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Synthesis and photophysical properties of two-photon chromophores containing 1H-benzimidazole residue



PIGMENTS

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ABSTRACT

The non-centrosymmetric, trans,trans-2-{4-[2-(1H-benzimidazol-2-yl)ethenyl]-styryl}-1,3-dimethylben zimidazole iodide and centrosymmetric, trans,trans-1,4-bis[4-(2-(1H-benzimidazol-2-yl)ethenyl)]benzene polymethine compounds based on 1H-benzimidazole residue were synthesized and characterized. Their photophysical properties in solvents of different polarity were thoroughly studied by means of absorption, emission and fluorescence quantum yield measurements. Analysis of the results clearly indicates that the compounds have strong one-photon absorption bands in the near ultraviolet region, relatively high fluorescence quantum yields and large Stokes' shifts due to the charge transfer effect.

The one- and two-photon absorption properties of a selected non-centrosymmetric dye were compared to those of a centrosymmetric polymethine dye. Their two-photon absorption cross-sections in DMF were determined to be ~330 GM and ~380 GM at ca. 650 nm for the centrosymmetric and noncentrosymmetric polymethine compounds, respectively.

Density functional theory calculations of one- and two-photon absorption electronic spectra of the tested compounds using CAM-B3LYP, LC-BLYP and LC-ωPBE functionals were carried out to support the experimental data.

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1. Introduction

The development of organic compounds with large twophoton absorption (TPA) cross-sections has recently been the focus of research interest due to their various applications in fields such as two-photon laser scanning microscopy [1,2], 3D microfabrication [3,4], optical data storage [5], optical limiting [6], and photodynamic therapy [7]. For all of these applications, molecules with large TPA cross-sections in the visible and near-infrared spectral region are desired [8-11]. Many strategies have been identified to maximize the TPA cross-section (σ_2) of organic materials. σ_2 is a measure of probability of simultaneous absorption of two photons by a molecule, usually expressed in Goeppert-Mayer units (1 GM = 10^{-50} cm⁴ s photon⁻¹ molecule⁻¹). From a fundamental point of view, the TPA cross-section is proportional the imaginary part of the second hyperpolarizability to

 $\gamma(-\omega;\omega,-\omega,\omega)$. This quantity can be maximized by combining three distinct structural elements: electron-donating (D) groups, electron-accepting (A) groups and conjugated π -bridges connecting donor and acceptor moieties [10–12]. Thus, based on the intra-molecular interactions, typical classes of non-linear optical molecules are non-centrosymmetric dipolar compounds (A- π -D), centrosymmetric quadrupolar compounds (D- π -D, A- π -A, D- π -A- π -D, A $-\pi$ -D $-\pi$ -A) and non-centrosymmetric octupolar compounds $(D-(\pi-A)_3, A-(\pi-D)_3)$ and there are also many more complex ones. Among the simplest nonlinear dyes with small molecule size and moderately large σ_2 one can mention stilbene derivatives which are based on a "push-pull" system. The nonlinear optical properties of these chromophores depend on the ability of the donor to provide electrons and the acceptor to withdraw electrons. An example of the donating group is a tertiary amine group whereas the methyl pyridinium group can constitute an electron acceptor [13–15].

The TPA cross-sections are most often determined either from two-photon excited fluorescence [16] or directly by transmission



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measurements in the Z-scan technique [17]. The two-photon fluorescence technique requires a suitable reference probe [18] and exclusion of one-photon excited fluorescence from the collected signal. On the other hand, the Z-scan technique can determine σ_2 also for non-fluorescent molecules and even in the range of wavelengths of excited state absorption [2,19].

The non-linear optical responses of new chromophores can be also predicted by theoretical calculations [20]. There are three main types of computational methods: a classical method, molecular mechanics, and two quantum chemical methods: ab initio and semiempirical. In turn, ab initio methods exist as two large families of methods: Hartree–Fock and density functional.

Semi-empirical methods are usually parametrized for the ground state (e.g. AM1) and the excited states active in the linear spectroscopy (e.g. INDO/S model, fitted to reproduce UV–vis absorption spectra at the CI singles (CIS) level). These models are often in error when applied to the two-photon transitions where higher excited-state energy levels are involved and double excitations are important [21–24]. Methods including higher-order correlated ground-state wave function [21,25]. In addition, size consistency is not guaranteed and special care needs to be taken when choosing the right configurations [21]. Alternatively, the TPA cross-section may be obtained as implemented for ab initio calculations – that is, by taking the residue of the second-order response function or the first hyperpolarizability [25].

The current method of choice for calculating the excited-state structure of large molecular systems is based on adiabatic time-dependent density functional theory (TD-DFT) [26] in the Kohn–Sham (KS) formalism [27–29]. TD-DFT was shown to give a better agreement with experiment than both semi-empirical and low level ab initio calculations for two-photon absorption (TPA) calculations in large quadrupolar conjugated organic chromophores [21] and small molecules [25,30].

We describe here investigations of new chromophores involving vinylidene-linked benzimidazole moieties. The BMe compound is based on push—pull system, which consists of 1*H*benzimidazole an electron-donating group (D) and 1,3dimethylbenzimidazolium iodide an electron-withdrawing group (A) coupled through a π -conjugated spacer. The BH is a centrosymmetric chromophore bearing on both sides 1*H*-benzimidazoles. Herein, we report the preparation and spectroscopic properties of these compounds. Their one- and two-photon absorption properties have been characterized by both experimental and theoretical methodologies.

2. Experimental

2.1. Materials and measurements

All reagents and solvents (spectroscopic grade) were purchased from Aldrich Chemical Co. or Alfa Aesar Co, and used without further purification.

The ¹H (200 MHz or 400 MHz) and ¹³C (50 MHz or 100 MHz) NMR spectra were recorded on a Varian Gemini 200 or Bruker AscendTM 400 NMR spectrometers, respectively. Dimethylsulfoxide (DMSO-d₆) was used as the solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm (δ). 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.

The elemental analysis was performed with an Elementar Analyser Vario EL III instrument (Germany) operating with the VARIOEL software (version 5.14.4.22). The purity of the dye was checked by TLC technique. The sample was dissolved in methanol-DMF 10:1 v/v mixture, applied on the plate (aluminium oxide IB-F) and eluted with methanol-chloroform 1:10 v/v mixture.

HPLC analyses were done by Waters HPLC systems equipped with Waters 2489 UV–Vis detector (detection wavelength was 370 nm), Waters 1525 Binary HPLC Pump and a Symmetry C18 column (3.5 μ m, 4.6 \times 75 mm). Separation was conducted under isocratic conditions with 0.8 ml/min flow rate, 25 °C, 10 μ l injection volume and HPLC grade methanol as a mobile phase.

Melting points were determined on the Buchi M-565 Melting Point apparatus.

Absorption and emission spectra were recorded at room temperature on 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 (AcMe); *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol (MeOH), acetonitrile (MeCN) and water (H₂O). The concentration of the dye in the solution was 1.0×10^{-5} M and 1.0×10^{-6} M for absorption and fluorescence measurements, respectively. All solvents were spectroscopic grade and were used without any additional purification. They were characterized by their static dielectric constant (ε) and refractive index (n) at 20 °C. The solvent polarity function, $f(\varepsilon, n)$, is given by Eq. (1) [31].

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

The fluorescence quantum yields (Φ) were measured by using a standard method under the same experimental conditions for all compounds. Dilute Coumarin 1 in ethanol ($\Phi_{ref} = 0.64$ [32]) at the same optical density as the other samples ($A \approx 0.1$ at 404 nm) was used as the reference. The quantum yield of the tested dye (Φ) was calculated using equation:

$$\Phi = \Phi_{ref} \frac{lA_{ref}}{I_{ref}A} \cdot \frac{n^2}{n_{ref}^2}$$
(2)

where:

 Φ_{ref} is the fluorescence quantum yield of the reference (Coumarin 1) sample in ethanol, *A* and A_{ref} are the absorbances of the compound under the study and reference sample at the excitation wavelength (404 nm), *I* and I_{ref} are the integrated emission intensity for the tested compounds and reference sample, *n* and n_{ref} are the refractive indexes of the solvents used for the compounds and the reference, respectively.

The fluorescence lifetimes were measured using an Edinburgh Instruments single-photon counting system (FLS920P Spectrometers). The excitation was provided by 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 it possible to analyse the fluorescence decay signals with a resolution of few picoseconds. The compounds were studied at concentration needed to provide absorbance of 0.2–0.3 in a 10 mm cell at 375 nm. The fluorescence decays were fitted as sums of two exponentials. The average lifetime, τ_{av} was calculated as $\tau_{av} = (\Sigma_i \alpha_i \tau_i)/(\Sigma_i \alpha_i)$, where α_i and τ_i are the amplitudes and lifetimes.

The two-photon absorption spectrum was determined using the open-aperture Z-scan technique [17] using a setup and procedures described elsewhere [33,34]. Briefly, a tunable amplified

femtosecond 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 closed-aperture Z-scan measurements on a 4.66 mm thick silica plate [33,34].

2.2. Computational details

The molecular geometry for considered molecules was carried out using the Gaussian 09 program package [35] and the hybrid exchange-correlation B3LYP [36] functional in conjunction with the 6-311++G(d,p) basis set for the ground and first excited state. The optimization of geometry was performed both *in vacuo* and with the inclusion of solvent effects by means of the Integral equation formalism for the polarizable continuum model (IEF–PCM) [37]. It was confirmed in all cases by means of harmonic vibrational analysis that the stationary points correspond to minima on the potential energy surface.

The electronic absorption and fluorescence spectra were obtained using time-dependent density functional theory (TD-DFT) using the Gaussian 09 suite of programs. The long-range corrected LC-BLYP [38,39], LC- ω PBE [40–42] and CAM-B3LYP [43] functionals, and the 6-311++G(p,d) 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 a 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 [44]:

$$\langle \delta^{OF} \rangle = \frac{1}{15} \sum_{ij} \left[S_{ii}^{OF} \left(S_{jj}^{OF} \right)^* + 2S_{ij}^{OF} \left(S_{ij}^{OF} \right)^* \right]$$
(3)

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

$$S_{ij}^{OF}(\zeta_{1},\zeta_{2}) = \frac{1}{\hbar} \sum_{K} \left[\frac{\langle \mathbf{0} | \zeta_{1} \cdot \widehat{\mu}_{i} | K \rangle \langle K | \zeta_{2} \cdot \widehat{\mu}_{j} | F \rangle}{\omega_{\alpha} - \omega_{1}} + \frac{\langle \mathbf{0} | \zeta_{2} \cdot \widehat{\mu}_{i} | K \rangle \langle K | \zeta_{1} \cdot \widehat{\mu}_{j} | F \rangle}{\omega_{\alpha} - \omega_{2}} \right]$$
(4)

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

It should be considered that determined experimental spectra ($\sigma^{(2)}$) with line broadening are connected to $\langle \delta^{OF} \rangle$ through [45]:

$$\sigma_{OF}^{(2)} = \frac{8\pi^3 \alpha^2 \hbar^3}{e^4} \cdot \frac{\omega^2 g(\omega)}{\Gamma_F/2} \langle \delta^{OF} \rangle$$
(5)

where α is a fine structure constant, ω is the frequency of absorbed photons (assuming one source of photons), Γ_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 δ -function.

In order to characterize the allowed TPA states, the quadratic response functions formalism [25,45] combined with the Kohn–-Sham method was used as implemented in the DALTON 2011 program [46,47]. Solvent effects were taken into account with the self-consistent reaction field (SCRF) model. All the TPA calculations

were carried out *e*mploying the CAM-B3LYP functionals and the 6-311++G(d,p) basis set.

2.3. Synthetic procedure

The procedure for the preparation of the compounds under study is shown in Scheme 1.

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



These compounds were obtained in parallel synthesis by the reaction of terephthaldialdehyde with 2-methyl-[1*H*]-benzimid-azole [48–50]. The detailed synthetic procedure together with spectroscopic and HPLC analysis is described in our previous paper [50].

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



1,2,3-Trimethylbenzimidazolium iodide (0.84 g, 3.4 mmol), 2-[2-(4-formylphenyl)ethenyl]benzimidazole (0.97 g, 3.4 mmol), and anhydrous methanol (25 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 precipitated and were collected by filtration under reduced pressure; 518.39 g/mol; 1.17 g, 66.7% yield, mp 283–285 °C, $R_f = 0.17$ and $R_f = 0.76$ for methanol-chloroform 1:10 v/v and 1:5 v/v, respectively. Elemental Anal. Calcd for C₂₆H₂₃N₄I: C, 60.2; H, 4.5; N, 10.8; I, 24.5%. Found: C, 60.19; H, 4.76; N, 10.83%.

¹H NMR (DMSO-d₆) δ (ppm): 3.54 (1H, NH), 4.17 (s, 6H, CH₃), 7.14 (m, 2H, Blm), 7.40–7.44 (d, ³J_{H,H} = 16.0 Hz, 1H, –CHdbnd), 7.54 (m, 2H, Blm), 7.63–7.59 (d, ³J_{H,H} = 16.0 Hz, 1H, –CHdbnd), 7.70 (m, 2H, Blm), 7.75–7.71 (d, ³J_{H,H} = 16.0 Hz, 1H, –CHdbnd), 7.84–7.82 (d, ³J_{H,H} = 8.0 Hz, 2H, Ar), 7.88–7.84 (d, ³J_{H,H} = 16.0 Hz, 1H, –CHdbnd), 7.99–8.01 (d, ³J_{H,H} = 8.0 Hz, 2H, Ar), 8.07 (m, 2H, Blm)

¹³C NMR (DMSO-d₆) δ (ppm): 33.0 (N⁺CH₃), 108.1, 113.0, 118.1, 119.4, 126.5, 127.6, 129.3, 133.3, 133.7, 145.7 (CH), 132.0, 134.6, 136.2, 138.4, 148.1, 150.7, 150.9 (C)

IR (KBr) (cm⁻¹): 3054, 1631, 1596, 1562, 1528, 1485, 1415, 1311, 1278, 1211, 1164, 1143, 1024, 968, 812, 741, 518.

3. Results and discussion

3.1. Preparation

The synthesis of BH was undertaken in acetic anhydride in the presence of acetic acid whilst the BMe compound was synthesized



Scheme 1. General route for the synthesis of 1H-benzimidazole derivatives.

in moderate yield (67%) from trans-2-[2-(4-formylphenyl)ethenyl] benzimidazole (BCHO) and 1,2,3-trimethylbenzimidazolium iodide on heating by using piperidine as a catalyst. Their chemical structures and purity were characterized by ¹H, ¹³C NMR and IR spectra and by thin layer and HPLC chromatography. The data were found to be in good agreement with the proposed structure. As expected, -CHdbndCH- bonds in both the centrosymetric and noncentrosymetric chromophores have a trans configuration, as evidenced by the value of coupling constants (J = 16 Hz) for olefinic protons (see Ref. [50] and Experimental section). All of the aromatic protons are observed around δ 7.0–8.2 ppm. Additionally, the ¹H NMR spectrum of the BMe dye exhibited a signal near δ 3.5 ppm which corresponds to the N-H proton of the benzimidazole ring and ca. $\delta 4.2$ ppm assigned to the methyl groups. The ¹³C NMR and IR spectral data of the dyes are summarized in the Experimental section and [50], and are also in good agreement with structures of the compounds.

The IR spectra showed typical vibrations for aromatic rings (CdbndC, 1600–1630, 1500–1530, 1400–1420 cm⁻¹; δ C–H, 700–900 cm⁻¹), resonance-conjugated unsaturated stretching modes in the chromophore (CdbndC, CdbndN, 1370–1480 cm⁻¹), chromophoric CH out-of-plane bending (CH, 940–1030 cm⁻¹) and bands for the appropriate functional group like the methyl group which gives low intensity absorptions around 1380 cm⁻¹ and 1480 cm⁻¹. They were identified as the deformation vibrations δ CH₃ sym. and δ CH₃ asym., respectively. The amine stretching

vibration for C–N bonds were observed in the $1250-1020 \text{ cm}^{-1}$ range, as medium bands,

The NMR and IR spectra together with HPLC analysis are presented in Supplementary Materials.

The studied molecules consist of a typical donor– π –donor structure, BH, and donor- π -acceptor structure, BMe, where the



Fig. 1. Normalized electronic absorption and fluorescence spectra of the heterocyclebased molecules recorded in DMF.

166

Spectral characteristic of BH and BMe compounds in solvents of different polarity ($\lambda_{ex} = 404$ nm).

$f(\varepsilon,n)$	THF	Acetone	DMF	DMSO	MeOH	MeCN	Water
	0.5491	0.7904	0.8356	0.8400	0.8546	0.8593	0.9137
BH							
$\lambda_{\max}^{ab}(nm)$	389	395	390	392	384	382	_
$\varepsilon (10^4 \text{ M}^1)$	5.29	_	5.16	4.72	4.37	5.28	_
cm ⁻¹)							
$\lambda_{\rm max}^{fl}$ (nm)	428; 454	427; 450	433; 458	439; 461	422; 446	427; 449	_
$\Delta \nu (\text{cm}^{-1})$	3681	3618	3807	3818	3620	3906	_
Φ_{fl}	0.855	0.609	0.775	0.630	0.738	0.679	_
τ_1^{fl} (ns)	0.386	0.44	0.432	0.4	0.482	0.477	_
$\alpha_1(\%)$	12.49	13.57	22.54	30.81	19.09	15.18	_
τ_2^{fl} (ns)	1.112	1.168	1.162	1.15	1.196	1.234	-
α_2 (%)	87.51	86.43	77.46	69.19	80.95	84.82	-
τ_{av}^{fl} (ns)	1.021	1.069	0.997	0.919	1.060	1.119	-
k _r	8.37	5.70	7.77	6.86	6.96	6.07	_
(10^8 s^{-1})							
k _{nr}	1.42	3.66	2.26	4.02	2.47	2.87	-
(10^8 s^{-1})							
f_{os}	0.94	-	0.95	0.87	0.84	0.99	-
BMe							
λ_{\max}^{aD} (nm)	363	386	389	392	381	377	376
$\varepsilon (10^4 \text{ M}^1)$	-	5.49	5.15	5.73	5.30	5.24	5.18
(cm')							
λ_{\max}^{n} (nm)	576	580	582	584	567	576	574
FWHMab	5694	4279	4281	4181	4102	4243	4136
(cm ⁻¹)	2002	2 400	0.505	0505	0.077	0554	2010
FWHMII	3082	3499	3527	3535	3677	3554	3918
(cm^{-1})	10 107	0.005	0525	0207	0.010	0164	0174
$\Delta \nu$ (cm)	10,187	8005	8525	838/	8010	9164	9174
Ψ_{fl}	0.157	0.103	0.120	0.114	0.067	0.109	0.044
$\tau_1(\Pi S)$	0.442	10.09	0.449	10 12	1724	11 452	0.564
$\alpha_1(\pi)$	12	19.08	21.01	18.13	17.34	11.45	1 552
τ_2 (IIS)	1.301	1.301	1.288	1.389	0.805	1.200	1.552
$d_2(\lambda)$	00	00.92	1 1 0 7	01.07	0 772	00.00	0.420
τ_{av} (IIS)	1.427	1.140	1.107	1.221	0.775	1.105	1.05
κ_r (10 ⁸ c ⁻¹)	0.98	0.94	1.02	0.90	1.01	0.94	1.05
(10 S)	6.03	7 78	8.01	7 73	110	7.66	228
(10^8 s^{-1})	0.05	1.10	0.01	1.25	11.5	1.00	22.0
for	_	1.25	1.18	1.29	1.14	1.17	1.11
200							

heterocyclic ring and styryl group are employed as acceptor and π conjugated moieties, respectively, while 1,3dimethylbenzimidazolium moiety constitutes an acceptor group. The two heterocycle-based molecules have been used in this work to investigate the effect of nitrogen alkylation on the one- and twophoton spectroscopic properties.

3.2. Optical properties

The normalized electronic absorption and fluorescence spectra of the heterocycle-based organic molecules under investigation at a concentration of $1.5-2 \times 10^{-5}$ M are presented in Fig. 1. Table 1 collects the photophysical properties of the studied compounds. There are: absorption (λ_{max}), emission (λ_{max}), Stokes' shift ($\Delta \nu$), relative fluorescence quantum yield (Φ_{fl}) fluorescence lifetimes (τ^{fl}) with their amplitudes (α), the radiative (k_r) and non-radiative (k_{nr}) rate constants and oscillator strength (f_{os}).

As can be seen in Fig. 1, the absorption spectrum of BH in DMF, with a maximum at 390 nm, shows a vibrational structure. Analysis of this complex vibronic spectrum with the use of the Gaussian function showed that the absorption bands occur at ca. 368 nm, 389 nm and 411 nm. The molar extinction coefficients of BH range from 4.37 to $5.29 \times 10^{-4} \, M^{-1} \, cm^{-1}$ in solvents of different polarity. On the other hand, the absorption spectrum of BMe is structureless and broad, having half-widths of 4281 cm⁻¹. The large bandwidth and the large extinction coefficient value (in the range of $5.15-5.73 \times 10^4 \, M^{-1} \, cm^{-1}$) for the BMe 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 benzimidazolium moiety through the conjugated π -system. The broadness of the absorption spectrum may arise due to a contribution from more than one electronic state to the absorption spectrum. Another reason may be that it reflects a broad distribution of conformers (solvent-solute or intramolecular) in the ground state [54].

As shown, the structural modification (BH vs. BMe) leads to negligible changes in the π -conjugated length and so results in linear absorption spectra with similar maximum position, λ_{max} . However, the emission maxima and the Stokes' shifts of methylated dye (BMe) were red-shifted by approximately 125 nm compared to those of non-methylated compound (BH). It is worth mentioning that the Stokes' shift is ca. three-times larger in BMe than in BH (Table 1, $\Delta \nu$). The observed large Stokes' shift suggests that the emitting state is not the Franck–Condon S₁ state reached in the absorptive transition and indicates that significant charge redistribution occurs upon excitation prior to emission. This suggests a quite substantial dipole moment change caused by the excitation [54].

Similar to the absorption spectrum, the fluorescence spectrum of BH shows vibrational structure for all used solvents at room temperature, while for BMe the fluorescence intensity distribution is described by a Gaussian shape. Such shape is characteristic for fluorescence spectra when the motions in the fluorophore environment occur simultaneously or faster than the emission. For these cases a very large number of different solute-environment space configurations are possible. They possess a large variation of interaction energies, forming an ensemble of sub-states. Each sub-state can possess a sharp maximum, but when added their contributions give a broadband emission spectrum of a Gaussian shape [55]. The range of the inhomogeneous broadening depends on the values of dipole moments of the dye molecule in the ground and excited states and on the dielectric properties and structure of the solvent [55]. The fluorescence emission spectra bands are somewhat narrower than the absorption spectra (see Table 1). Its fluorescence full-width at half-maximum FWHM^{fl} values are smaller than that determined for the long-wave absorption band, FWHM^{ab}. The difference between FWHM^{fl} and FWHM^{ab} amounts to 46% for low-polar THF, 15% for polar nonprotic DMSO and 10% for polar protic MeOH. If the broadening of the spectra is understood as deriving from the population of the thermally available conformers, then according to Rettig [56], the observed results can be taken as the evidence that some of these conformers are non-emissive (reduction of fluorescence band width). This type of conformer is obtained by twisting of the olefinic double bonds. The deactivation of this state should occur mainly by radiationless processes because the energy gap between its excited state and the ground state is verv small [56,57].

The steady-state absorption and emission spectra of BH and BMe in the fairly limited range of solvent polarity show small variations as a function of polarity. Generally, the BH and BMe dyes, which include a strongly electron donating benzimidazole nucleus, should rather possess negative solvatochromism. 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 fluorescence quantum yields of the conformers [58].

The observed hypsochromic shift occurring in methanol relative to THF or acetone can be a result of the solute-solvent interaction through intermolecular hydrogen bond formation between methanol and the lone pair electrons of benzimidazole nitrogen atom. This slightly decreases the electron density on the benzimidazole nitrogen atom, and consequently decreases to some extent the mobility of the attached π electrons over the conjugated pathway. The same is realized when the spectra recorded in aqueous solution are compared to those recorded in methanol.

Likewise as the fluorescence maxima the fluorescence quantum yield (Φ_{fl}) shows changes with increasing solvent polarity. Fluorescence quantum yields are higher for the non alkylated compound BH compared to the ionic dye BMe. The modification of the symmetrical compound with N-methyl groups leads to ca. sevenfold decrease in fluorescence quantum yield. Solvent choice also has a considerable influence on the fluorescence quantum yield of the compounds. BH and BMe in water are the samples with the lowest fluorescence quantum yields, whereas BH and BMe in THF are the samples with the highest Φ_{fl} values. In general, the quantum yields of the synthesized compounds decreased in protic solvents like methanol and water and in solvents of high polarity as compared to THF.

Apart from fluorescence quantum yields, the fluorescence lifetimes of the two chromophores were determined as described in the Experimental section. The fluorescence decays were fitted with the minimum number of exponential terms that resulted in random residuals. Consistent with a previous paper [50], the fluorescence decays measured with the compounds under the study were two-exponential (Fig. 2). The results of the individual fits,



Fig. 2. Fluorescence decay curves of BH and BMe in solvents of different polarity ($\lambda_{Ex} = 373 \text{ nm}, \lambda_{EM} = 450 \text{ or } 550 \text{ nm}$ for BH and BMe, respectively).

summarized in Table 1, show the contributions of the long (ca. 1.2 ns) and the short (ca. 0.4 ns) lifetime components. The amplitude of the short lifetime component is the highest in the sample displaying the fastest decay and the amplitude of the long lifetime component is the highest in the sample displaying the slowest decay.

Fig. 2 shows the fluorescence decays of BH and BMe in solvents of different polarity. From this figure, it is clear that the fluorescence lifetimes of BMe significantly decrease with increasing solvent polarity (from THF to water). However, there is only a little change in lifetimes of BH with applied solvents. Using the experimental $\Phi_{\rm fl}$ and $\tau_{\rm av}$ values, one can calculate values for the radiative (k_r) and nonradiative (k_{nr}) rate constants. The values of k_r are in the range from 8.37 \times 10⁸ s⁻¹ to 0.64 \times 10⁸ s⁻¹ for BH and from 0.94×10^8 s⁻¹ to 1.05×10^8 s⁻¹ for BMe (Table 1). For the BMe dye, the k_r value does not vary much as a function of solvent properties. The largest k_r value is found in lower polarity solvents (Table 1). This is due to the fact that, for a constant transition dipole, k_r is proportional to the square of the refractive index of the medium [59]. The fluorescence quantum yield and lifetime for the studied compounds decrease when the solvent changes from THF to water, due to an increase of the nonradiative rate constant k_{nr} in more polar solvents. The large k_{nr} values for both BMe and BH in polar solvent indicate that the nonradiative channel is dominant in the excited-state deactivation.

To get a deeper insight into fluorescence behaviour of BH and BMe, the fluorescence decay traces in DMF were recorded at different emission wavelengths, λ_{EM} (Fig. 3). The decays were found to be dependent on the monitoring wavelengths. Thus, a fast decay, as compared to that at 458 nm and 582 nm for BH and BMe, respectively, was observed at the blue edge, and a fast growth followed by a relatively slow decay was observed at the red edge of the emission spectra.

To reveal the reason behind the wavelength-dependent changes in the emission characteristics, fluorescence transient decays were converted to time-resolved emission spectra (TRES) (Fig. 4).

The analysis of the TRES spectra indicates that initially an increase in the fluorescence intensity is observed, followed by gradual decreases. There is a small discrepancy in the maximum wavelengths between the TRES and the steady state spectra, but it does not influence the overview of the dynamic properties of the system.

Normalized fluorescence spectra of BH and BMe in DMF are shown in Fig. 5 for various time delays after electronic excitation. The data are fitted by log-normal functions. The spectra are slightly shifted to the red with an invariant shape and show only one isoemissive point which is observed at 465 nm and 565 nm for BH and BMe, respectively. Observation of an iso-emissive point in time-resolved area-normalized emission spectra (TRANES) is an unambiguous confirmation for the presence of two emissive species in the sample, irrespective of their origin [60].

3.3. Photostability

To characterize photophysical properties of the studied compounds it is very important to check their photostability in solution. The photostability arises primarily as a consequence of molecular flexibility about the central carbon–carbon double bonds in the singlet excited state and accounts for the characteristic photochemical reaction shown by *trans-cis* photoisomerization. It was found that the optical properties of the compounds in the dark at room temperature remained constant for over 3 days but photodegradation was observed upon irradiation of the dye solutions with a 20 mW DPSS laser beam ($\lambda_{\rm EM} = 408$ nm). Fig. 6 shows photofading behaviour of BH and BMe in acetonitrile.



Fig. 3. Fluorescence decay profile for BH (top) and BMe (bottom) in aqueous DMF at different emission wavelengths.

The results indicate that visible light irradiation of BMe and BH in MeCN causes distinct changes in the electronic absorption spectra, i.e. after 200 s of irradiation, BMe showed a 30% decrease in maximal absorbance accompanied by hypsochromic shift of about 16 nm whereas the BH showed 25% photofading with blue shift of ca. 12 nm.

3.4. Theoretical approach

To gain further insight into the correlation between structure and the physical properties, quantum chemistry computations were conducted. The optimized parameters (bond lengths, bond angles and dihedral angles) of the investigated molecules in their ground and first excited state (cf. Fig. 7) in selected solvents are listed in Table S1 (See Supporting Information).

When the geometries of the S_0 and S_1 states are compared, the following observations are made: (a) the molecular structure of the BMe is not planar, in both the ground and excited state. In the first case, the rotation is bigger; (b) during the excitation of the molecule, the dihedral angle between C6-C7-C8-N9 decreases and in the same time C6–C7–C8–N11 increases. Simultaneously there is an increase of C7-C8-N9 and C7-C8-N11 bond angles while C8-N9-C10 and C8-N11-C10 are reduced. These differences make the benzimidazole fragment with methyl groups more twisted in the ground state and flatter in the excited state BMe; (c) in the case of carbon–carbon π -bridges, transition of the molecule from the ground to the excited state causes the single bonds to become shorter, and the double bonds longer in BMe. These observations do not apply to BH; (d) in both cases, the molecule is characterized by a planar structure and its excitation does not influence its geometry significantly.

Table 2 contains theoretically determined spectroscopic parameters characterizing the lowest-lying singlet excited states. It



Fig. 4. Time-resolved emission spectra (TRES) of BH (top panel) and BMe (bottom panel) in DMF at room temperature at various times after excitation ($\lambda_{Ex} = 373$ nm). Direction of the arrow indicates from 0 to 10 ns every 0.1 ns.



Fig. 5. Time-resolved area-normalized emission spectra (TRANES) with time for BH (top) and BMe (bottom) in DMF.

was found that for both molecules the first excited state is the charge-transfer (CT) state of $\pi - \pi^*$ character and characterized by the highest value of the oscillator strength. This transition is dominated by HOMO \rightarrow LUMO excitation (see Fig. 8). The figure shows that the HOMO is localized on the fragment without substituents, while the LUMO is focused on a part with methyl groups. Thus, during the excitation to the S₁ state there is a substantial shift of the electron density distribution in direction of the benzimidazole with substituents and this constitutes an intramolecular charge transfer. Despite the fact that the methyl groups are electron-donating, it accumulates on the opposite side of the positive charge of the molecule which results from the fact that hydrolysis of iodide salt is so strong that it produces the charge shift from the benzimidazole part, yielding the form of D- π -A. In the case of centrosymmetric BH compound, the HOMO is stretched across the entire molecule but LUMO is focused on the central phenyl ring, with the result that there is little intramolecular charge transfer.

The wavelengths of the absorption maxima $(S_0 \rightarrow S_1)$, oscillator strengths, fluorescence maxima $(S_0 \rightarrow S_1)$ and Stokes' shifts calculated in vacuum and solvents are presented in Table 2. Comparison of functionals used in the evaluation of one-photon absorption bands (OPA) indicates that the LC functionals give similar values,



Fig. 6. Changes in absorbance intensity for BH and BMe, respectively, after irradiation with a blue DPSS laser (line at 408 nm) with the power of 20 mW.

while CAM-B3LYP overestimates them, about 45 nm for BMe and 38 nm for BH. On the other hand, the latter gives the values nearest to the experimental ones. Using CAM-B3LYP gives values at the level of the average relative error of 3.5% for non-centrosymmetric compound, which decreases to 0.5% for centrosymmetric. Similarly good performance of this functional in computing spectra of π conjugated organic molecules has also been reported by other authors [61-65]. More importantly, the values contained in the presented tables indicate that, while in the case of BMe passing from the gas phase to the solvent is accompanied by a decline of the OPA value (hipsochromic shift), for BH these values increase (batochromic shift). The performed theoretical studies indicate that for the first molecule there is a gradual but slight increase in the value of the excitation energy, which allows for searching after negative solvatochromism. However, the presence of MeCN and DMF solvents caused a slight shift of the absorption band maximum in the direction of longer wavelength relative to the less polar solvents $(\Delta E_{MeCN-MeOH} = -0.0004 \text{ eV} \text{ and } \Delta E_{DMF-MeCN} = -0.0146 \text{ eV})$, so a further shift to a more polar DMSO and water results in the regrowth of the excitation energy ($\Delta E_{\text{DMSO-DMF}} = +0.0055 \text{ eV}$). This behaviour of BMe might be discerned in the nature of solute-solvent interaction.

Fig. 9 shows a comparison of the absorption spectra determined experimentally and theoretically (TD/CAM-B3LYP) in methanol and DMF. Firstly, if the calculated maximum absorption band is shifted slightly in the direction of longer wavelengths, in the case of the BMe compound in both the media the obtained spectra have similar shapes. Furthermore, a rather intense band at



Fig. 7. Optimized geometries of BMe (top) and BH (bottom).

211 nm was recorded in methanol, which is much less intense in theoretical spectrum and occurs at the wavelength of 283 nm. As mentioned earlier, this band is probably associated with the formation of H-bonds in more polar DMF and for this reason it disappears in this solvent. For BH, an almost identical position of the absorption band peaks was obtained, determined both theoretically and experimentally. However, in this case, the calculation does not provide additional bands that appear during the measurements. This proves the existence of specific interactions in the solute-solvent system, for which the TD-DFT method is not sensitive.

Table 3 collects the computed emission wavelengths λ_{EM} in gas phase and the solvent effect on the position the emission peaks. Similarly to the OPA, when changing from gas phase to the solvent, the position of the emission shifted. In the case of BMe it is a blueand for BH a red-shift. The change in peak position in different solvents is an indication that the emission wavelengths are sensitive to the environmental factors of the solvents. For this reason, for both molecules with increasing solvent polarity a hypsochromic effect is observed. On the other hand, it can also be seen that λ_{EM} exhibits the red-shift when going from less polar MeOH to more polar MeCN or DMF and then a blue-shift when the most polar solvents are taken into account. Comparing the determined λ_{EM} for both compounds it is easy to see that the presence of the two methyl groups causes a red shift on the position of the emission peaks. In addition, BMe is characterized by higher values of the Stokes' shift.

The data presented in Table 3 indicate that LC-BLYP and LC- ω PBO describe the position of the emission peak at a similar level, and the differences between them are lower than 0.9 nm (1.4 in the gas phase) and 0.5 nm for BMe and BH respectively. On the other hand, CAM-B3LYP overestimates the value of λ_{EM} relative to LC-functionals by about 52 nm (BMe) and 46 nm (BH). Taking into

account the value of the Stokes' shift, its higher value was obtained in the case of LC-BLYP and LC- ω PBE. Generally, it can be concluded that in the presence of solvents, the CAM-B3LYP functional provides the value on average 0.63/0.61, LC-BLYP 0.72/0.70 and LC- ω PBE 0.70/0.68 for BMe and BH, respectively. Only in the case of BMe, the Stokes' shift value determined in the least polar THF is slightly undervalued by an average of about 12%.

The dipole moments for the ground (μ_1) and the first excited state (μ_2) for the investigated compounds calculated within the TD-DFT formalism are listed in Table 4. Firstly, in each of the media the dipole moments obtained for the BH molecule are zero, for both the S₀ and S₁ state (symmetry). In the case of the BMe structure, for the S₀ and S₁, an increase in the value of the dipole moment during transition from the gas phase to the solvent is observed. The values collected in Table 4 indicate that with an increase of the solvent polarity the ground state dipole moment increases. However, analysis of the CT shows that, while the transition from vacuum to THF is characterized by an increase in μ_2 , the transition to the more polar environment is accompanied by a decrease of the dipole moment, and is more than 3D. This observation seems to be a little surprising because it is not associated with any observation resulting from the absorption and fluorescence analysis, where growth trends were observed for MeCN and DMF. Further enhancing polarity of the medium results in an increase of μ_2 , although initially increases are becoming smaller ($\Delta \mu_2^{(MeOH-Acetone)} = 0.47$ D; $\Delta \mu_2^{(MeCN-MeOH)} = 0.07 \text{ D}; \Delta \mu_2^{(DMF-MeCN)} = 0.04 \text{ D}) \text{ and from the DMF}$ was getting bigger ($\Delta \mu_2^{(DMSO-DMF)} = 0.15 \text{ D}; \Delta \mu_2^{(Water-DMSO)} = 0.22 \text{ D}).$ It also clear that the excitation of the charge-transfer (CT) state is accompanied by a decrease of the dipole moment values. For the CAM-B3LYP functional this value is more than 16D and 9D less relative to the μ_1 , for the gas phase and solvents, respectively. However, for THF $\Delta \mu_{1-2}$ is three times smaller compared to the other polar media. It is also worth mentioning that polarity of the low**Table 2** Calculated values of excitation energies (in nm, λ_{max}) and oscillator strengths (f_{OS}) for the BMe and BH molecules.

		CAM-E	3LYP	LC-BLYP		LC-ωPBE	
		λ_{max}	fos	λ_{max}	fos	λ_{max}	fos
BMe							
Gas chase	$\pi{-}\pi^*$	473	1.79	397	2.12	402	2.11
	$n-\pi^*$	357	0.047	289	0.028	292	0.037
THF	$\pi - \pi^*$	405	2.29	359	2.37	361	2.40
	$n-\pi^*$	306	0.038	280	0.0066	282	0.0064
Acetone	$\pi - \pi^*$	394	2.31	352	2.36	354	2.39
	$n-\pi^*$	300	0.028	276	0.0067	279	0.0065
MeOH	$\pi - \pi^*$	392	2.31	350	2.35	352	2.38
	$n-\pi^*$	299	0.026	276	0.0067	278	0.0065
MeCN	$\pi - \pi^*$	392	2.32	350	2.36	352	2.39
	$n-\pi^*$	299	0.026	276	0.0068	278	0.0066
DMF	$\pi - \pi^*$	394	2.34	352	2.38	354	2.41
	$n-\pi^*$	301	0.026	277	0.0071	279	0.0069
DMSO	$\pi - \pi^*$	393	2.34	351	2.37	353	2.41
	$n-\pi^*$	300	0.025	277	0.0071	279	0.0069
Water	$\pi - \pi^*$	391	2.32	349	2.36	351	2.39
	$n-\pi^*$	299	0.025	275	0.0069	278	0.0066
BH							
Gas chase	$n-\pi^*$	379	2.26	342	2.25	343	2.29
	$\pi - \pi^*$	299	0.000	274	0.000	276	0.000
THF	$n-\pi^*$	389	2.44	350	2.40	351	2.45
	$\pi - \pi^*$	304	0.000	280	0.000	282	0.000
Acetone	$n-\pi^*$	387	2.43	348	2.40	350	2.44
	$\pi - \pi^*$	303	0.000	279	0.000	281	0.000
MeOH	$n-\pi^*$	386	2.43	348	2.39	349	2.44
	$\pi - \pi^*$	302	0.000	278	0.000	280	0.000
MeCN	$n-\pi^*$	386	2.43	348	2.40	349	2.44
	$\pi - \pi^*$	303	0.000	279	0.000	281	0.000
DMF	$n-\pi^*$	388	2.45	350	2.41	351	2.46
	$\pi - \pi^*$	304	0.000	280	0.000	282	0.000
DMSO	$n-\pi^*$	388	2.45	349	2.41	351	2.46
	$\pi - \pi^*$	304	0.000	280	0.000	282	0.000
Water	$n-\pi^*$	386	2.43	348	2.39	349	2.44
	$\pi - \pi^*$	302	0.000	278	0.000	280	0.000

lying excited state is decreasing with the polarity of the solvent. 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. Similar results were obtained for *trans,trans*-2-{4-[2-(1*H*-benzimidazol-2-yl) ethenyl]-styryl}-*N*-methylpyridine iodide (BTP1) [50]. The presented conclusions, as well as studies carried out by the group of Bartkowiak [66] and our research conducted for the BTP1 molecule allow to classify the investigated BMe compound as one exhibiting negative solvatochromism.

3.5. NLO characterization

In addition to the linear spectral calculations presented and discussed above, two-photon absorption spectra are also of interest. As mentioned earlier, for the compounds with positive solvatochromism, the two-photon absorption spectrum shifts toward longer wavelengths with increasing polarity of the solvent [67]. All presented conclusions indicate that the studied molecule, similarly as BTP1 described previously [50], is characterized by a negative solvatochromism. Because there is not enough detailed reports in the subject literature on the impact of the environment with different polarity on the two-photon absorption cross-section value for this class of compounds [43,68,69], the results presented below should be treated as demonstrative and a continuation of the ones provided for the BTP1 molecule.

The TPA cross-sections in a.u. (δ^{OF}) and in GM ($\sigma_{\text{OF}}^{(2)}$) for the compounds considered in this study are given in Table 5 for two lowest singlet excited states. The values indicate that in the case of BMe the most dominating TPA state is S₁, which is also the most dominating in OPA. This is accordance with observation about other asymmetric compounds presented by Agren and co-workers [70]. However, for BH a different relation is observed. This molecule exhibits efficient TPA under excitation into the second excited state which is not unexpected for a centrosymmetric structure. Indeed, because of the presence of the centre of symmetry the mutual exclusion selection rule is operative in the case of BH: since transition S_0-S_1 is one-photon allowed, it is two-photon disallowed, on the other hand, two-photon excitation into S₂ is possible but this transition is not one-photon allowed. However, it needs to be noted that while the selection rules lead to differences between OPA and TPA for BH and BMe, the chromophores reach different excited states upon absorption but, due to fast radiationless relaxation they emit from the same, lowest excited state.

Organic solvatochromic compounds may exhibit significant changes under the influence of the solvent in terms of not only structural and linear optical properties (OPA) but also of the nonlinear optical properties, such as TPA. Considering the values expressed in atomic units, in both cases the transition from vacuum to solvent is accompanied by an increase of the δ^{OF} by more than 60,000 a.u. In general, increasing the dielectric constant of the environment causes a gradual increase in the value of δ^{OF} . For the BMe molecule a deviation from this dependence is observed, because least polar THF leads to the TPA almost identical as in the case of more polar water. The transition from THF to acetone is accompanied by a fall of two-photon cross-section by about 2500, but further increase of the solvent polarity contributes to the



Fig. 8. The plots of orbital contour surfaces for BMe (left panel) and BH (right panel). 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.)



Fig. 9. The comparison of the absorption spectra determined experimentally (the solid line) and theoretically (the dotted line) for BH (right panel) and BMe (left panel).

Table 4

growth of δ^{OF} . In the case of a centrosymmetrical compound (BH) the two-photon cross-section values are almost twice lower as compared to the asymmetric chromophore (BMe). Electronic excitation of BH molecule induces a transfer of a significant electron density from the benzimidazole part in the direction of the centre of the π -bridge. Such excitation results in a change of the quadrupole moment and thus leads to the enhancement of the δ^{OF} value.

Table 5 shows the values of TPA cross-section also in GM units that are more useful for comparisons to the measured values. In all simulations, the following values of Γ_F (see Eq. (5)), determined on the basis of our experimental data, were used: THF - 0.554 eV,

acetone – 0.477 eV, methanol – 0.464 eV, MeCN – 0.467 eV, DMF – 0.479 eV, DMSO – 0.472 eV and water – 0.464 eV. Looking closely at this table one finds that, as in the case δ^{OF} , the change of the environment is accompanied by change in the value of $\sigma_{OF}^{(2)}$. It should be noted, that in both cases the cross-section tends to increase with the polarity of the solvent, but only up to MeCN. Then, the transition from DMF to the more polar solvents results in a gradual increase of this parameter. In the case of BMe, in order to clarify these discrepancies, one should refer to the two-state approximation [67,71,72]. According to this, the TPA depends on three parameters: oscillator strength, the transition energy and the polarity of the excited state. As presented earlier, in any environment f_{OS} value is very high and almost equal in all solvents. On the

Table 3 Calculated emission values (in nm, λ_{EM}) and oscillator strengths (f_{OS}) for the BMe and BH molecules

	CAM-B3LYP		LC-BLYP		LC-wPBE	
	λ_{EM}	fos	λ_{EM}	fos	λ_{EM}	fos
BMe						
Gas phase	507	1.88	455	1.84	457	1.85
THF	495	2.40	439	2.44	441	2.46
Acetone	492	2.44	441	2.44	442	2.46
MeOH	491	2.44	440	2.44	441	2.46
MeCN	491	2.44	441	2.44	441	2.46
DMF	495	2.46	444	2.46	445	2.48
DMSO	495	2.46	443	2.46	444	2.48
Water	491	2.44	441	2.44	441	2.46
BH						
Gas phase	446	2.29	404	2.25	404	2.30
THF	479	2.49	433	2.41	433	2.46
Acetone	478	2.48	433	2.41	433	2.45
MeOH	477	2.48	433	2.40	432	2.45
MeCN	478	2.48	433	2.41	433	2.45
DMF	482	2.50	436	2.42	436	2.47
DMSO	481	2.50	436	2.42	435	2.47
Water	478	2.48	433	2.41	433	2.45

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

		CAM-B3LYP	LC-BLYP	LC-ωPBE
Gas phase	μ_1	23.30	24.60	24.57
	μ_2	6.59	12.06	11.36
THF	μ_1	28.34	28.82	28.85
	μ_2	25.34	26.50	26.34
Acetone	μ_1	28.98	29.35	29.39
	μ_2	19.24	23.56	23.15
MeOH	μ_1	29.11	29.46	29.50
	μ_2	19.71	23.88	23.49
MeCN	μ_1	29.13	29.47	29.51
	μ_2	19.78	23.93	23.54
DMF	μ_1	29.14	29.48	29.52
	μ_2	19.82	23.94	23.55
DMSO	μ_1	29.17	29.51	29.55
	μ_2	19.97	24.04	23.65
Water	μ_1	29.23	29.56	29.60
	μ_2	20.19	24.20	23.82

Table 5

Values of two-photon absorption (TPA) cross-section $\langle \delta^{OF} \rangle$ in atomic units and $\sigma_{OF}^{(2)}$ in GM obtained using Eqs. (3) and (5) respectively for the BMe and BH calculated at the CAM-B3LYP/6-311++G(d,p) level of theory.

	BMe				BH			
	$\delta^{\rm OF} \times 10^{-3}$		$\sigma_{0F}^{(2)}$		$\delta^{OF} imes 10^{-3}$		$\sigma_{OF}^{(2)}$	
	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂	<i>S</i> ₁	<i>S</i> ₂
Gas phase	301.8	1.3	314.3	2.4	0.0	113.7	0.0	296.7
THF	368.9	7.3	355.3	12.8	0.0	176.9	0.0	398.8
Acetone	365.4	7.6	418.4	15.7	0.0	193.7	0.0	500.2
MeOH	367.1	8.1	431.4	17.2	0.0	197.1	0.0	519.9
MeCN	367.2	8.1	428.7	17.2	0.0	197.9	0.0	518.6
DMF	367.1	8.1	417.8	16.8	0.0	197.9	0.0	505.4
DMSO	367.8	8.3	428.6	17.5	0.0	198.9	0.0	516.6
Water	368.7	8.6	436.4	18.3	0.0	200.7	0.0	529.4

other hand, the dipole moment differences increase with the dielectric constants. Thus in this case, the excitation energy value has a decisive influence on the two-photon absorption. Therefore, the characteristic $\sigma_{OF}^{(2)}$ in terms of environmental impact on the obtained value analogous resulting conclusions as in the case of OPA. It is also worth mentioning that higher values of two-photon absorption (TPA) cross-section $\sigma_{OF}^{(2)}$ in solutions are obtained for BH than for BMe.

It is known that the value of TPA expressed in GM is affected by the $\Gamma_{\rm F}$. When the only theoretical work are presented, the value of the broadening of the final state is unknown and is assumed to be constant for all solvents. For this reason, we also calculate the value of the two-photon absorption cross-section for constant value of $\Gamma_{\rm F}$. The obtained results are illustrated in Fig. 10. It is clear that the higher values of $\sigma_{OF}^{(2)}$ are obtained for BH compound.

The results of theoretical calculations were compared to the experimental data. As shown in Fig. 1, the experimental one-photon absorption (OPA) spectra of BMe and BH in DMF are very similar to each other in peak positions and intensities (see data in Table 1). This is also true for the two-photon absorption (TPA) spectra (Figs. 11 and 12). The largest OPA peaks are observed at 3.18 eV and 3.19 eV for BH and BMe, respectively with the second small peak located at 4.13 eV. In the TPA spectra, both compounds have a main peak at 1.91 eV, with almost the same magnitude of the cross-section (330 and 380 GM for BH and BMe, respectively). Moreover, at a photon energy lower than 1.8 eV, a smaller peak is also found in both spectra. Both the TPA bands are well reproduced in



Fig. 10. Comparison of the values the two-photon absorption expressed in GM at a constant value of the broadening of the final state. The solid line refers to BMe and the dotted line to BH.



Fig. 11. Two-photon absorption spectrum of BMe derived from Z-scan measurements in DMF. The data are compared with one-photon spectrum replotted against the doubled wavelength.

the OPA spectra replotted against the doubled wavelength, except for their intensity. The reason for this similarities, despite the differences in the selection rules due to different symmetries of the molecules are not clear at this stage. Nevertheless, it can be concluded that both BMe and BH are found to be moderate strength two-photon absorbers.

Summing up, the non-linear optical properties of the noncentrosymmetrical dipolar compound (BMe) and centrosymmetric quadrupolar compound (BH) revealed very similar twophoton properties, thus, 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 and there is no nonlinear absorption at longer wavelengths (1000–1600 nm).

4. Conclusion

Optical properties of two compounds based on the benzimidazole skeleton have been investigated. The dyes were synthesized, in reasonably good yields, by the Knovenagel condensation reaction. They show the typical absorption and emission features of styryl fluorophores, i.e., absorption bands that are blue-shifted with increasing solvent polarity, a highly Stokes-shifted emission band



Fig. 12. Two-photon absorption spectrum of BH derived from Z-scan measurements in DMF. The data are compared with one-photon spectrum replotted against the doubled wavelength.

of mirror image shape and a relatively high fluorescence quantum yield which decreases with increasing solvent polarity.

The two-photon absorption measurements show no significant change in cross-section as a result of substituting alkyl (dye BMe) groups onto the nitrogen of the benzimidazole ring. The non-centrosymmetrical dipolar compound (A- π -D, BMe) and the centrosymmetric quadrupolar compound (D- π -D, BH) have moderate TPA cross-section of ca. 350 GM at around 625 nm.

The one- and two-photon experimental data were supported by the results of quantum chemical calculations based on the density functional theory with CAM-B3LYP, LC-BLYP and LC- ω PBE functionals. The theoretical calculations show differences in the absorption and fluorescence peak position between BMe and BH chromophores. Furthermore, the quantum-chemical calculations allowed the estimation of the TPA cross-section for studied compounds.

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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.2014.06.007.

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