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# Styryl dye possessing donor- $\pi$ -acceptor structure – Synthesis, spectroscopic and computational studies

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# 1. Introduction

Two-photon absorption (TPA) is a nonlinear absorption process wherein two photons are absorbed simultaneously. Characteristic features are adherence to even-parity selection rules and quadratic intensity dependence, while one-photon absorption processes typically conform to odd-parity selection rules and linear intensity dependence. An important consequence of two-photon absorption is the possibility of the presence of upconverted fluorescence emission [1,2].

Although the two-photon absorption process was predicted theoretically by Göppert-Mayer as early as in 1931 [3] and experimentally observed [4] in the 1960s, organic molecules exhibiting significant nonlinear optical effects are still an intensely investigated subject of various scientific studies.

Research into novel frequency upconversion materials has been of considerable interest due to their potential use in emerging applications. These new technologies include three-dimensional optical data storage [5], photodynamic therapy [6], two-photon

# ABSTRACT

A novel hemicyanine dye possessing donor- $\pi$ -acceptor structure that features a fixed benzimidazole ring as an electron donor and pyridinium moiety as an electron acceptor was synthesized. The structure of the hemicyanine was elucidated by means of NMR and IR spectroscopy. The dye was studied using steadystate absorption and emission spectroscopy. The analysis of experimentally recorded spectra was supported by quantum chemical calculations using density functional theory with CAM-B3LYP, LC-BLYP, LC- $\omega$ PBE and PBE0 functionals. The measurements and calculations were performed in solvents of different polarity. In particular, we found that the CAM-B3LYP and LC- $\omega$ PBE excitation energies are in very good agreement with the experimental data. Two-photon absorption of the dye was studied by Z-scan measurements.

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optical power limiting [7], and two-photon three-dimensional microfabrication [8–10]. All of the applications are primarily based on accessing higher-energy excited states using relatively low-energy laser sources.

To realize these applications, intense worldwide effort has been focused on the design of organic materials with a large TPA crosssection ( $\delta$ ) at desirable wavelengths. Up to now, several efficient design strategies have been put forward to enhance  $\delta_{\text{TPA}}$  [11]. One of the most successful types of two-photon organic dyes is constituted by the push-pull architecture, based on a dipolar D- $\pi$ -A structure: the donor group (D) is an electron-rich unit, linked through a  $\pi$  bridge spacer to the electron-acceptor group (A). The vast majority of push-pull chromophores are neutral organic molecules, with fluorene, biphenyl, or naphthyl groups used as the electron bridge [12]. At the same time, organic salts with an NLOactive cation have also received considerable attention. They usually contain the N-methylpyridinium cationic moiety as an acceptor and are known as "stilbazolium" derivatives. This group of NLO chromophores brings several interesting features: (1) cationic quaternary nitrogen is a very strong acceptor; (2) variation of counter ions is an easy way to tune the crystalline packing, (3) they are promising as amphiphilic materials for NLO-active Langmuir-Blodgett (LB) films [13-15].







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An extremely powerful and comparably low cost tool in the design of new organic molecules with large two-photon absorption cross-sections are ab initio or quantum mechanical calculations which are able to accurately foresee the electronic and spectroscopic properties of the chromophores. The computational methodologies based on density functional theory (DFT) and time-dependent density functional theory (TD-DFT) provide accurate results and accurately reproduce the optical properties of compounds allowing us to predict and screen, in some cases, novel synthetic approaches [16].

In this paper we describe the synthesis and spectral properties of a novel compound belonging to the class of styryl dyes. Our intention was to support experimental data with an analysis of the nature of the photoexcitation, with a view towards assessment of the reliability of predictions of electronic spectra for this compound calculated using the frequently applied conventional global hybrid PBE0 functional, as well as the **hybrid exchange–correlation** CAM-B3LYP and long-range corrected LC- $\omega$ PBE and LC-BLYP functionals. In addition to the linear optical properties, nonlinear optical properties are also considered.

# 2. Experimental

# 2.1. Measurements

All reagents and solvents (spectroscopic grade) were purchased from Aldrich Chemical Co. and used without further purification. For thin layer chromatography, aluminium oxide IB-F flexible sheets (thickness 0.2 mm) were purchased from J.T. Baker Chemical Co., Germany.

The <sup>1</sup>H (200 MHz or 400 MHz) and <sup>13</sup>C (50 MHz or 100 MHz) NMR spectra were recorded with the use of a Varian Gemini 200 or Bruker Ascend<sup>TM</sup> 400 NMR spectrometers, respectively. Dimethylsulfoxide (DMSO-d<sub>6</sub>) was used as the solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm ( $\delta$ ). Coupling constants, *J*, are reported in Hz.

The IR spectra of the synthesized salts were recorded using a Bruker Vector 22 FT-IR spectrophotometer (Germany) in the range  $400-4500 \text{ cm}^{-1}$ , by KBr pellet technique.

HPLC analyses were done by Shimadzu HPLC systems equipped with UV–Vis detector (detection wavelength was 370 nm) and a Supelcosil LC-NH<sub>2</sub> column (250 mm  $\times$  4.6 mm  $\times$  5 µm) Supelco. Separation was conducted under isocratic conditions with 0.8 ml/min flow rate, 30 °C, 20 µl injection volume and HPLC grade methanol as a mobile phase.

Melting points (uncorrected) were determined on the Boëthius apparatus (type PHMK 05, Germany).

Absorption and emission spectra were recorded at room temperature using a Shimadzu UV-vis Multispec-1501 spectrophotometer (Japan) and a Hitachi F-4500 spectrofluorimeter (Japan). respectively. The spectra were recorded in the following solvents: tetrahydrofuran (THF), acetone; 1-methyl-2-pyrrolidone (MP), N,Ndimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol (MeOH), acetonitrile (MeCN), formamide (FA) and water (H<sub>2</sub>O). The final concentration of the dye in the solution was  $1.0\times10^{-5}$  M. The spectroscopic measurements were also performed in the studied solvents containing either 10% or 20% of methanol. In that case the samples were prepared as follows: the appropriate amount of the chromophore was dissolved in methanol, then 0.1 mL (or 0.2 mL) of the concentrated (ca. 1 mM) stock solution was added to a 10 mL volumetric flask containing spectroscopic grade solvents under the study. All solvents were the spectroscopic grade and were used without any additional purification. They were characterized by their static dielectric constant ( $\varepsilon$ ) and refractive index (n) at 20 °C. The solvent polarity function,  $f(\varepsilon, n)$ , is given by Eq. (1) [17,18].

$$f(\varepsilon, n) = \frac{(2n^2 + 1)}{(n^2 + 2)} \cdot \left[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} - \frac{(n^2 - 1)}{(n^2 + 2)} \right]$$
(1)

The fluorescence quantum yields for the dyes in solvents of different polarity were determined as follows. The fluorescence spectrum of a dilute dye solution ( $A \approx 0.1$  at 404 nm) was recorded by excitation at the absorption band maximum of the standard. Dilute Coumarin 1 in ethanol ( $\Phi = 0.64$  [19]) was used as reference. The fluorescence spectrum of Coumarin 1 was obtained by excitation at its absorption maximum at 404 nm. The quantum yield of the tested dye ( $\Phi_{dye}$ ) was calculated using equation:

$$\Phi_{\rm dye} = \Phi_{\rm ref} \frac{I_{\rm dye} A_{\rm ref}}{I_{\rm ref} A_{\rm dye}} \cdot \frac{n_{\rm dye}^2}{n_{\rm ref}^2}$$
(2)

where: $\Phi_{ref}$  is the fluorescence quantum yield of the reference (Coumarin 1) sample in ethanol,  $A_{dye}$  and  $A_{ref}$  are the absorbances of the dye and reference samples at the excitation wavelength (404 nm),  $I_{dye}$  and  $I_{ref}$  are the integrated emission intensity for the dyes and reference samples,  $n_{dye}$  and  $n_{ref}$  are the refractive indexes of the solvents used for the dyes and the reference, respectively.

The fluorescence lifetimes were measured using an Edinburgh Instruments, single-photon counting system (FLS920P Spectrometers). The apparatus utilizes for the excitation a picosecond diode laser generating pulses of about 55 ps at 375 nm. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals with a resolution of few picoseconds possible. The dyes were studied at concentration able to provide equivalent absorbance at 375 nm (0.2–0.3 in the 10 mm cell) to be obtained. The fluorescence decays were fitted to two exponentials. The average lifetime,  $\tau_{av}$  is calculated as  $\tau_{av} = (\Sigma_i \alpha_i \tau_i)/(\Sigma_i \alpha_i)$ , where  $\alpha_i$  and  $\tau_i$  are the amplitudes and lifetimes.

The two-photon absorption spectrum was determined using the open-aperture Z-scan technique using a setup and procedures described elsewhere [20–22]. Briefly, a tunable amplified femto-second laser system consisting of a Quantronix Integra regenerative amplifier (800 nm, 1.2 mJ/pulse, 130 fs pulse length) and a Quantronix Palitra optical parametric amplifier was used and the spectral range of the measurements was 600–1600 nm. The Z-scan data obtained on a solution of the dye were calibrated against measurements on a 4.66 mm thick silica plate [20,21].

According to Coe et al., a two-state analysis of ICT transitions gives [23]:

$$\Delta\mu_{ab}^2 = \Delta\mu_{12}^2 + 4\mu_{12}^2 \tag{3}$$

where  $\Delta \mu_{ab}$  is the dipole-moment change between the diabatic states and  $\Delta \mu_{12}$  is the observed (adiabatic) dipole-moment change. The value of  $\mu_{12}$  can be determined from the oscillator strength  $f_{os}$  of the transition by:

$$|\mu_{12}| = \left(\frac{f_{\rm os}}{1.08 \times 10^{-5} E_{\rm max}}\right)^{1/2} \tag{4}$$

where  $E_{\text{max}}$  is the energy of the ICT maximum (in wavenumbers) and  $\mu_{12}$  is in e Å. The latter is converted into Debye units upon multiplying by 4.803. The degree of delocalization  $c_b^2$  and electronic coupling matrix element  $H_{\text{ab}}$  for the diabatic states are given by

$$c_b^2 = \frac{1}{2} \left[ 1 - \left( \frac{\Delta \mu_{12}^2}{\Delta \mu_{12}^2 + 4\mu_{12}^2} \right)^{1/2} \right]$$
(5)

$$|H_{ab}| = \left|\frac{E_{max}(\mu_{12})}{\Delta\mu_{ab}}\right|$$
(6)

If the hyperpolarizability tensor  $\beta_0$  has only nonzero elements along the ICT direction, then this quantity is given by

$$\beta_0 = \frac{3(\Delta\mu_{12})\mu_{12}^2}{(E_{\text{max}})^2} \tag{7}$$

#### 2.2. Computational details

The geometry optimization of all molecules in their ground state was carried out both *in vacuo* and with the inclusion of solvent effects by means of the polarizable continuum model (PCM) [24] as implemented in the Gaussian 09 package [25]. The geometry of the solute was optimized using the hybrid exchange-correlation B3LYP [26] functional with the 6-311++G(d,p) basis set, whereas in the case of a complex containing the solute molecule with two methanol molecules, the optimization was performed using the B97D [27] functional which includes the correction for dispersion interaction as suggested by Grimme. The latter calculations employed 6-31 + g(d) basis set. In all cases, the Hessian was computed in order to confirm that the stationary points correspond to minima on the potential energy surface.

Spectroscopic parameters characterizing one-photon excitation spectra, i.e. oscillator strengths and excited state dipole moments were determined using time-dependent density functional theory (TD-DFT) using the Gaussian 09 suite of programs. The standard hybrid PBE0 [28], long-range corrected LC-BLYP [29], LC- $\omega$ PBE [29–31] and CAM-B3LYP [32] functionals, and the 6-311++G(d,p) basis set were employed for these calculations, carried out both *in vacuo* and with the inclusion of the solvents effect using the PCM model.

In the case of molecule absorbing two photons of the same energy in isotropic media, the degenerate two-photon transition probability in an isotropic medium using a linearly polarized laser beam is given by Ref. [33]:

$$\left\langle \delta^{\rm OF} \right\rangle = \frac{1}{15} \sum_{ij} \left[ S_{ii}^{\rm OF} \left( S_{jj}^{\rm OF} \right)^* + 2 S_{ij}^{\rm OF} \left( S_{ij}^{\rm OF} \right)^* \right] \tag{8}$$

In this equation,  $S_{ij}^{OF}$  is the second-order transition moment given by:

$$S_{ij}^{\text{OF}}(\zeta_{1},\zeta_{2}) = \frac{1}{\hbar} \sum_{K} \left[ \frac{\left\langle \mathbf{0} \middle| \zeta_{1} \cdot \widehat{\mu}_{i} \middle| K \right\rangle \left\langle K \middle| \zeta_{2} \cdot \widehat{\mu}_{j} \middle| F \right\rangle}{\omega_{\alpha} - \omega_{1}} + \frac{\left\langle \mathbf{0} \middle| \zeta_{2} \cdot \widehat{\mu}_{i} \middle| K \right\rangle \left\langle K \middle| \zeta_{1} \cdot \widehat{\mu}_{j} \middle| F \right\rangle}{\omega_{\alpha} - \omega_{2}} \right]$$
(9)

where  $\hbar\omega_1 + \hbar\omega_2$  should satisfy the resonance condition and  $\langle 0|.\zeta_1 \cdot \hat{\mu}_i|.K \rangle$  stands for the transition moment between electronic states  $|0\rangle$  and  $|K\rangle$ , respectively.  $\zeta$  is the vector defining polarization of photons.

In order to compare the calculated values of the two-photon absorption probability with the two-photon absorption cross-section which was determined experimentally $\sigma_{OF}^{(2)}$ , the following relation might be used [34]:

$$\sigma_{\rm OF}^{(2)} = \frac{8\pi^3 \alpha^2 \hbar^3}{e^4} \cdot \frac{\omega^2 g(\omega)}{\Gamma_F/2} \left\langle \delta^{\rm OF} \right\rangle \tag{10}$$

where  $\alpha$  is a fine structure constant,  $\omega$  is the frequency of absorbed photons (assuming one source of photons),  $\Gamma_F$  is the broadening of

the final state (*F*) due to its finite lifetime and  $g(\omega)$  provides the spectral line profile, which often is assumed to be a  $\delta$ -function.

In this study we present calculations of two-photon absorption probability (computed as single residue of quadratic response functions) which were done using the DALTON 2011 program [35,36]. Solvent effects were taken into account with the selfconsistent reaction field (SCRF) model.

# 2.3. Synthetic procedure

2.3.1. Synthesis of trans-2-[2-(4-formylphenyl)ethenyl] benzimidazole (**BT**)



The compound was obtained based on the synthesis described in literature [37,38]. A mixture of terephthalaldehyde (2.68 g, 0.02 mol) and 2-methylbenzimidazole (2.66 g 0.02 mol) was stirred at 120 °C for 6 h in a mixture of acetic acid (3 mL) and acetic anhydride (6 mL) solvents. The reaction mixture was cooled down to room temperature. After adding concentrated hydrochloric acid (30 mL), the mixture was left for an hour. The resulting precipitate was collected and subsequently washed repeatedly with copious water. The filtrate was neutralized with 30% NaOH (60 mL) and gave yellowish precipitate that was filtered and dried. The crystals were dissolved in hot ethyl acetate, and the insoluble materials were removed by filtration to yield trans, trans-1, 4-bis[4-(2-benzimidazolyl) ethenyl]benzene (BTI) (see supporting information). The filtrate was evaporated to dryness. The crude product was recrystallized from CHCl<sub>3</sub>/acetone to yield 2.7 g (54%) of the trans-2-[2-(4-formylphenyl)ethenyl]benzimidazole; C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O; 248.28 g/mol.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ (ppm): 7.1990 (m, 2H, Ar), 7.3912-7.4324 (d, J = 16.48 Hz, 1H, -CH=), 7.4974–7.5162 (d, J = 7.52 Hz, 1H, Ar), 7.6103–7.6291 (d, J = 7.52 Hz, 1H, Ar), 7.7129–7.7542 (d, J = 16.52 Hz, 1H, -CH=), 7.8797–7.9001 (d, J = 8.16 Hz, 2H, Ar), 7.9460–7.9666 (d, J = 8.24 Hz, 2H, Ar), 10.0211 (s, 1H, CHO), 12.7248 (s, 1H, NH).

2.3.1.1. <sup>13</sup>C NMR (DMSO- $d_6$ )  $\delta$  (ppm): 192.387 (CHO), 113.104, 113.804, 125.893, 128.487, 130.116, 140.775 (CH), 131.627, 136.989, 139.337, 141.6205 (C). IR (KBr): 3052, 2890, 2837, 1693, 1600, 1568, 1505, 1419, 1388, 1310, 1279, 1212, 1169, 1144, 1032, 1001, 969, 919, 810, 735, 506, 441.

2.3.2. Synthesis of trans,trans-2-{4-[(2-(1H-benzimidazol-2-yl) ethenyl]-styryl}-N-methylpyridine iodide (**BTP1**)



1,2-Dimethylpyridinium iodide (0.59 g, 2.5 mmol), 2-[2-(4formylphenyl)ethenyl]benzimidazole (0.62 g, 2.5 mmol), and methanol (20 mL) were placed in a 100 mL one-necked flask with a stirrer and a condenser. Then three drops of piperidine were added as a catalyst and the resultant mixture was heated under reflux for 12 h. Upon cooling in a refrigerator, orange microcrystals of the iodide salt were collected by filtration under reduced pressure [39,40]; C<sub>23</sub>H<sub>20</sub>N<sub>3</sub>I; 465.33 g/mol; 0.71 g, 65.2% yield, mp 267– 270 °C. The purity of the dye was checked by TLC (methanol-DMF 5:0.5 v/v, aluminum oxide IB-F,  $R_f = 0.25$ ). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ (ppm): 4.4065 (s, 3H, N<sup>+</sup>CH<sub>3</sub>), 7.1781 (m, 2H, Ar), 7.3633–7.4045 (d, J = 16.48 Hz, 1H, -CH=), 7.5003–7.5186 (d, J = 7.32 Hz, 1H, Ar), 7.6056–7.6245 (d, J = 7.56 Hz, 1H, Ar), 7.6621–7.7021 (d, J = 16.00 Hz, 1H, -CH=), 7.7295–7.7707 (d, J = 16.48 Hz, 1H, -CH=), 7.8122–7.8332 (d, J = 8.4 Hz, 2H, Ar), 7.9070 (1H, Ar), 7.9374–7.9582 (d, J = 8.32 Hz, 2H, Ar), 7.9779 (d, J = 16.0 Hz, 1H, -CH=), 8.5207 (1H, Ar), 8.5524–8.5693 (d, J = 6.76 Hz, 1H, Ar), 8.9347–8.9501 (d, J = 6.16 Hz, 1H, Ar), 12.8129 (s, 1H, NH).

2.3.2.1. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>)  $\delta$  (ppm): 46.055 (N<sup>+</sup>CH<sub>3</sub>), 111.157, 117.745, 118.718, 119.343, 121.657, 122.724, 124.942, 125.158, 127.581, 129.220, 133.325, 142.233, 144.268, 146.154 (CH), 134.581, 135.139, 138.140, 143.998, 150.723, 152.306 (C). IR (KBr): 3081, 1633, 1616, 1569, 1522, 1459, 1415, 1326, 1278, 1214, 1175, 1145, 1007, 962, 817, 771, 744, 538.

# 3. Results and discussion

# 3.1. Synthesis

Synthesis of benzimidazolium chromophore BTP1 is depicted in Fig. 1.

Starting 2-methyl-[1H]-benzimidazole and terephthaldialdehyde are available commercially, while 1,2-dimetylpyridinium iodide was prepared from 2-methypyridine according to the typical procedure [40]. Styrylbenzimidazole with formyl group, the key compound in the preparation of the BTP1 chromophore, was obtained by the reaction of terephthaldialdehyde with 2-methyl-[1H]-benzimidazole. The condensation was carried out in acetic anhydride – acetic acid mixture to yield *trans*-2-[2-(4-formylphenyl)ethenyl]benzimidazole as a major product, accompanied by the formation of byproduct, *trans*,*trans*-1,4-bis[4-(2-benzimidazolyl)ethenyl]benzene.

BTP1 chromophore was prepared via Knoevenagel condensation of *trans*-2-[2-(4-formylphenyl)ethenyl]benzimidazole with 1,2-dimethylpyridinium iodide in methanol in the presence of a few drops of piperidine used as catalyst according to the procedures described in literature [39–41].

Structures and purity of BTP1 was confirmed by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra, and by thin layer and HPLC chromatography. The data were found to be in good agreement with the proposed structure. According to the <sup>1</sup>H NMR data, BTP1 crystallizes as a solvent free molecule. As expected, CH = CH bonds in the chromophore have a *trans* configuration, as evidenced by the value of coupling constants for olefinic protons (see experimental part and supplementary materials).

The IR spectra indicate some characteristic bands for the synthesized compounds. Thus, the aromatic stretching vibrations for C=N and C=C bonds were observed in the frequency range of 1600–1430 cm<sup>-1</sup>, as a strong or medium band and for C–H in the 3090–3000 cm<sup>-1</sup> region as a weak band. The peaks corresponding to aromatic bending vibrations out-of-plane for C–H appeared at about 540 cm<sup>-1</sup>, 740 cm<sup>-1</sup> and 820 cm<sup>-1</sup> and were of medium or strong intensity. Absorption for the ethylenic group was located within the same range. Stretching vibrations of the aromatic C–C bond gave a strong band between 1597 cm<sup>-1</sup> and 1616 cm<sup>-1</sup>. The aromatic bonds were also to be found between 1500 and 1540 cm<sup>-1</sup> and around 1450 cm<sup>-1</sup>.

The methyl group gives low intensity absorptions around 1380 cm<sup>-1</sup> and 1480 cm<sup>-1</sup>. They were identified as the deformation vibrations  $\delta$ CH<sub>3</sub> sym. and  $\delta$ CH<sub>3</sub> asym., respectively. The amine stretching vibration for C–N bonds were observed in the 1250–1020 cm<sup>-1</sup> range, as strong or medium bands.

The characteristic stretching vibration of O=C in the BT was located at 1695 cm<sup>-1</sup> whereas the O=C-H stretching vibration gave absorption band at 2743 cm<sup>-1</sup>.

The NMR and IR spectra as well as HPLC chromatograms of the compounds are presented in Supplementary materials.

The chromophore was poorly soluble in many organic solvents of low or medium polarity such as dichloromethane, chloroform, THF, ethyl acetate, *n*-hexane, benzene and toluene at room temperature.

# 3.2. Spectral properties

Fig. 2 displays a few typical sets of steady-state absorption and fluorescence spectra of BTP1 in formamide. DMF and AcCN at room temperature. The absorption spectra are structureless and broad, having half-widths of about 4000 cm<sup>-1</sup>. The large bandwidth and the large extinction coefficient values (about  $5.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) for the absorption probably indicate involvement of charge transfer, most likely involving partial donation of the nitrogen lone pair of electrons in the benzimidazole residue to the charged pyridinium moiety through the conjugated  $\pi$ -system. The absorption band around 300 nm is due to localized  $\pi \rightarrow \pi^*$  transition of the stilbene moiety. The broadness of the absorption spectrum may arise due to a contribution from more than one electronic state to the absorption spectrum. The other reason is that it probably reflects a broad distribution of conformers (solvent-solute or intramolecular) in the ground state [42]. The photophysical characteristics of BTP1 are listed in Tables 1 and 2.

As expected for this highly polar chromophore, its solubility is limited to the more polar solvents. For that reason, only medium and high polarity solvents have been used in this study. The steadystate absorption spectra of BTP1 in the fairly limited range of solvent polarity show small variations as a function of polarity



Fig. 1. Synthesis of the chromophore.



Fig. 2. Normalized electronic absorption and one-photon fluorescence spectra BTP1 in formamide, DMF and AcCN at 293 K.

(Table 1). Generally, with increasing solvent polarity the maxima of the absorption spectra shift to the blue.

Solvatochromism is generally explained through differential solvation of the ground state and Franck-Condon excited state. Negative solvatochromism will result from better stabilization by polar solvents of the ground state in comparison to the excited state. The molecular orbitals involved in intramolecular charge transfer (ICT) in BTP1 are depicted in Fig. 3. The HOMO, as expected, is dominated by benzimidazolium group, and the LUMO by the quaternary pyridinium moiety. On excitation, electron density is transferred from the donor end of the molecule to the positively charged quaternary heterocyclic moiety, providing charge compensation, and thus indeed resulting in an excited state that is less polar than the ground state, and hence less stabilized by polar solvents. Therefore, negative solvatochromism should be expected [12,42– 44]. On the other hand, the methyl substituent (electron-donating) is also attached to the pyridine fragment which may cause the opposite effect. However, the tested compound in its ground state is a cation derived from an iodide salt, and the iodide anion is associated with the pyridine ring. Consequently, positive charge formed

Spectral characteristic of BTP1	compound in solvents of different polarity ( $\lambda_{ex} = 404 \text{ nm}$	1).

Table 1

	THF	Acetone	MP	DMF	DMSO	MeOH	MeCN	FA	Water
<i>f</i> (ε,n)	0.5491	0.7904	0.8125	0.8356	0.8400	0.8546	0.8593	0.8948	0.9137
$\lambda_{\max}^{ab}(nm)$	402.5	399.5	403.5	402.5	402.5	394.5	395.0	396.5	387.5
$\epsilon (10^4 \text{ M}^1 \text{ cm}^{-1})$			4.72	5.09	5.35	5.68	4.54	4.32	5.78
FWHM <sup>ab</sup> (cm <sup>-1</sup> )	5001	4194	4275	4033	3952	3710	3952	4113	3871
$\lambda_{\rm max}^{\rm fl}(\rm nm)$	618.4	619.4	619.8	623.4	625.2	610.6	621.4	617.2	603.4
$FWHM^{fl}$ (cm <sup>-1</sup> )	2904	3388	3388	3468	3468	3629	3468	3468	3871
$\Delta v (cm^{-1})$	8674	8887	8649	8804	8850	8971	9224	9018	9234
$\Phi_{ m fl}$	0.164	0.294	0.199	0.124	0.119	0.135	0.186	0.080	0.019
$\tau_1^{fl}(ns)$	0.339	0.433	0.484	0.536	0.400	0.492	0.382	0.617	0.178
$\alpha_1$ (%)	4.11	3.65	3.62	3.41	2.16	10.72	2.21	48.1	98.23
$\tau_2^{fl}(ns)$	1.797	1.542	1.408	1.197	1.361	0.936	1.686	0.878	0.802
$\alpha_2$ (%)	95.89	96.35	96.38	96.59	97.84	89.28	97.79	51.90	1.77
$\tau_{av}^{fl}(ns)$	1.74	1.50	1.37	1.17	1.34	0.89	1.66	0.75	0.19
$k_r (10^8 \text{ s}^{-1})$	0.94	1.96	1.45	1.05	0.89	1.52	1.12	1.06	1.01
$k_{\rm nr} (10^8  {\rm s}^{-1})$	4.81	4.70	5.83	7.46	6.57	9.74	4.91	12.2	51.9
$f_{os}$			1.15	1.15	1.19	1.24	1.01	1.00	1.22
μ <sub>12</sub> (D)			9.88	9.87	10.08	10.14	9.16	9.16	9.98
$\beta_0 (10^{-30} \text{ esu})$			-235	-233	-240	-234	-194	-195	-221
$c_h^2$			0.15	0.15	0.15	0.15	0.14	0.13	0.15
$ \bar{H}_{ab} (10^3 \text{ cm}^{-1})$			8.8	8.9	9.0	9.2	8.7	8.6	9.2

 $\lambda_{ex} = 404$  nm; FWHM – full with at half maximum;  $\Delta \mu_{12}$  dipole moment change between excited and ground states was taken from quantum chemical calculation for gas faze and is equal to -19.44 D.

#### Table 2

The electronic absorption and one photon emission spectra parameters for BTP1 compound in solvents of different polarity. Each sample contained either 10 or 20% of methanol ( $\lambda_{ex} = 404$  nm).

Solvent	$\begin{array}{l} \lambda^{ab}_{max}(nm);\\ \epsilon~(10^4~{\rm M}^{-1} \end{array}$	cm <sup>-1</sup> )	$\lambda_{max}^{fl}(nm)$		$\Delta v (cm^{-1})$	
	10% MeOH	20% MeOH	10% MeOH	20% MeOH	10% MeOH	20% MeOH
THF	403.5;	404;	614.6	608.6	8512	8321
	4.52	4.54				
Acetone	397.5;	398;	621.2	621.4	9059	9033
	4.85	4.80				
DMF	400;	402;	622.6	624.0	8938	8850
	5.13	5.35				
DMSO	403;	402;	623.2	624.8	8768	8871
	4.72	4.91				
MeCN	393.5;	394;	625.2	624.4	9418	9365
	4.82	4.91				
Water	386.5;		602.4		9273	
	4.78					

in this part produces the electron distribution from the benzimidazole fragment, producing the form of  $D-\pi$ -A.

The experimentally observed negative solvatochromism of BTP1 constitutes convincing evidence for a ground state that is more polar than the charge-transfer excited state, and hence lower dipole moment value of the latter state as compared to the former is evident. These results are in perfect agreement with previous observations on many other chromophores [12,42–44].

The fluorescence spectra of BTP1 were recorded in the same solvents as the steady-state absorption spectra. Generally, a broad and structureless band was observed whose position depends on the excitation wavelength and the solvent (see Figs. 1 and 4). The solvent dependent shape of the emission spectra indicates the possibility of the presence of more than one conformer, with either or both in the ground and excited electronic states [42].

As shown in Fig. 2, the relationship between the absorption and the emission spectra displays, to some extent, a mirror image suggesting a weak geometrical relaxation of Franck-Condon singlet excited state. It should be underlined, however, that the maximum of the emission spectrum recorded in each of the solvents at room temperature shows a large red shift, more than ca. 8000 cm<sup>-1</sup> with respect to the absorption maximum. The observed large Stokes'



**Fig. 3.** The plots of orbital contour surfaces for model A. The molecular orbitals were calculated at the CAM-B3LYP/6-311++G(d,p) level of theory. The lower plot presents contour surface of HOMO and the upper presents contour surface of LUMO. Shown are the contour surfaces of orbital amplitude 0.02 (red) and -0.02 (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shift indicates that significant charge redistribution occurs upon excitation, prior to emission, and suggests a quite substantial dipole moment change caused by the excitation [42].

The compound has a moderate fluorescence quantum yield ( $\phi$ , Table 1), which also depends on the solvent polarity. It was found that the fluorescence intensity of the chromophore gradually decreases with increasing solvent polarity from THF to DMF. These results indicate that the chromophore shows typical asymmetric chromophore behaviour [45].

In order to clarify the role of solvent polarity in modifying both the ground and excited states of molecule, we tested the fluorescence excitation and emission characteristics of BTP1 in selective solvents. As illustrated in Fig. 4, right panel, for molecule under study dissolved in polar and highly polar solvents, only a single fluorescence band is observed and the location of the fluorescence peak remains invariant on  $\lambda_{exc}$ . Fluorescence measurements carried out in medium polar solvents (THF) yield two partially overlapping emission bands.

Fig. 4 shows the excitation wavelength dependence of fluorescence spectra (fluorescence maxima positions and shape of the spectra) of BTP1 in THF at room temperature. Upon increasing the excitation wavelength, the intensity of the short-wavelength band at about 444 nm decreases. This behaviour is accompanied by an increase of the long-wavelength emission band intensity at 618 nm.



Fig. 4. Electronic absorption, excitation (left panel) and fluorescence (right panel) spectra of BTP1 in selected solvents.

The observation of the dual fluorescence indicates the existence of two emitting species characterized by the molecules possessing different spatial conformations.

As can be seen (Fig. 4), the steady-state fluorescence excitation spectrum of the title compound is not only solvent dependent but also depends on the observation wavelength. The fluorescence excitation spectra were recorded for two emission wavelengths (detection at the maximum of the short-wavelength and long-wavelength bands of the emission spectrum). As can be seen in Fig. 4, fluorescence excitation and absorption spectra are superimposable when recorded for long-wavelength emission band [46].

The differences between absorption and excitation spectra of BTP1 show the existence of the excited molecules that differ in spatial conformations and/or differ in solvent relaxation [46].

The steady-state fluorescence maximum slightly shifts to the red, due to an increase in solvent polarity, which is evident from Table 1. However, no reasonable correlation has been found between either the absorption or fluorescence peak maxima and the solvent polarity parameter,  $f(\varepsilon,n)$ . The same is true for the dependence of the Stokes' shift parameter on  $f(\varepsilon,n)$ . The possible reason behind the lack of correlation between the fluorescence maxima or the Stokes' shift and the solvent polarity parameter (Table 1), is the emission from more than one conformer formed following optical excitation. Since the solvent effect on the fluorescence maxima of the undecomposed spectra is not a simple reflection of the solvent dependence of a particular excited state conformation, the spectral shape as well as the solvent shift can also depend on the relative quantum yields of the conformers [47].

To further understand the excited state dynamics, fluorescence decay lifetimes of the BTP1 were measured in the studied solvents. These measurements were performed on an Edinburgh FLS920 spectrofluorimeter with a picosecond diode laser as the excitation source. The fluorescence lifetimes ( $\tau_f$ ) have been determined by single photon counting technique. The fluorescence decay function is seen to be double exponential when monitoring the fluorescence decay at 615 nm (Fig. 5). For all the decays in this experiment,  $\chi^2$  is bigger than 1.0 and less than 1.3, which indicates a good fit. The lifetime of the longer component may be considered as the lifetime of the S<sub>1</sub> state of the most stable conformer of BTP1 molecule.

Fig. 5 shows the fluorescence decays of BTP1 in various solvents. From this figure and data collected in Table 1, it is clear that the fluorescence lifetimes decrease with increasing solvent polarity (from THF to water).

We noted that the fluorescence average lifetimes do not correlate well with the fluorescence quantum yields for this chromophore in different solvents. However, the results from the quantum yield measurement and lifetime calculation of the compound can clearly demonstrate the sensitivity of its fluorescence behaviour to the solvents. The fluorescence quantum yield and lifetime for BTP1 decreases with increase of solvent polarity due to the strong interaction between the strongly polarized molecule and solvents in the excited state. Moreover, the much lower fluorescence quantum yield in a proton solvent, water, can be attributed to the hydrogen bond interaction between the molecule and surrounding solvent, which results in an additional non-radiative decay as observed in other molecules [48,49].

Based on the average lifetimes and quantum yields of fluorescence data, radiative  $(k_r)$  and nonradiative  $(k_{nr})$  rate constants have been calculated according to Eqs. (11) and (12). The values are collected in Table 1.

$$k_{\rm r} = \frac{\Phi_{\rm fl}}{\tau_{\rm av}} \tag{11}$$



Fig. 5. Fluorescence decay curves of BTP1 in solvents of different polarity ( $\lambda_{ex}=375$  nm,  $\lambda_{em}=615$  nm).

$$k_{nr} = \frac{\left(1 - \Phi_{\rm fl}\right)}{\tau_{\rm av}} \tag{12}$$

In aprotic solvents,  $k_r$  and  $k_{nr}$  is not so well correlated with viscosity of the solvents used. The radiative rate constant is rather independent of the medium which, indicates that the electronic structure of the fluorescent state is insensitive to the environmental perturbation induced by the solvents. The non-radiative rate constant can be represented as a sum of the rates associated with internal conversion, photoisomerization, intersystem crossing and specific solvent effects. A closer inspection of Fig. 6 suggests that the nonradiative rate constant increases with increasing solvent viscosity. These facts indicate that in the deactivation process of the S<sub>1</sub> state, the nonradiative relaxation process dominates, however, in addition to this process, the intramolecular rearrangements, e.g., solvation phenomena as well as other specific kinds of solute—solvent interactions might also play a role [42,45].

Fig. 7 shows the absorbance spectra of BTP1 in MeCN, before and after different irradiation times. The photoreactions were carried out in quartz cells (1 cm in width) where the sample solution was irradiated with a blue DPSS laser with an intensity of light of 20 mW at room temperature.



**Fig. 6.** Radiative (solid sign) and non-radiative (open sign) rate constants as a function of viscosity of the aprotic solvents. The lines are used to guide the eye.

Visible light irradiation of BTP1 in MeCN do not cause distinct changes in the electronic absorption spectra, i.e. after 20 s of irradiation, BTP1 showed 5% decrease in maximal absorbance accompanied by hypsochromic shift of about 4 nm. After irradiation times higher than 20 s, no further changes were observed. This suggests that obtained from synthesis in the *trans* configuration, BTP1 is photochemically stable and does not undergo isomerization to *cis* form.

The BTP1 compound shows a blue shift in the absorption band and very low emission in the protic solvent, water, with its excited state decaying non-radiatively, involving the hydrogen bond interactions. The strong hydrogen bonding solvent forms hydrogen bonds with the nitrogen lone pair of the dye molecule, which reduces the magnitude of the ICT interaction within the dye molecule. However, when the investigated compound BTP1 was dissolved in solvents containing either 10% or 20% of methanol no significant changes in the spectral properties were observed as shown in Table 2.

The intensity and maximum of the absorption and fluorescence band depend on the solvent but do not depend on methanol content. Fig. 8 presents the examples of the absorption spectra of the BTP1 compound in pure DMF and after addition of 10% or 20% of methanol to each sample.

It has long been recognized that the longest wavelength absorption band of "push-pull" compounds is responsible for the second-order NLO response, according to the well-known and widely used "two-level model" [50]. In this model, the hyperpolarizability ( $\beta_0$ ) can be described in terms of a ground and first excited-state having charge-transfer character and is related to the energy of the optical transition (*E*), its oscillator strength ( $f_{os}$ ), and the difference between ground and excited-state dipole moment  $(\Delta \mu_{12})$  [51]. It should be noted that this analysis constitutes a major oversimplification because the compounds that reveal multiple low-energy excited states, cannot be accurately described as twostate systems [23]. Nevertheless, it is notable that the chromophore does display one dominant visible maximum, and the derived  $\beta_0$  values are rather large. As we can conclude from Table 1, the indirectly derived  $\beta_0$  values are slightly dependent on the polarity of the solvent.

#### 3.3. Theoretical calculations

The compound studied in this work (BTP1, see Fig. 9) belongs to the D- $\pi$ -A class of compounds. Similarly to other molecules of this



**Fig. 7.** Changes in absorbance intensity for BTP1 dye after irradiation of a Blue DPSS laser (line at 408 nm) with intensity of light of 20 mW.



Fig. 8. Normalized electronic absorption spectra of BTP1 in pure DMF and with addition of MeOH at 293 K.

type, the electronic spectrum of BTP1 exhibits very intense band associated with so-called intramolecular charge-transfer. It was mentioned in the experimental section, that BTP1 was dissolved in solution containing 10% of methanol in order to improve its solubility. Therefore, it was very important to verify how this addition affects the computed electronic structure parameters. In our theoretical calculations, the presence of admixture of methanol was taken into account by placing explicitly two methanol molecules near the nitrogen atoms from benzimidazole groups. Hereafter, the solute molecule surrounded by dielectric continuum will be denoted as model A, while the complex of a solute and two methanol molecules surrounded by dielectric continuum will be denoted as model B.

Tables 3 and 4 contain the values of the theoretically determined spectroscopic parameters characterizing the lowest-lying singlet excited states, obtained using model A and B, respectively. In the case of both models, we found that the first electronic excited state is the charge transfer-state of  $\pi$ - $\pi$ \* character and the corresponding transition is dominated by the HOMO  $\rightarrow$  LUMO excitation as was mentioned earlier (cf. Figs. 3 and 10). Fig. 10 presents the plots of orbital contour surfaces for model B. The results show that for BTP1 compound the lowest one-photon transition *in vacuo*, which is an allowed transition, does not change for the calculations including the presence of two methanol molecules.

Spectroscopic parameters assembled in Tables 3 and 4 show that transition to the first excited state is accompanied by the largest value of oscillator strength. Experimental studies have shown the inability to classify it as a chemical exhibiting a positive or negative solvatochromism. The same observation is confirmed by the theoretical calculations using four different functionals. Although the comparison of the data computed for BTP1 in vacuo and in solvent show the increase in the excitation energy (hypsochromic shift), changing the solvent from less to more polar does not result in significant changes in the position of the band maximum. The presence of two methanol molecules slightly increases the values of oscillator strength but shifts the absorption band towards longer wavelengths with an average of 60 nm in the gas phase and 30 nm in all solvents. On the other hand, this batochromic shift results in the values obtained for the complex with two methanol molecules being slightly closer to the experimental values.

In both cases, the functional PBEO gives values of the transition energy ( $\Delta E$ ) significantly underestimated relative to the experimental value. The average difference of  $\Delta \Delta E$  between them is



Fig. 9. Chemical structure of the investigated molecule a) monomer and b) with two-methanol compounds obtained after optimization in G09.

 $3710.1 \text{ cm}^{-1}$  for the monomer and  $5162 \text{ cm}^{-1}$  for the complex. The asymptotically corrected CAM-B3LYP, LC-BLYP and LC-wPBE functionals give the results more comparable with those obtained experimentally. Here the average deviation is 403.2 cm<sup>-1</sup> and -1532.5 cm<sup>-1</sup> for CAM-B3LYP, 3548.8 cm<sup>-1</sup> and 1371.1 cm<sup>-1</sup> for LC-BLYP, 3387.5 cm<sup>-1</sup> and 1290.5 cm<sup>-1</sup> for LC- $\omega$ PBE, in the case of the monomer and the complex, respectively. Among these three, the LC functionals give similar values, while the CAM-B3LYP on average predicts the absorption band maximum to be 40 nm larger than that observed experimentally. On the other hand, the values obtained in the case of model A using CAM-B3LYP, and in the case of model B using LC- $\omega$ PBE are closer to the experimental ones. In general, the values for the complex are closer to the experimental ones and the presence of two molecules of methanol causes an overestimation of the  $\lambda$  value using the CAM-B3LYP in comparison with experiment, therefore LC-wPBE more correctly describes the spectroscopic parameters of this compound.

The dipole moments for the ground  $(\mu_1)$  and first excited state  $(\mu_2)$  for the investigated monomer and complex calculated within TDDFT formalism are presented in Tables 5 and 6, respectively. Firstly, the presence of two molecules of methanol does not affect significantly the obtained values of the dipole moment. In the gas phase differences in the values of this parameters between the investigated systems are in the region of 2–5 D, but the presence of the solvent minimizes to less than 0.7 D, except for the PBE0. In

addition, we can see that for the ground state these differences are smaller ( $\Delta \mu < 0.3$  D), and slightly larger for the CT excited state  $(\Delta \mu > 0.3 \text{ D})$ . In both cases, for  $S_0$  and  $S_1$ , an increase in the value of the dipole moment during transition from the gas phase to the solvent is observed. In general, it can be stated that the increase of the solvent polarity is followed by the increase of the value of  $\mu_1$ and  $\mu_2$ , and these differences are minimal with an average of 0.03– 0.1 D. It is also clear, that in both cases the excitation to the CT excited state is accompanied by a decrease of the dipole moment values, and its value is more than 6 D less relative to the  $\mu_1$ . It is worth mentioning, that the polarity of the low-lying excited state is decreasing with the polarity of the solvent. The values contained in Tables 5 and 6 indicate, that for the gas phase  $\Delta \mu_{12}$  is more than 2 times smaller than for water. The presence of two molecules of methanol does not change significantly the value of  $\Delta \mu_{12}$  if solvent effects are taken into account; however, one should not overlook that reduction of  $\Delta \mu_{12}$  roughly by a factor of two is found for the molecule in vacuo. This observation indicates that the ground state is better stabilized by the polar solvent than the CT excited state, which leads to the enhancement of the excitation energy of the solute. In this connection, according to research carried out by Bartkowiak and others [52], we classify the investigated system as the one exhibiting negative solvatochromism.

In the case of compounds with a positive solvatochromic behaviour, the two-photon cross-section (TPA) increases with

#### Table 3

Calculated and experimental values of excitation energies (in nm,  $\lambda_{max}$ ) and oscillator strengths ( $f_{os}$ ) for the molecule without two-methanol compounds (model A). The bold type was distinguished values of DFT functionals giving more reliable results in relation to experimental values.

Solvent		CAM-B3LYP		LC-BLYP		LC-ωPBE		PBEO	
		$\lambda_{max}$	$f_{os}$	$\lambda_{max}$	$f_{os}$	$\lambda_{max}$	$f_{os}$	$\lambda_{max}$	$f_{os}$
Gas phase	$\pi - \pi^*$	494.05	1.0804	385.33	1.7229	391.59	1.6831	747.61	0.4923
	$n-\pi^*$	368.67	0.0443	298.52	0.0278	302.38	0.0311	608.78	0.0091
	$\pi - \pi^*$	367.24	0.3590	265.55	0.1273	272.23	0.1596	534.05	0.3147
THF	$\pi - \pi^*$	398.64	1.9197	351.71	2.0800	353.83	2.0914	488.94	1.1870
	$n-\pi^*$	281.07	0.1707	287.04	0.0153	289.30	0.0178	376.21	0.1061
	$\pi - \pi^*$	314.45	0.0328	256.61	0.0152	259.49	0.0143	375.81	0.3912
Acetone	$\pi - \pi^*$	390.73	1.9664	347.85	2.0833	349.65	2.0986	466.81	1.3213
	$n-\pi^*$	310.27	0.0260	284.74	0.0120	286.84	0.0139	362.71	0.4584
	$\pi - \pi^*$	277.25	0.0263	255.94	0.0147	258.75	0.0138	358.36	0.0313
MeOH	$\pi - \pi^*$	388.70	1.9694	346.71	2.0782	348.45	2.0940	461.91	1.3442
	$n-\pi^*$	309.08	0.0248	283.96	0.0113	286.03	0.0130	359.94	0.4529
	$\pi - \pi^*$	276.88	0.0205	255.78	0.0143	258.56	0.0134	354.79	0.0347
MeCN	$\pi - \pi^*$	388.86	1.9758	346.90	2.0828	348.63	2.0989	461.72	1.3560
	$n-\pi^*$	309.23	0.0244	284.14	0.0112	286.20	0.0130	359.71	0.4493
	$\pi - \pi^*$	276.86	0.0203	255.77	0.0145	258.57	0.0136	354.30	0.0356
DMF	$\pi - \pi^*$	390.59	2.0006	348.26	2.1047	350.00	2.1215	463.53	1.3920
	$n-\pi^*$	310.50	0.0234	285.29	0.0111	287.36	0.0128	360.26	0.4371
	$\pi - \pi^*$	276.95	0.0217	255.86	0.0155	258.65	0.0146	354.18	0.0379
DMSO	$\pi - \pi^*$	389.92	2.0005	347.87	2.1027	349.60	2.1196	462.00	1.3981
	$n-\pi^*$	273.57	0.0670	285.01	0.0109	287.08	0.0125	359.41	0.4353
	$\pi - \pi^*$	310.09	0.0231	255.81	0.0153	258.59	0.0144	353.11	0.0390
Water	$\pi - \pi^*$	387.52	1.9823	346.21	2.0823	347.89	2.0990	458.07	1.3822
	$n-\pi^*$	308.46	0.0232	283.69	0.0106	285.73	0.0123	357.56	0.4416
	$\pi - \pi^*$	276.59	0.0180	255.66	0.0144	258.44	0.0134	351.39	0.0389

#### Table 4

Calculated and experimental values of excitation energies (in nm,  $\lambda_{max}$ ) and oscillator strengths ( $f_{os}$ ) for the molecule with two-methanol compounds (model B). The bold type was distinguished values of DFT functionals giving more reliable results in relation to experimental values.

Solvent		CAM-B3LYP		LC-BLYP		LC-ωPBE		PBEO	
		$\lambda_{max}$	$f_{os}$	$\lambda_{max}$	$f_{os}$	$\lambda_{max}$	$f_{os}$	$\lambda_{max}$	$f_{os}$
Gas phase	$\pi - \pi^*$	540.18	1.6078	449.97	1.9404	455.50	1.9163	680.05	1.0715
	$n-\pi^*$	387.89	0.0320	314.24	0.0061	317.62	0.0032	588.63	0.0476
	$\pi - \pi^*$	356.03	0.2530	278.02	0.0715	286.85	0.0504	516.92	0.0004
THF	$\pi - \pi^*$	434.67	2.0462	383.91	2.1462	385.94	2.1568	523.61	1.5012
	$n{-}\pi^*$	321.48	0.0114	296.04	0.0348	298.14	0.0363	404.74	0.0355
	$\pi - \pi^*$	293.74	0.1072	264.06	0.0184	267.40	0.0186	371.34	0.6709
Acetone	$\pi - \pi^*$	422.25	2.0723	376.04	2.1442	377.73	2.1578	499.13	1.5784
	$n{-}\pi^*$	316.62	0.0135	292.84	0.0287	294.79	0.0302	384.95	0.0418
	$\pi - \pi^*$	287.11	0.0810	262.72	0.0170	265.93	0.0171	361.31	0.6256
MeOH	$\pi - \pi^*$	419.17	2.0712	374.01	2.1379	375.62	2.1528	493.41	1.5890
	$n-\pi^*$	315.24	0.0134	291.84	0.0269	293.76	0.0281	380.87	0.0434
	$\pi - \pi^*$	286.35	0.0496	262.42	0.0165	265.60	0.0165	359.16	0.6100
MeCN	$\pi - \pi^*$	419.31	2.0774	374.16	2.1426	375.77	2.1578	493.29	1.5996
	$n{-}\pi^*$	315.41	0.0135	292.03	0.0269	293.94	0.0282	380.31	0.0439
	$\pi - \pi^*$	286.29	0.0472	262.40	0.0167	265.58	0.0167	358.96	0.6050
DMF	$\pi - \pi^*$	421.53	2.1033	375.87	2.1653	377.50	2.1809	495.90	1.6367
	$n{-}\pi^*$	316.90	0.0144	293.33	0.0283	295.26	0.0297	380.15	0.0452
	$\pi - \pi^*$	286.38	0.0482	262.50	0.0179	265.68	0.0179	359.29	0.5937
DMSO	$\pi - \pi^*$	420.53	2.1022	375.20	2.1627	376.81	2.1785	494.08	1.6391
	$n{-}\pi^*$	316.43	0.0143	292.98	0.0277	294.90	0.0290	378.93	0.0457
	$\pi - \pi^*$	286.18	0.0432	262.41	0.0177	265.58	0.0177	358.63	0.5885
Water	$\pi - \pi^*$	417.21	2.0813	372.82	2.1415	374.37	2.1572	489.07	1.6163
	$n{-}\pi^*$	314.53	0.0135	291.43	0.0256	293.32	0.0269	376.94	0.0457
	$\pi - \pi^*$	285.79	0.0359	262.18	0.0164	265.34	0.0164	357.27	0.5874

increasing polar environment [53]. Conclusions presented in this work indicate that the molecule tested by us should exhibit negative solvatochromism. For this group of compounds, there are no detailed reports in the subject literature on the value of  $\sigma_{OF}^{(2)}$  in various media. To our best knowledge, there is only one theoretical work regarding TPA in the gas phase and in the polar solvent and in most cases the works concern the impact of polar environment on the first- ( $\beta$ ) and second- ( $\gamma$ ) order hyperpolarizabilities for the non-centrosymmetric organic molecules [33,54,55]. Despite the



**Fig. 10.** The plots of orbital contour surfaces for molecule with presence of twomethanol compounds. The molecular orbitals were calculated at the CAM-B3LYP/6-311++G(d,p) level of theory. The lower plot presents contour surface of HOMO and the upper presents contour surface of LUMO. Shown are the contour surfaces of orbital amplitude 0.02 (red) and -0.02 (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fact that there are difficulties in the dissolution of the compound, the TPA spectra discussed below should be treated as demonstrative and indicating the impact of the solvent polarity on the nonlinear response.

Fig. 11 presents the comparison of the values of the TPA crosssection for monomer and the complex with two molecules of methanol in selected environments. Similarly to the results of onephoton absorption calculations, in the case of functional CAM-B3LYP almost identical values of this parameters were obtained for both systems. For this reason, further discussions will be focused solely on the complex. The CAM-B3LYP was designed to predict charge-transfer excitations more accurately by improving the long range behaviour of the exchange potential, so for this reason, further consideration will be based on values obtained using this functional [56].

Two-photon absorption cross-sections in a.u. ( $\delta^{OF}$ ) and in GM  $(\sigma_{OE}^{(2)})$  for the molecule in this study are given in Table 7. In all simulations, the following values of  $\Gamma_F$  (see eq. (10)), determined on the basis of our spectroscopic data for BTP1 solution containing 10% of methanol, were used: THF - 4470.7 cm<sup>-1</sup>, acetone - 3844 cm<sup>-1</sup>, methanol - 3744.8 cm<sup>-1</sup>, acetonitrile - 3769.8 cm<sup>-1</sup>, DMF - $3867.4 \text{ cm}^{-1}$ , DMSO -  $3805.3 \text{ cm}^{-1}$  and water -  $3745.6 \text{ cm}^{-1}$ . Looking closely at this table one finds that the most dominating TPA state is also the most dominating one-photon absorption state (OPA). These observation are in accordance with the results presented by Agren and co-workers, i.e. for asymmetric compounds both the dominant OPA and the dominant TPA state are the same [57]. Considering the CT excited state, it is difficult to clearly determine the impact of the environment on the obtained value of the TPA cross-section. First, quite a surprising observation is that the obtained values of both parameters do not differ significantly from each other in the following media. These small differences can be related to change of position of absorption band maxima. The presence of the solvent, as it has been shown previously, does not affect substantially the value of excitation energy. In accordance with the two-state approximation [31,50,58], the obtained value of  $\delta^{OF}$  depends on three factors: oscillator strength, dipole moment difference and transition energy. Because of the fact that  $\Delta \mu_{12}$  and

Solvent	Ground state $\mu_1$			First excited state $\mu_2$						
	CAM-B3LYP	LC-BLYP	LC-ωPBE	PBEO	CAM-B3LYP	LC-BLYP	LC-ωPBE	PBEO		
Gas phase	24.77	26.33	26.10	22.66	5.33	11.77	10.71	5.72		
THF	30.59	31.24	31.15	29.70	17.46	24.1	23.38	6.70		
Acetone	31.31	31.86	31.77	30.56	19.95	25.76	25.11	7.86		
MeOH	31.47	31.99	31.91	30.75	20.49	26.13	25.49	8.26		
MeCN	31.49	32.01	31.93	30.76	20.58	26.18	25.55	8.35		
DMF	31.50	32.02	31.94	30.79	20.66	26.21	25.58	8.51		
DMSO	31.55	32.06	31.98	30.84	20.83	26.32	25.7	8.65		
Water	31.63	32.13	32.05	30.93	21.05	26.49	25.88	8.77		

 Table 5

 Values of dipole moments for the ground and first lowest-ling singlet electronic states for the model A calculated at the TDDFT/6-311++G(d,p) level of theory. All values are given in D.

 $f_{\rm os}$  are almost equal in case of all solvents, the energy transition will be a factor responsible for saturation of the two-photon cross-section.

In the case of the values expressed in atomic units the transition from gas phase to solvent is accompanied by a slight decline of the  $\delta^{\text{OF}}$ . However, in the case of  $\sigma_{\text{OF}}^{(2)}$ , it can be attributed to the upward trend. These observations, which may be due to the presence of the negative solvatochromism, are significantly different from the molecules with positive solvatochromism, where there is a clear increase in both parameters [53]. Referring to the azobenzene, stilbene and benzilideneanilines derivatives, in the case of the studied molecule the values of both  $\delta^{\text{OF}}$  and  $\sigma_{\text{OF}}^{(2)}$  are several times higher. This indicates that the tested molecule is characterized by a nonlinear response at a much higher level and it should be expected for the higher values of the molecular hyperpolarizabilities. Moreover, the component of the first hyperpolarizability is associated with TPA by equation (13), therefore similar trends in the obtained values are expected.

$$\left(\delta_{g-CT}^{ZZ}\right) \sim \beta_{ZZZ} \Delta \mu_{12,Z} \tag{13}$$

The two-photon absorption cross-section values in GM determined in both theoretical and experimental are in good agreement. In the case of CAM-B3LYP functional the obtained value is about 54 GM lower and for the B3LYP about 70 GM higher relative to the value measured in DMSO. Considering the computational methods used in the function of the average relative deviation of the method, the best value of the TPA cross-section appears to be provided by CAM-B3LYP functional. The use of this method leads to a  $\sigma_{OF}^{(2)}$ affected by an error of 13%, while for B3LYP this value increases to 16%. The type of model solvent used may be partly responsible for these discrepancies and in particular, the parameters that define a cavity solvation in SCRF method. In the context of computational validation protocol, it should be mentioned that the Z-scan method, by which the experimentally determined TPA cross-sections has been flawed, gives error values often exceeding 20%. Moreover, this discrepancy has its roots in the applied functional. It is expected that, as in the case of spectroscopic parameters, the LC- $\omega$ PBE would be more appropriate, but it is not available in the applied computing program. However, these differences are insignificant and overall agreement is quite satisfactory. Therefore, it is believed that the values of determined for the other solvents are not burdened with a bigger mistake, and the calculation scheme used provides a correct value of this parameters and thus supports experimental research.

The results discussed above are obtained using the values of  $\Gamma_F$ from the one-photon absorption calculations. As a consequence of eq. (10), this coefficient has influence on the values of TPA obtained in GM. It is easy to assume that if this factor changes, the  $\sigma_{OF}^{(2)}$  will change significantly. For this reason, the TPA was also calculated using  $\Gamma_F = 3892.4 \text{ cm}^{-1}$ , which is an average value of the broadening of the final state for all solvents. The results are presented in parenthesis in Table 5. When different values of  $\Gamma_F$  are used, the TPA in water is about 50 GM higher than in THF. In the case of constant absorption line width, the TPA in water is about 16 GM smaller than in THF so the relation is reversed. Moreover, for a medium of relative permittivity there are observed almost the same values of TPA cross-sections with increasing solvent polarity when  $\Gamma_F$  = const is used. However, first calculations indicated more nonmonotonic behaviour of the TPA with respect to solvent polarity which is characteristic for the solvatochromic reversal [58]. In the second case, the values of  $\sigma^{(2)}_{\rm OF}$  show a monotonic decrease with increasing solvent polarity which is characteristic for either negative or positive solvatochromic shifts. This observation indicates that for BTP1 the direct solvent effect has significant influence on behaviour of the TPA cross-section, but it is effectively reduced by the other factors like the broadening of the final state. On the other hand, these discrepancies clearly illustrated the importance of  $\Gamma_F$  in correct description of the TPA cross-section.

# 3.4. Comparison with experimentally derived two-photon spectra

Fig. 12 shows the comparison of the experimentally obtained two-photon absorption spectrum with the one-photon absorption

Table 6

Values of dipole moments for the ground and first lowest-ling singlet electronic states for the model B calculated at the TDDFT/6-311++G(d.p) level of theory. All values are given in D.

Solvent Ground state $\mu_1$								
	CAM-B3LYP	LC-BLYP	LC-wPBE	PBEO	CAM-B3LYP	LC-BLYP	LC-wPBE	PBEO
Gas Phase	22.19	24.06	23.9	19.82	10.99	16.07	15.63	15.69
THF	30.19	31.02	30.93	29.06	20.46	24.85	24.44	13.17
Acetone	31.24	31.94	31.85	30.28	20.93	25.32	24.73	13.02
MeOH	31.47	32.15	32.06	30.55	20.96	25.77	25.18	13.33
MeCN	31.51	32.18	32.09	30.59	21.04	25.83	25.24	13.39
DMF	31.52	32.19	32.10	30.61	21.09	25.84	25.26	13.48
DMSO	31.59	32.26	32.17	30.69	23.57	25.97	25.45	13.59
Water	31.71	32.36	32.26	30.82	21.50	26.20	25.63	13.69

δ (a.u.) 450000

400000

350000

300000

250000

200000

150000

100000

50000

0

-B - complex

DMSO

monomer



THE

#### Table 7

Values of two-photon absorption (TPA) cross-section ( $\delta^{OF}$ ) in atomic units and  $\sigma^2_{OF}$  in GM calculated using Eqs. (9) and (10) respectively for the complex with two methanol molecules.

Solvent	CAM-B3LYP		B3LYP		
	$\delta  imes 10^{-50}$	σ	$\delta imes 10^{-50}$	σ	
Gas Phase	4.16	364.4	4.49	190.5	
THF	3.71	330.95 (381.41)	8.42	380.42 (438.42)	
Acetone	3.48	373.81 (370.41)	8.82	484.20 479.80)	
MeOH	3.50	381.86 (368.62)	8.90	506.65 (489.08)	
MeCN	3.49	381.17 (370.41)	8.92	504.38 (490.15)	
DMF	3.49	371.60 (370.47)	8.92	491.60 (490.10)	
DMSO	3.48	376.23 (369.05)	8.94	500.86 (491.31)	
Water	3.46	379.95 (366.86)	8.98	516.31 (498.52)	

replotted at twice the wavelength. The results can be seen to confirm some of the theoretical predictions although there are also some striking features of the experimental spectrum that may be considered not fully understood at the present stage. Indeed, BTP1



**Fig. 12.** Two-photon absorption spectrum of BTP1 derived from Z-scan measurements in DMSO solvent. The data are compared with the one-photon spectrum re-plotted against the doubled wavelength. The data for the wavelength greater than  $\sim$ 850 nm contained contributions from a three-photon process.

is found to be a strong two-photon absorber in the expected wavelength range, i.e. at twice the wavelength of the main onephoton absorption band. It is comforting to find that the peak value of the two-photon absorption in this range is found to be ~430 GM, quite close to the predicted theoretically range of values. However, the experimental spectrum appears to be split into two bands, the actual peak value being found in the shorter wavelength component of the composite band. In addition, at the long wavelength tail of the two-photon absorption process, tentatively ascribed to three-photon absorption (within ~850–950 nm, the  $\sigma_3$  value at 950 nm appeared to be about 1.2  $10^{-77}$  cm<sup>6</sup> s<sup>2</sup>). There was no nonlinear absorption at longer wavelengths (1000–1600 nm).

# 4. Conclusions

Synthesis, spectral and photophysical properties of BTP1 were studied in medium and high polarity solvents. It has been found that negative solvatochromizm in the absorption spectra and bathochromic shifts of the emission bands occurs with increased solvent polarity which is a well-known manifestation of the charge transfer character of the solvent-relaxed emissive state. However, the plot of the emission maxima vs. polarity of the solvents is not linear but this plot of the absorbance maxima is much more linear, indicating that the specific interactions between solvent and solute occur rather in the excited state than in the ground state. Performed theoretical calculations showed that TD-DFT properly describes the one-photon absorption of the investigated compound. Obtained transition energies are in good agreement with experimental data, and in the same way indicate the trends in the behaviour of the molecule in the presence of solvent.

Additionally, Stark spectroscopy of the ICT bands affords estimated static first hyperpolarizabilities  $\beta_0$  of the compound in solvent of different polarity. The indirectly derived  $\beta_0$  values are large and slightly depend on the polarity of the solvent. The two-photon absorption cross-section for the investigated compound were determined using the quadratic response functions formalism combined with density functional theory. For the DMSO, the theoretical value in terms of the average relative deviation does not exceed of 16%, relative to the experimental value. This coefficient is quite satisfactory and indicates the possibility of applying the presented computational scheme in prediction of two-photon absorption cross-section for this class of compounds.

The experimental and theoretical results indicate that this unsymmetrical cyanine dye is thus a promising candidate for applications as a nonlinear absorber.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.06.008.

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σ (GM)

390

380

370

360

350

340

330

320

310

300

Gas Phase

monomo

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