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Raman spectra, electrochemical redox potentials and intramolecular reorganization due to ionization and excitation of benzodifuranone chromophore

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Dedicated to Professor Miloš Nepraš on the occasion of his 80th birthday

ABSTRACT

Experimental Raman spectrum of 3,7-diphenyl substituted benzodifuranone (BDF) was assigned based on the density functional theory. The first electrochemical redox potentials in acetonitrile relate well with DFT adiabatic HOMO and LUMO energies, computed by polarized continuum model including solvent effect. DFT computed changes of bond lengths of central *para*-benzoquinodimethane (BQM) core upon ionization correspond to the most intense stretching modes. Simple algebraic relations between the bond lengths of BQM core in neutral, ionized and excited species were found.

1. Introduction

Although the first organic semiconductors were of *p*-type[1],-one can see a considerable progress in the area of *n*-type ones during the past years [2–4]. Among other properties the energy of LUMO falling into relatively sharp interval [4,5] is the crucial attribute making *n*-type semiconductors air-stable. The required values of LUMO are not common, but they were obtained e.g. for various tetracarboxydiimides with aromatic hydrocarbon core, like naphtalene (NDI) [3], anthracene (ADI) [6], perylene (PDI) [3] or even terrylene (TDI) [7], sometimes substituted by electron-accepting cyano groups.

para-Benzoquinodimethane (BQM) is a reactive molecule, that was never isolated. There was recently shown to be sufficiently stable in a dilute solution, so its NMR spectrum could be measured [8]. If terminal hydrogens of BQM are substituted either with strong electron acceptors (e.g. tetracyano, TCNQ [9]), resp. donors (e.g. tetrathia [10]), more or less stable compounds with extremely low LUMO, resp. high HOMO, energy levels are obtained. Their combinations can be interesting in the area of organic conductors [11]. *para*-Benzodithiophenes (BDT) with central BQM core were recently tested for the use in the area of *n*-channel organic semiconductors. While dicyanomethylene end-capped BDT (CNBDT) [12] showed poor characteristics in a thin film organic field-effect tranzistor (OFET), the symmetrical substitution of two cyano groups in CNBDT with two carboxy ester groups brought considerably higher *n*-mobilities [13] in vapor-processed OFETs.

Disperse dyes based on 3,7-diphenyl substituted *para*-benzodifuranone (BDF, Table 1) [14], among which C.I. Disperse Red 356 (with one propoxy substituent in *para* position of one of the pendant phenyl rings) was the first commercialized product [15], also contain BQM core. Moreover, isomeric *ortho*-benzodifuranones were also reported [14], but not commercialized. Bathochromic shifts of the absorption spectra for the dyes with central 2,6-naphtoquinodimethane core [16,17] or for derivatives with pendant phenyls substituted by electron-donating groups [17,18] were observed. The effect of the conjugation extension on the absorption spectra of BDFs using time dependent density functional theory (TD DFT) [19] was theoretically studied. Excitation energies of push–pull substituted BDFs were theoretically simulated by TD DFT, because of their potential interest in dye sensitized solar cells (DSSC) [20]. Benzodifuranone dyes were also found as the perspective compounds for nonlinear optical applications [21] and the extreme positive solvatochromism of amino derivatives made it interesting as a solvent polarity probe [22]. Fullerene–benzodifuranone dyad was studied in *p*–*n* heterojunction photovoltaic device [23]. Copolymerization of *para* and *ortho* BDFs with thiophene [24], EDOT and EDTT [25] formed low-bandgap polymers with unusually low LUMO energies.

Raman spectra, which are useful tools to obtain a fundamental information on the conjugated system of aromatic [26] or quinoid [27] conjugated compounds, were not studied for BDFs. Due to our interest on the relations between the structure and Raman spectra [28–30] we present here a combined experimental/theoretical study, based on an assignment of Raman spectrum using density functional theory (DFT) computations. Experimental energies of HOMO and LUMO, obtained by cyclic and rotating disc voltamme-

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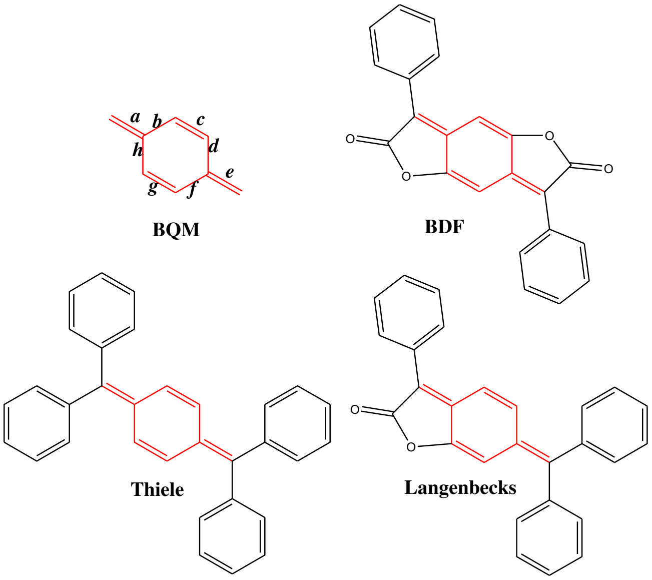
Table 1
DFT B3LYP/6-311G(d,p) computed bond lengths (Å) of central BQM core of the compounds under study together with experimental X-ray data, where available.



Compound	Theor/Exp.	Bond lengths (Å)							
		a	b	c	d	e	f	g	h
D_{2h} – BQM	B3LYP	1.353	1.460	1.347					
C_i – Thiele	B3LYP	1.385	1.453	1.354					
	X-ray [35]	1.382	1.450	1.347					
C_1 – Langenbecks	B3LYP	1.378	1.434	1.359	1.456	1.389	1.451	1.350	1.442
	X-ray [34]	1.387	1.422	1.352	1.448	1.384	1.448	1.347	1.427
C_i – −BDF	B3LYP	1.374	1.437	1.352	1.455				

try, were also interpreted using DFT adiabatic energies including the effect of solvent with continuum polarized model (PCM). As the theoretical approach produced quite realistic interpretation of the experimental data, structural changes accompanying the electron-transfer were also studied.

2. Experimental and theoretical methodology

Compound BDF was the same as in Ref. [19].

2.1. Instrumental equipment

The room temperature Raman spectrum of polycrystalline sample was measured by FT-IR spectrophotometer IFS 55 provided with Raman FRA-106 accessory (Bruker) for back scattering method. The YAG: Nd^{3+} laser line (1064 nm) was used for excitation.

Electrochemical measurements were carried out in acetonitrile containing 0.1 M Bu_4NPF_6 in a three electrode cell by cyclic voltammetry (CV) and rotating disc voltammetry (RDV). The working electrode was platinum disc (2 mm in diameter) for CV and RDV experiments. As the reference and auxiliary electrodes were used saturated calomel electrode (SCE) separated by a bridge filled with supporting electrolyte and Pt wire, respectively. Voltammetric measurements were performed using a potentiostat PGSTAT 128N (AUTOLAB, Metrohm Autolab B.V., Utrecht, The Netherlands) operated via Nova software.

2.2. Computational procedures

All calculations were carried out using DFT. No constraints were preliminary employed, but, if the non-constrainted computations converged to symmetrical structures, the final computations were carried out with these symmetry constraints. All methods were taken from Gaussian09w program suite [31] and the default values of computational parameters were used. The results were analyzed using GaussViewW from Gaussian Inc, too.

The ground state geometry of neutral compounds in vacuum was optimized using hybrid three-parameter B3LYP functional in combination with 6-311++G(d,p) basis set. Harmonic fundamental frequencies and Raman intensities in static approximation were computed on these optimized geometries at the same level of theory. Calculation of vibrational spectra of two smaller model compounds including an anharmonic correction were computed on the same level of theory.

For the calculations of adiabatic energies the geometrical optimization in vacuum of the closed-shell (neutral molecule, dianion and dication in singlet ground state), resp. open-shell (radical anion and cation in dublet states, neutral molecule in triplet state), species was carried out on restricted, respectively unrestricted, level with the same functional but only with 6-311G(d,p) basis set. No imaginary frequencies were found for any of these species, computed at C_i symmetry, by vibrational analysis. Closed-shell TD DFT calculations of S_1 state geometry were carried out with 6-311G(d,p) basis set. Diffuse function (6-311++G(d,p)) were introduced for following estimation of single-point energies either in vacuum or including solvent effect of acetonitrile introduced by PCM (with dielectric constant $\varepsilon = 35.688$) for an interpretation of electrochemical redox potentials.

3. Results and discussion

An ability of DFT to calculate the optimized geometries close to the experimental ones is crucial for a successful assignment of Raman peaks. We carried out the optimizations of BDF together with