitrogen before use. Column chromatography was carried out on Merck silica gel. Thin-layer chromatography (TLC) was performed on silica gel (Merck TLC Silica Gel 60). NMR spectra were recorded with a Bruker Avance 400 MHz instrument by using $CDCl_3$ as solvent. 2,7-diiodofluorene [14], 2,7-diiodo-9,9-dioctylfluorene [15], 2-iodo-7-(9H-carbazole-9-yl)-9,9-dioctylfluorene [16], N,N'-bis(2-ethylheksyl)-3,4,9,10-perylene diimide [17] were prepared to the literature procedures. Synthesis details for 2-(trimethylsilylethynyl)-7-(9H-carbazol-9-yl)-9,9-dioctylfluorene (**1**) can be found in SI. Both synthesis pathways are summarize in Figs. 1 and 2 for compounds (**1**) and (**2**), respectivelly. UV/Vis spectra were recorded with a Hewlett–Packard model 8453 UV/Vis spectrophotometer in dichloromethane solution. Electrochemical measurements were carried out with an Eco Chemie Autolab PGSTAT128n potentiostat using glassy carbon, gold, platinum (all with diam. 2 mm) or Indium tin oxide(ITO, with 10 Ω per square) as working electrode. For thin film preparation, substances were spin-coated on the cleaned electrode surface from fresh solution (2 mg/cm^3 in methylene chloride (DCM)) and baked 30 min at 60 °C. Platinum coil, and silver wire were used as auxiliary and reference electrode, respectively. Potentials are referenced with respect to ferrocene (Fc), which was used as the internal standard. Cyclic and differential pulse voltammetry experiments were conducted in a standard one-compartment cell, in CH_2Cl_2 (Carlo Erba, HPLC grade), under argon. Bu_4NPF_6 (Aldrich; 0.2 M, 99%) was used as the supporting electrolyte. The quantum theoretical calculations were performed with use of density functional theory (DFT), with an exchange correlation hybrid functional B3LYP and the basis 6–311 + G(d,p) for all atoms. The calculations were carried out with use of Gaussian 09 program.

3. RESULTS

For the measurement, two compounds with very different physical and chemical properties have been chosen, although they both belong to the intensively investigated for use in organic electronics groups of compounds. Compound **1** (carbazole



(i) 2-ethylhexylamine, DMF, reflux, 8h.

Fig. 2. Synthetic pathway for 2.