CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.201200539

Benzo[1,2-*d*:4,5-*d*′]bisimidazoles as a Convenient Platform Towards Dyes that are Capable of Excited-State Intramolecular Proton Transfer and of Two-Photon Absorption

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Abstract: New, strongly fluorescent benzo[1,2-*d*:4,5-*d*′]bisimidazoles have been prepared by the reaction of Bandrowski's base with various aldehydes. Their structures were carefully designed to achieve efficient excited-state intramolecular proton transfer and good two-photon-absorption (2PA) cross-sections. Functional dyes that possessed both high fluorescence quantum yields and large Stokes shifts were prepared. A π-expanded D-A-D derivative that possessed $\Phi_{fl} = 50\,\%$ and $\sigma_2 =$ 230 GM in the spectroscopic area of interest for biological imaging is an excellent candidate as a fluorescent probe. Thanks to the presence of two reactive amino groups, such compounds can be easily transformed into probes for bioconjugation. All of these benzo[1,2-*d*:4,5-*d*′]bisimidazoles were also strongly fluorescent in the solid state.

Keywords: absorption · dyes/pigments · fluorescence · fluorescent probes · nitrogen heterocycles

Introduction

The development of new luminescent platforms for applications in bioimaging has been one of the major focal points in organic chemistry over the last few decades. Highly selective fluorescent probes have opened new avenues in monitoring key functions and dynamic changes within living organisms.[1] One of the problems in fluorescence microscopy is the relatively small Stokes shift of many commercially available dyes. In this case, the absorption- and emission spectra overlap, thereby leading to self-absorption and poor distinction between excitation- and emission light in the sample. As a consequence, typical multicolor (multiple-dye) imaging presents a true challenge. A possible solution involves modifying the core of the fluorescent probe so as to allow excited-state intramolecular proton transfer (ESIPT) to occur. In most classical examples, ESIPT involves the transfer of a hydroxy proton to a neighboring nitrogen- or oxygen atom, which leads to a significant increase in the Stokes shift.[2] This phenomenon has been utilized in the design of fluorescent sensors,[3] laser dyes,[4] ultraviolet stabilizers,[5] probes for biological environments,[6] and, recently, in organic light-emitting devices.[7] Among the many compounds that display ESIPT, benzoxazoles,[8] flavones,[9] imidazoles,[10] imidazo[1,2-a]pyridines,[11] and benzoquinolines[12] have attracted the most attention. Unfortunately, the majority of these compounds absorb in the UV region, which is highly undesirable in biological applications. Ideally, a fluorescent probe should absorb in the so-called "biological window" (650–900 nm), which allows for deep tissue penetration and low background fluorescence without the photochemical side-effects that are often observed after ultraviolet irradiation.[13] This combination can be accomplished without substantial modification of the parent fluorescent platform by exploiting the nonlinear properties of the desired material, in particular, two-photon absorption. Two-photon absorbing materials have found many applications in various fields, such as optical limiting, multiphoton-pumped frequency-upconversion lasing, polymerization microfabrication, 3D data storage, photodynamic therapy, and two-photon excited fluorescence.[14] Surprisingly, there are very few reports on molecules that simultaneously undergo both of these aforementioned phenomena.[15] Herein, we present our preliminary studies on two-photon absorbing benzobisimidazoles and their excited-state intramolecular proton-transfer properties.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201200539.

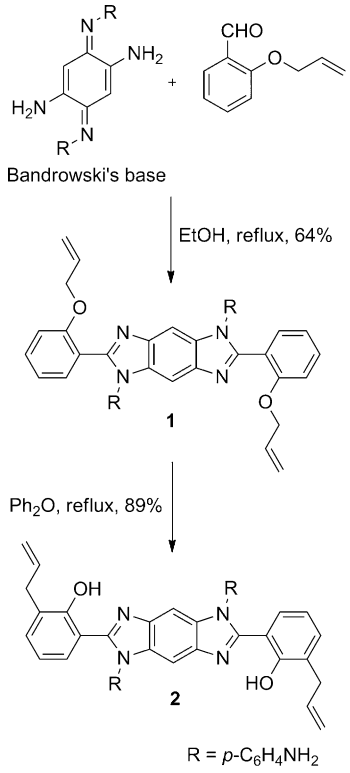
Results and Discussion

Design and Synthesis

To the best of our knowledge, benzo[1,2-*d*:4,5-*d*′]bisimidazoles have not been subjected to ESIPT or 2PA studies. Their core can be considered as relatively electron poor. The facile attachment of electron-rich groups at the periphery of this heterocycle through ethenyl or ethynyl linkers should lead to classical quadrupolar D-π-A-π-D systems (where D and A are electron donors and -acceptors, respectively, and π denotes a π-conjugated bridge), which are known to effectively promote simultaneous two-photon absorption.[14a–c] It has been shown that derivatives of benzo[1,2-*d*:4,5-*d*′]bisimidazole can be utilized as sensing molecules and that they interact with G-quadruplex DNA.[16] Their quaternary salts were found to be strongly fluorescent.[17] We envisioned that benzo[1,2-*d*:4,5-*d*′]bisimidazoles, if suitably substituted, should be an ideal core for the construction of two-photon absorbing and ESIPT-capable materials.

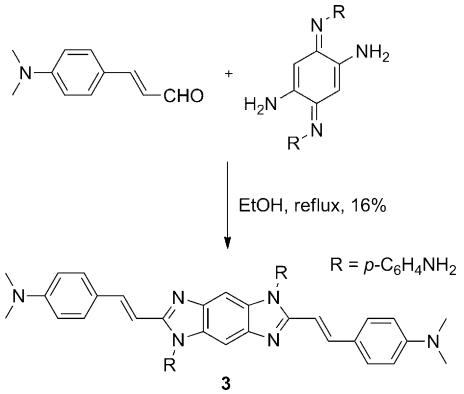
The synthesis of substituted benzo[1,2-*d*:4,5-*d*′]bisimidazoles has been much less explored than similar benzo[1,2-*d*:4,5-*d*′]bisoxazole systems.[18] They have usually been synthesized from 1,2,4,5-tetraaminobenzene[16a,b] or, more recently, by Pd-catalyzed tandem coupling/ring closure.[19] However, very recently, Siri and co-workers proposed a new, elegant synthetic route to these heterocycles,[20] starting from the readily available Bandrowski's base[21] and an appropriate aldehyde. The desired compounds were prepared in just one step (as a result of nucleophilic addition followed by prototropic rearrangement, cyclization, and oxidation in air), and possessed two *N*-(4-*a*minophenyl) substituents that could be used for further functionalization. This last feature is particularly attractive because it affords easy access to compounds that are suitable for bioconjugation.

We initially focused our attention on benzobisimidazoles for ESIPT studies. Unfortunately, the simple reaction of Bandrowski′s base with salicylaldehyde did not lead to the expected product. We suspected that phenol protection would help to overcome this problem and assumed that simple methyl ethers would not be sufficient for this purpose because their deprotection in the presence of amino groups might be problematic. Therefore, we decided to use an allyl ether that can be removed thermally. Indeed, the reaction of 2-allyloxybenzaldehyde with Bandrowski′s base, followed by Claisen rearrangement, gave the expected product (**2**) in moderate overall yield (Scheme 1).



Scheme 1. Synthesis of 2-hydroxyphenyl-substituted benzobisimidazole **2**.

Subsequently, we prepared a model compound for 2PA studies. The condensation of Bandrowski′s base with 4-(*N*,*N*-dimethylamino)cinnamaldehyde yielded the expected π-expanded product (**3**, Scheme 2). Unfortunately, similar reactions with phenylpropargyl aldehyde derivatives only led to tar-like products. Thus, we decided to prepare compound **4** from trimethylsilylpropynal (Scheme 3). Subsequent alkyne deprotection yielded highly insoluble compound **5**, which was completely unreactive to palladium-catalyzed coupling



Scheme 2. Synthesis of π-expanded benzobisimidazole **3**.

Abstract in Polish: W wyniku reakcji odpowiednio podstawionych aldehydów z zasadą Bandrowskiego otrzymano nowe, silnie fluoryzujące benzobisimidazole. Ich struktura została starannie zoptymalizowana pod kątem uzyskania wydajnego przeniesienia protonu w stanie wzbudzonym, następującego w wyniku jednoczesnej absorpcji dwóch fotonów. Dzięki obecności dwóch reaktywnych grup aminowych zsyntetyzowane związki dają możliwości dalszych modyfikacji i użycia w dwufotonowej mikroskopii fluorescencyjnej.

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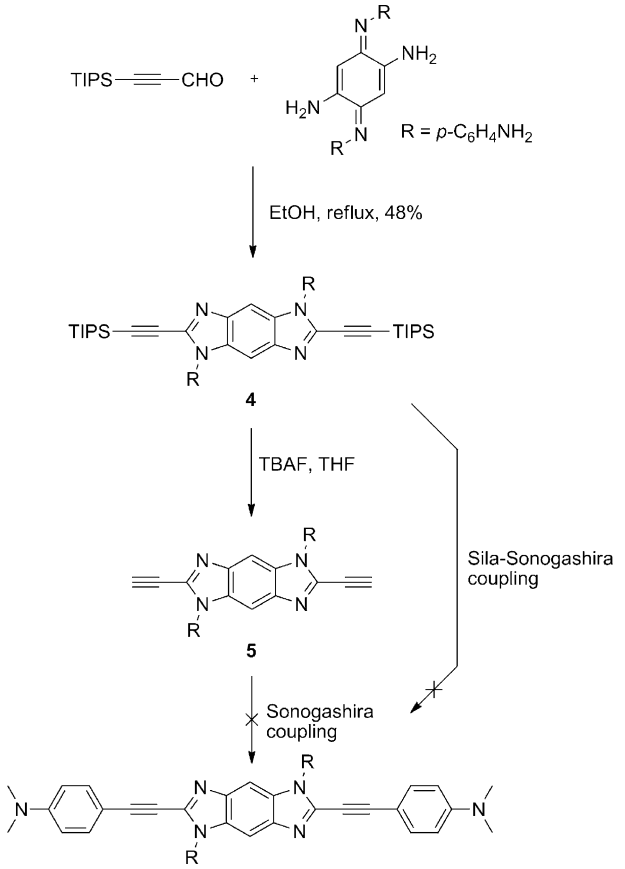


Scheme 3. Attempted approach to another π-expanded benzobisimidazole.

with 4-bromo-*N*,*N*-dimethylaniline. For this reason, we attempted a "sila"-Sonogashira coupling reaction with highly soluble compound **4**, but all attempts were met with failure. It is worth pointing out that the prepared compounds can very often be purified by simple crystallization from the reaction mixture.

Linear Photophysical Properties

The spectroscopic properties of the prepared benzo[1,2-*d*:4,5-*d*′]bisimidazoles are summarized in Table 1 and Figures 1–3. 2-(2′-Hydroxyphenyl)benzimidazole is a prototype of molecules that exhibit ESIPT.[22] When compared with this model compound, compound **2** exhibits both shifted absorption (380 nm versus 330 nm) and emission spectra (506 nm versus 430 nm). The enol *syn* form exhibits ESIPT owing to favorable electronic and structural properties, whereas ESIPT is prohibited in both the *anti* and open forms owing to unfavorable thermodynamic parameters.

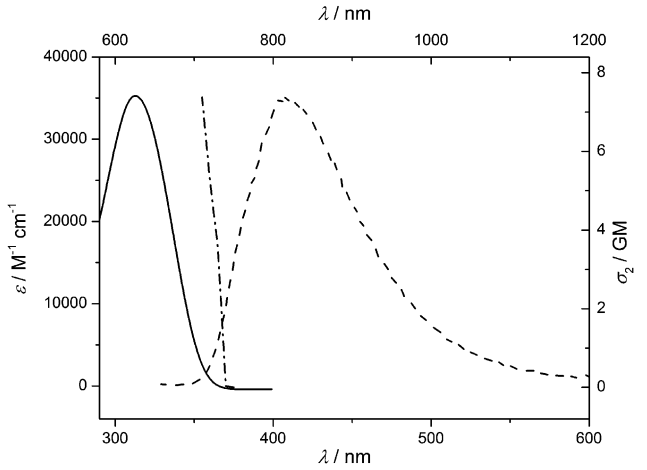


Figure 1. Absorption (solid line), emission (dashed line), and 2PA spectra (dashed–dotted line) of compound **1**.

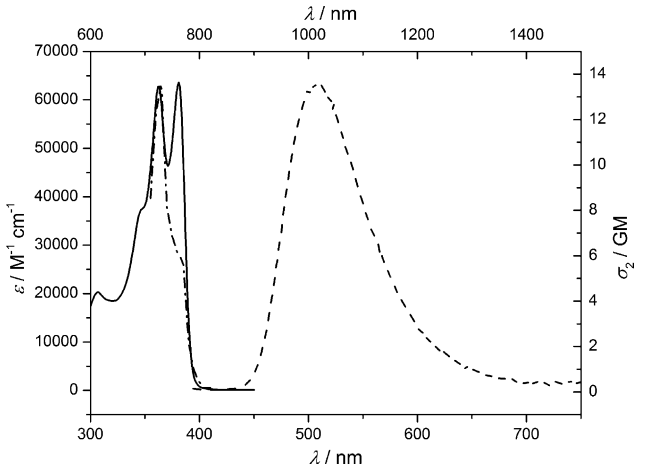


Figure 2. Absorption (solid line), emission (dashed line), and 2PA spectra (dashed–dotted line) of compound **2** in CH_2Cl_2.

Although the formation of the enol *anti* conformer in compound **2** is blocked, the overall number of possible conformers is four. The distribution of the conformers is governed by the substitution pattern and by the polarity of the solvent, with polar and/or protic solvents favoring the enol open conformer (stabilized by intermolecular hydrogen bonds with the sol-

Table 1. Spectroscopic data for compounds **1**, **2**, and **3** in CH_2Cl_2.

Compound	λ_{abs}^{max} [nm]	ε^{max} [$M^{-1}cm^{-1}$]	λ_{em}^{max} [nm]	Stokes shift [cm^{-1}][a]	Φ [%]
1	313	3.53×10^4	407	7380	19.7[b]
2	383[d]/381/378[e]/376[f]	6.36×10^4	500[d]/506	6480	16.5[b]
	365[d]/363/360[e]/360[f]	6.28×10^4	501[e]/501[f]		14[b,d]
	307	2.03×10^4			7[b,e]
					1.5[b,f]
3	437	3.26×10^4	488	2390	50[c]
	301	1.34×10^4			

[a] Stokes shift $=1/\lambda_{abs}-1/\lambda_{em}$; [b] standard: quinine bisulfate; [c] standard: fluoresceine; [d] measured in toluene; [e] measured in MeCN; [f] measured in MeOH.

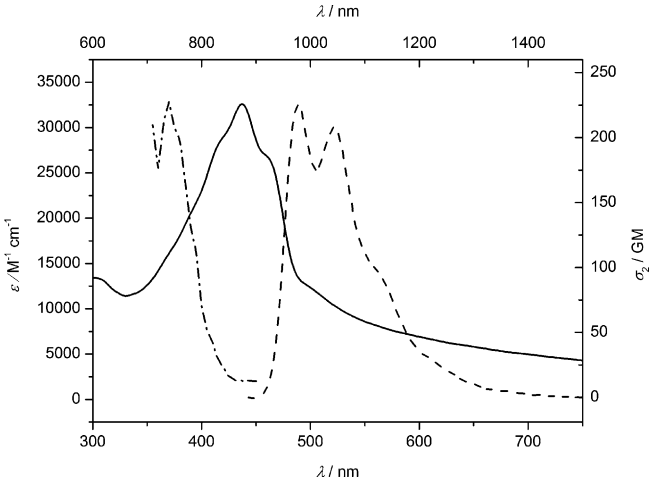
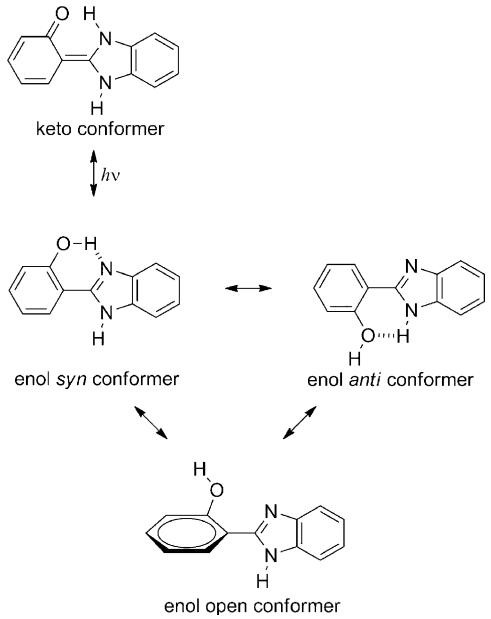


Figure 3. Absorption (solid line), emission (dashed line), and 2PA spectra (dashed–dotted line) of compound **3**.



Scheme 4. Three possible 2-(2′-hydroxyphenyl)benzimidazole conformers.

vent) and non-polar solvents favoring the enol *syn*- and *anti* conformers (Scheme 4). The absorption spectrum of compound **2** was measured in four different solvents and its maximum was around 380 nm (π–π* transition). The fluorescence spectra of compound **2** in CH_2Cl_2 and in toluene only showed a single ESIPT band (at 506 and 501 nm, respectively, Figure 2). These bands were shifted to longer wavelengths by almost 100 nm compared to compound **1** and had a Stokes shift of 6480 cm^{-1}.

Additional bands appeared in MeCN (403 nm, 17% of the overall fluorescence intensity) and MeOH (405 nm, 2% of the overall fluorescence intensity), thereby indicating conformational equilibrium in solution in the ground state. The fluorescence quantum yield of compound **2** was surprisingly high in non-polar solvents, even though ESIPT very often causes a significant decrease in emission strength owing to competitive internal conversion followed by vibrational relaxation. The fluorescence quantum yield decreased with an increase in the polarity of the solvent (Table 1). Park and co-workers showed that tetrasubstituted imidazole derivatives (and compound **2** can be considered as such) that contain a 2-hydroxyphenyl substituent at position 2 undergo ESIPT and display unusually high fluorescence quantum yields (0.18).[7] Interestingly, compound **1**, in which ESIPT is blocked, possesses a relatively large Stokes shift, thus suggesting a highly distorted excited state.

Compared to compounds **1** and **2**, the absorption of compound **3** in CH_2Cl_2 is significantly red-shifted as a result of extended π-conjugation, although, surprisingly, ε^{max} is not larger (Figure 3). The strongest absorption band of compound **3** has several shoulders, which may either be due to aggregation or to the existence of different conformers. Aggregation typically leads to emission-quenching, so the fact that compound **3** is strongly fluorescent in solution (with the quantum yield reaching 50%) favors the second possibility. Compared to polymers of similar benzobisoxazoles, both the absorption- and emission maxima of compound **3** are blue-shifted by more than 70 nm.[18d] Such behavior may be explained by the stronger electron-withdrawing character of the benzobisoxazole, which leads to a more polarized structure. Similarly, compound **2** has a rich, red-shifted absorption spectrum in CH_2Cl_2 with three major bands and one shoulder. This behavior is commonly interpreted as being a result of the presence of different conformers (Scheme 4).

Non-Linear Photophysical Properties

Two-photon absorption measurements of compounds **1–3** were performed by using the TPEF method (Table 2). As expected, compound **3** gave the highest 2PA cross-section (228 GM) owing to extended π-overlap and pronounced dipolar character. In combination with high fluorescence quantum yield, this property leads to relatively good two-photon brightness. On the other hand, the results obtained for compound **2** suggest that the 2-hydroxyphenyl substituent in the enol *syn* conformer is not an efficient electron donor in the D-A-D system. Apparently, the decreased rigidity, together with moderate conjugation in compound **2**, causes a significant drop in 2PA cross-section.

Table 2. Two-photon data for **1**, **2** and **3** measured in CH_2Cl_2.

Compound	$2\lambda_{OPA}^{max}$ [nm]	λ_{TPA}^{max} [nm]	σ_2^{max} [GM][a]	$\sigma_2^{max}\Phi$ [GM]
1	626	≤710	≥7.4	>1.5
2	762	730	14	2
	726			
	614			
3	874	740	228	114
	602			

[a] GM = Goeppert-Mayer unit; 1 GM = 10^{-50} cm^4 s photon^{-1}.

Conclusions

In summary, three new benzo[1,2-*d*:4,5-*d*′]bisimidazoles were synthesized and their optical properties were studied. Compound **2**, which contained two 2-hydroxyphenyl units and emitted yellow–green light, underwent efficient ESIPT, although the Φ_{fl} value remained remarkably high (16.5%). Ground-state conformational equilibrium in solvents of different polarity and proticity was observed, although, after excitation, the dominant radiative decay pathway was ESIPT. A benzo[1,2-*d*:4,5-*d*′]bisimidazole-based D-π-A-π-D system was also synthesized for the first time. The introduction of this rarely seen building block as an electron acceptor inside the two-photon absorbing scaffold was successfully investigated, thereby resulting in the formation of a new dye that displayed good two-photon brightness.

Experimental Section

*Synthesis of Compound **1***

A mixture of Bandrowski′s base (1.27 g, 4 mmol) and 2-allyloxybenzaldehyde (1.43 g, 8.8 mmol) in absolute EtOH (100 mL) was heated at reflux for 24 h under an Ar atmosphere. The reaction mixture was cooled to RT and left undisturbed for a further 24–48 h to allow slow crystallization of the product. The precipitate was filtered off and washed with EtOH to give 1.55 g (64%) of compound **1** as off-white crystals. M.p.: 255 °C (dec./Claisen rearrangement); ^{1}H NMR (500 MHz, CF_3COOD): δ = 4.53 (d, J = 5.5 Hz, 4H; CH_2CH=CH$_2$), 5.22 (d, J = 16.5 Hz, 2H; CH$_2$CH=CH_2), 5.27 (d, J = 9.5 Hz, 2H; CH$_2$CH=CH_2), 5.81–5.85 (m, 2H; CH$_2$CH=CH$_2$), 7.05–7.11 (m, 4H; C_6H_4), 7.41 (d, J = 1.5 Hz, 2H; C_6H_4), 7.63–7.67 (m, 2H; C_6H_4), 7.75, 7.87 (AA′BB′, J = 8.5 Hz, 8H; $C_6H_4NH_2$), 8.07 ppm (s, 2H; benzobisimidazole), NH_2 signal was not detected; ^{13}C NMR (125 MHz, CF_3COOD): δ = 72.4, 101.1, 110.6, 115.7, 121.3, 124.0, 128.4, 131.3, 131.5, 132.8, 133.4, 133.9, 135.2, 136.8, 139.4, 155.2, 159.6 ppm; UV/Vis (CH_2Cl_2): λ (ε) = 313 nm (3.53×10^{-4} dm^{3}mol^{-1}cm^{-1}); emission max: 407 nm; IR (KBr): $\tilde{\nu}$ = 757, 1360, 1431, 1518, 1633, 3462 cm^{-1}; HRMS (ESI): m/z calcd for $C_{38}H_{33}N_6O_2$: 605.2659 [M+H$^+$]; found: 605.2676.

*Synthesis of Compound **2***

Ether **1** (420 mg, 0.5 mmol) was added in one portion to boiling Ph_2O (20 mL). The reaction mixture was heated to reflux under an Ar atmosphere for 10 min. After that time, the mixture was cooled and hexanes (80 mL) was slowly added. The resulting pale-yellow precipitate was filtered off and washed with plenty of hexanes to give 376 mg (89%) of compound **2**. M.p.: >300 °C; ^{1}H NMR (500 MHz, CF_3COOD): δ = 3.76 (d, J = 6.5 Hz, 4H; CH_2CH=CH$_2$), 5.43–5.48 (m, 2H; CH$_2$CH=CH_2), 5.56 (dd, ^2J = 1 Hz, ^3J = 10.2 Hz, 2H; CH$_2$CH=CH_2), 6.21–6.29 (m, 2H; CH$_2$CH=CH$_2$), 7.26 (t, J = 7.8 Hz, 2H; C_6H_3), 7.44 (dd, ^3J = 1.3 Hz, ^4J = 8.1 Hz, 2H; C_6H_3), 7.78 (dd, ^3J = 1 Hz, ^4J = 7.5 Hz, 2H; C_6H_3), 8.11, 8.22 (AA′BB′, J = 8.7 Hz, 8H; C_6H_4), 8.32 ppm (s, 2H; benzobisimidazole), NH_2 and OH signals were not detected; ^{13}C NMR (125 MHz, CF_3COOD): δ = 36.7, 100.8, 109.6, 120.1, 124.2, 128.6, 130.0, 131.2, 131.38, 131.41, 134.0, 135.3, 136.0, 136.9, 140.0, 154.4, 156.6 ppm; UV/Vis (CH_2Cl_2): λ (ε) = 381 (6.36), 363 (6.28), 307 nm (2.03×10^{-4} dm^{3}mol^{-1}cm^{-1}); emission max: 506 nm; IR (KBr): $\tilde{\nu}$ = 750, 1170, 1248, 1367, 1422, 1460, 1518, 1618, 3371, 3470 cm^{-1}; HRMS (ESI): m/z calcd for $C_{38}H_{33}N_6O_2$: 605.2659 [M+H$^+$]; found: 605.2679.

*Synthesis of Compound **3***

A mixture of Bandrowski′s base (954 mg, 3 mmol) and 4-dimethylaminocinnamaldehyde (2.1 g, 12 mmol) in absolute EtOH (60 mL) was heated at reflux for 24 h under an Ar atmosphere. The reaction mixture was cooled to RT and left undisturbed for 24–48 h to allow for slow crystallization of the product. The precipitate was filtered off and then recrystallized from $CHCl_3$ and DMSO. The resulting orange crystals were washed with EtOH and dried under high vacuum to give 300 mg (16%) of compound **3**. M.p.: >300 °C; ^{1}H NMR (500 MHz, CF_3COOD): δ = 3.42 (s, 12H; NCH_3), 6.98 (d, J = 16.5 Hz; CH=CH), 7.67, 7.79 (AA′BB′, J = 7.8 Hz, 8H; C_6H_4), 7.93 (s, 2H; benzobisimidazole), 7.96, 8.08 (AA′BB′, J = 7.8 Hz, 8H; C_6H_4), 8.17 ppm (d, J = 16.5 Hz; CH=CH), NH_2 signal was not detected; ^{13}C NMR (125 MHz, CF_3COOD): δ = 49.3, 100.7, 110.8, 123.3, 129.1, 131.9, 133.3, 134.9, 135.9, 138.1, 146.4, 149.1, 153.9 ppm; UV/Vis (CH_2Cl_2): λ (ε) = 437 (3.26), 301 nm (1.34×10^{-4} dm^{3}mol^{-1}cm^{-1}); emission max: 488 nm; IR (KBr): $\tilde{\nu}$ = 811, 1184, 1363, 1433, 1518, 1606 cm^{-1}; HRMS (ESI): m/z calcd for $C_{40}H_{39}N_8$: 631.3292 [M+H$^+$]; found: 631.3262.

*Synthesis of Compound **4***

A mixture of Bandrowski′s base (1.27 g, 4 mmol) and 3-(tris-isopropylsilyl)-2-propynal (3.36 g, 16 mmol) in absolute EtOH (60 mL) was heated at reflux for 24 h under an Ar atmosphere. The reaction mixture was cooled to RT and left undisturbed for 24–48 h to allow for slow crystallization of the product. The precipitate was filtered off to give 881 mg of compound **4** as off-white crystals. The supernatant was evaporated with silica and purified by column chromatography on silica gel (CH_2Cl_2 then CH_2Cl_2/MeOH, 98:2) and crystallized from EtOH to give an additional 477 mg of the product. Overall yield: 1.36 g, 48%; M.p.: >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00–1.02 (m, 42H; CH(CH_3)$_2$), 3.89 (s, 4H; NH_2), 6.80, 7.28 (AA′BB′, J = 8.6 Hz, 8H; C_6H_4), 7.52 ppm (s, 2H; benzobisimidazole); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.1, 18.4, 96.1, 99.0, 99.3, 115.3, 126.4, 127.9, 134.2, 138.3, 141.4, 146.9 ppm; IR (KBr): $\tilde{\nu}$ = 740, 1361, 1428, 1518, 1627, 2161, 2864, 2942, 3215, 3339 cm^{-1}; HRMS (ESI): m/z calcd for $C_{42}H_{56}N_6NaSi_2$: 723.3997 [M+Na$^+$]; found: 723.4027.

*Synthesis of Compound **5***

Alkyne **4** (881 mg, 1.25 mmol) was dissolved in THF (30 mL) and TBAF (1 M solution in THF, 3 mL, 3 mmol) was added whilst stirring. A heavy, amorphous precipitate was immediately formed. After 1 h, the solvent was removed under reduced pressure and the residue was triturated with MeOH, thereby yielding fine crystals that were filtered off and washed with plenty of MeOH. This product was not further purified owing to its low solubility in common organic solvents and was subjected in this form to Pd-catalyzed coupling reactions. ^{1}H NMR (500 MHz, CF_3COOD): δ = 4.34 (s; CCH), 7.98, 8.04 (AA′BB′, J = 8.7 Hz, 8H; C_6H_4), 8.15 ppm (s, 2H; benzobisimidazole), NH_2 signal was not detected; ^{13}C NMR (125 MHz, CF_3COOD): δ = 66.1, 101.4, 102.0, 128.7, 131.1, 132.1, 134.8, 135.0, 135.1, 138.4 ppm; HRMS (ESI): m/z calcd for $C_{24}H_{17}N_6$: 389.1509 [M+H$^+$]; found: 389.1518.

Acknowledgements

Financial support from the Foundation for Polish Science (Grant no. TEAM/2009-4/3) is gratefully acknowledged.

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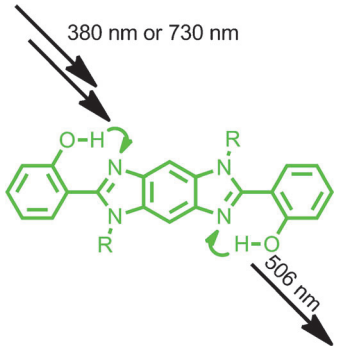
Received: June 18, 2012
Published online: ■■ ■■, 0000

FULL PAPER

Or dye trying: Strongly fluorescent benzobisimidazoles were prepared by the reactions of Bandrowski's base with various aldehydes. Their properties were carefully tuned to achieve efficient excited-state intramolecular proton transfer and strong two-photon absorption. Their superb optical properties, in addition to the presence of two reactive amino groups, make them good candidates to be transformed into probes for bioconjugation.



Functional Dyes

Mariusz Tasior, Vincent Hugues, Mireille Blanchard-Desce, Daniel T. Gryko** _____ ▮▮▮▮–▮▮▮▮

Benzo[1,2-*d*:4,5-*d*′]bisimidazoles as a Convenient Platform Towards Dyes that are Capable of Excited-State Intramolecular Proton Transfer and of Two-Photon Absorption

