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The first route towards pyrrolo[3,2-*b*]pyrroles possessing two azulene moieties at positions 2 and 5 has been developed. The key step of this approach is the three-step transformation of pyridine scaffolds into azulene *via* sequential *N*-arylation followed by ring-opening and reaction with cyclopentadiene. The resulting quadrupolar acceptor-donor-acceptor compounds possess interesting optical properties such as bathochromically shifted absorption with the magnitude of the red-shift strongly depending on linkage position. Two-photon absorption of these functional dyes differs markedly from previously described pyrrolo[3,2-*b*]pyrroles. The experimental optical spectra have been rationalized using Time-Dependent Density Functional Theory calculations of both linear and non-linear optical properties.

#### Introduction

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Azulene, as the most known non-alternant aromatic hydrocarbon, attracts significant attention ever since its discovery.<sup>1</sup> Its polarized structure, being an exception to the Kasha's rule, and bathochromically shifted absorption have become particularly interesting at the time of rise of the interest in polycyclic aromatic hydrocarbons<sup>2</sup> and their heterocyclic analogs.<sup>3</sup> Photophysics,<sup>4</sup> chemistry<sup>5</sup> and applications<sup>6</sup> of azulene derivatives were intensively investigated during the last decades. Many azulenes conjugated with other aromatic scaffolds have been obtained<sup>7</sup> including porphyrinoids.<sup>8</sup>

Pyrrolo[3,2-*b*]pyrroles<sup>9</sup> are a class of nitrogen containing heterocycles that are one of the most  $\pi$ -electron-rich systems. New methods for the synthesis of both pyrrolo[3,2-*b*]pyrroles<sup>10</sup> and their  $\pi$ -expanded analogs<sup>11</sup> induced a renaissance<sup>12</sup> in the chemistry of these previously elusive compounds.<sup>13</sup> The very electron-rich pyrrolo[3,2-*b*]pyrrole core is a valuable building block in the synthesis of acceptor-donor-acceptor systems,<sup>14</sup> possessing interesting optical properties. We have previously proven that for 2,5-diphenyl-pyrrolo[3,2-*b*]pyrroles, the interaction between all segments of the molecule through biaryl linkage is rather strong

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Figure 1. Formal resonance forms of azulene-containing pyrrolo[3,2-b]pyrrole derivatives.

and intramolecular charge transfer occurs both in quadrupolar and in dipolar compounds of this family.<sup>15</sup> As a result, the character of chemical groups attached to the phenyl substituents strongly affects the photophysical properties of these molecules.<sup>14,15</sup> Inspired by these observations, we decided to synthesize pyrrolo[3,2-*b*]pyrroles possessing azulene moiety linked to the core *via* electron-deficient seven-membered ring (Fig. 1). We reckoned that the introduction of azulene moieties into pyrrolo[3,2-*b*]pyrrole framework can largely modify its photophysical properties as azulene possesses a charge separated structure.

### **Results and discussion**

Conceptually the simplest strategy leading to the targeted dyes would be use of our tandem process where aromatic amines, aromatic aldehydes and butano-2,3-dione are combined to form tetraaryl-pyrrolo[3,2-*b*]pyrroles (TAPPs). However, the substrates essential for the synthesis of the desired dyes, *i.e.*, azulene derivatives containing aldehyde groups are either not readily accessible (azulene-6-carboxaldehyde),<sup>16</sup> substituted azulene-5-carboxaldehydes<sup>17</sup>

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or even unknown (unsubstituted azulene-5-carboxaldehyde). Additionally, we found that the easily available 1-formyl-3,8-dimethyl-5-(2-propyl)azulene<sup>18</sup> did not form Schiff's bases with aromatic amines and hence no conversion towards TAPP derivatives was monitored. Faced with these two difficulties we came up with an alternative strategy in which azulene moieties are built after assembling pyrrolo[3,2-*b*]pyrrole core. This pathway towards azulene initially described by Jutz and Schweiger,<sup>19</sup> requires TAPPs substituted with pyridine moieties, as starting material.

Though compound **4a** was previously described,<sup>20</sup> it was obtained with 1% yield only. We found, that the reaction yield can be significantly increased by the following modification of the synthetic procedure: first the formation of a Schiff base in the neat, followed by tandem reaction with butane-2,3-dione



Figure 2. Identified reaction products in synthesis of TAPP 4b.



Figure 3. Molecular structure of **4bbb** based on X-ray diffraction analysis.

under the acidic catalysis. This approach allowed us to obtain isomeric pyrrolo[3,2-b]pyrrole derivatives 4a and 4b in 19% and 11% yields, respectively (Scheme 1). The synthesis of the 4b illustrates the complexity of the TAPP formation reaction. Indeed, after a work-up analogous to the one used for 4a, compound 4b was separated in the form of the 1:1 mixture with its reduced form 4bb (Figure 2) by the column chromatography. Besides compounds 4b and 4bb, a side-product of this reaction has been separated (Figure 2). Heterocycles 4b, 4bb and 4bbb present reaction yields of 15%, 11% and 6%, respectively. A set of analytical data including mass spectrometry, NMR spectroscopy (COSY, NOESY, HSQC, HMBC) and X-ray diffraction<sup>‡</sup> prove the structure of product **4bbb** (Figures 2-3). To allow further modifications, the pyridine derivatives 4a and 4b were arylated by the Zincke reaction<sup>21</sup> to form pyridinium salts 5a and 5b in 90% and 41% yields, respectively. The pyridinium ring system was opened by treating with a solution of dimethylamine in methanol to form functional analogues of glutaconaldehyde 6a and 6b in the form of iminium salts (Scheme 2).

Though the ESI-MS spectra of compounds **6a** and **6b** show peaks corresponding with disalts, NMR spectroscopy at RT did not confirm the structure as the spectra of these compounds showed broad non-resolved signals. The most likely reason of this outcome is the flexibility of the terminal chains that undergo the free rotation at RT. Indeed, the peaks are getting narrower with increasing the temperature of the measurement. At 80°C, the NMR spectrum of **6b** shows resolved peaks corresponding to the expected chemical structure (Scheme 2). Similarly to the previous reports,<sup>19</sup> salts **6a** and **6b** showed a sufficient reactivity towards cyclopentadiene to form azulene derivatives of pyrrolo[3,2-*b*]pyrrole **7a** and **7b** using the two-step process.

The UV/Vis spectra of the azulene derivatives **7a** and **7b** display some similarities with the classical TAPP molecules,<sup>10,15,22-24</sup> however as expected, the presence of terminal azulene rings introduces a new electronic transition. Indeed, the absorption spectra of compounds **7a,b** show several electronic transitions: the short wavelength band

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Scheme 2. The synthetic transformation of heterocycles **4a** and **4b** into the bisazulenyl TAPPs **7a,b**.

(around 290 nm) and the weak band at ca. 600-700 nm corresponding to the azulene  $\pi$ -system (Figure 4) whereas the sharp bands in the visible domain are attributed to the TAPP chromophore (see also theoretical calculations below). In particular in both cases the main band is bathochromically shifted versus 1,2,4,5-tetraryl-TAPPs lacking electronwithdrawing substituents where it is typically located ~350 nm.  $^{10,15,23,24}$  The  $\lambda_{\text{max}}$  of the TAPP related bands on the spectrum depends on the structure of the TAPP derivatives as the diverse positions in the azulene system drastically alter the effects. Indeed, dye 7a shows a TAPP band around 420 nm, while in case of the compound **7b** the TAPP is strongly redshifted ( $\lambda_{max}$ = 504 nm) partially masking the azulene transition at long wavelengths (Figure 4). Compounds 7a and 7b do not exhibit any fluorescence at room temperature.

As stated in the Introduction, the azulene ring system is characterized by a polarized structure with the electron-rich five-membered and the electron-deficient seven-membered rings.<sup>25</sup> We found that the addition of the strong acid into the



Figure 4. Absorption spectra of compounds 7a (black) and 7b (red) in DCM.

solutions of compounds **7a,b** gives rise to the protonation of the position 1 in the azulene ring (Scheme 3). This protonation process was observed by means of electronic spectroscopy (Figure 5). On the addition of the excess of trifluoroacetic acid in DCM the spectral band corresponded to the TAPP system weakened in favor of the long wavelength band. We found that the above-mentioned effect is reversible, as after approaching the saturation the addition of triethylamine causes the growth of the TAPP band along with diminishing the long wavelength absorption.

The protonation process was also monitored by the NMR spectroscopy (Figure 6). Upon the addition of deuterated trifluoroacetic acid to a  $CD_2Cl_2$  solution of compound **7b**, the NMR spectrum shows the formation of tropylium system at one azulene ring system (NMR monitored protonation of **7a** is available in the ESI).

As chromophores **7a,b** present a polarized quadrupolar structure, their nonlinear optical properties were studied. In particular, two-photon absorption cross-section ( $\sigma_2$ ) values were determined in CH<sub>2</sub>Cl<sub>2</sub> using Z-scan technique. As both compounds are centrosymmetric, their two-photon absorption (2PA) maxima are not expected to correspond to twice their linear optical absorption maxima, as theoretically



Scheme 3. Reversible protonation of compounds 7a,b

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predicted<sup>26</sup> and seen in the experimental spectra for other centrosymmetric molecules obtained by Z-scan<sup>27</sup> or twophoton excited fluorescence (TPEF).<sup>28</sup> This is indeed what is observed in our case (Figure 7). In case of **7a**, the 2PA spectrum does not present very distinct peaks in the 800-1200 nm region, which contrasts with **7b**. One can nevertheless distinguish three peaks, centered at 875, 975 and 1150 nm, with  $\sigma_2$  being ca. 400 and 250 GM. Moreover, **7a** shows non-zero 2PA in 1200-1600 nm region with  $\sigma_2$  being in the range 100-200 GM. The features in this spectral range correspond crudely to the 1PA peaks in 500-800 nm. In contrary to **7a**,



Figure 6. <sup>1</sup>H NMR observed protonation of compound **7b** in CD<sub>2</sub>Cl<sub>2</sub>.



Figure 7. 2PA cross-sections (red) of compounds 7a and 7b plotted vs. Laser wavelength overlaid with linear absorption (black) plotted vs. 1 $\lambda.$ 

the 2PA spectrum of 7b presents three distinctive peaks, centered at 875, 950 and 1200 nm. The most intense band of two-photon absorption is centered at 875 nm, with a 2PA crosssection,  $\sigma_2$ , around 500 GM. The 2PA cross-section at 950 nm is smaller (ca. 200 GM). Finally, the third distinctive band is located at 1200 nm and the corresponding  $\sigma_2$  is also close to 200 GM. It seems that there is non-zero absorption at wavelength longer than 1300 nm, but one needs to keep in mind that the error bars of these measurements are quite big. It is noteworthy to add that the 2PA spectra of dyes 7a and 7b are distinctly different than analogous spectra for all other previously studied TAPPs, which possess only one broad signal with maximum ca. 700 nm and tail reaching no more than 900 nm.<sup>15a</sup> This difference results from the azulene group working as an electron acceptor substituent. It is worth to mention that, thanks to strong charge-transfer, the 2PA spectrum is not only expanded to longer wavelengths, but also the values of twophoton absorption cross-sections are higher than those reported for TAPP molecules end-capped with other moieties.15a

Let us now turn to theoretical calculation. According to DFT, the ground-state twisting angle between the azulene moieties and pyrrolopyrrole groups are similar for both **7a** (40.6°) and **7b** (41.8°) indicating a moderate conjugation between the both moieties. That means that conjugation is similar to that of 2,5-diphenyl-pyrrolo[3,2-b]pyrroles where the twisting angles were found to be 35.6° *via* X-ray crystallography.<sup>15a</sup> For both dyes, theory foresees three low-lying excited-states. The

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Figure 8: Representation of the density difference plots for the three lowest-lying states of **7a** (top) and **7b** (bottom) compounds. The blue (red) regions indicate decrease (increase) of electron density upon absorption. Contour threshold: 0.008 au.

two first consists in energetically nearly-degenerated transitions, one being weakly-allowed and one being dipoleforbidden. These two excited-states are mainly localized on the azulene moieties (see Figure 8), though the TAPP parts play a minor role in 7a. The third excited-states are strongly dipoleallowed and are more delocalized on the  $\pi$ -conjugated path: they present a partial charge-transfer character, the TAPP playing the role of the donor and the azulene moieties the role of the acceptor. According to Figure 8, one notes a stronger delocalization in 7b compared to 7a for this third state. To quantify the intensity of the CT between the azulene and TAPP, we have determined the amount of transferred charged,  $q^{CT}$ using a well-known model.<sup>29</sup> The  $q^{CT}$  attains 0.49 e in **7a** but 0.66 e in 7b, indicating a significantly stronger (+35%) chargetransfer in the latter dye. In all three excited-states the tolyl substituents do not play any role.

In Table 1, we report the vertical transition energies and oscillator strengths determined with TD-DFT for both **7a** and **7b**. Though one notes the expected blueshift of the theoretical values compared to experiment (this is due to the selected functional, see experimental section), the trends are nicely reproduced. First, the azulene band is rather intense (f=0.08) and well separated from the intense  $S_3$  band ( $\Delta$ =0.95 eV) in **7a**. In contrast, in **7b**, this azulene band is four times weaker (f=0.02) and closer to the very intense absorption ( $\Delta$ =0.46 eV), which explains why it is almost unseen experimentally (see Figure 4): it is hidden by the strong absorption.

Table 1: Vertical transition wavelength (in nm) and oscillator strengths for thethree lowest states of 7a and 7b and their protonated forms.

Second, the strong visible band becomes more intense (±50%) and is bathochromically shifted (-0.40 eV) When going From 77a to 7b and these trends clearly follow experimental data (+57% and -0.48 eV, see Figure 4). The variations of the positions of the absorption bands in the two compounds follow well the delocalization of the corresponding excited-states shown in Figure 8 as well as the intensity of the CT between azulene moieties and TAPP (see above): the strong redshift of the TAPP band in 7b is thus related to a stronger interaction and CT with the azulene groups compared to 7a. Upon protonation of the azulene, one notices on Table 1, a very strong redshift of the dipole-allowed band is obtained in both dyes. In 7a + H<sup>+</sup> the two first states are strongly-allowed, which fits the broad band noticed in Figure 5 whereas in 7b + H<sup>+</sup> only the second singlet state is strongly-allowed, which explains the sharper absorption. We also underline that theory foresees that the strong difference between the positions of the intense visible bands in the neutral forms are strongly decreased in the protonated forms, consistently with experiment.

No emission was observed experimentally from these two molecules. In unsubstituted azulene, it is well-known that fluorescence originates from the second excited-state, a violation of Kasha's empirical rule related to the large gap between the second and first singlet excited-states. However, in 7a and 7b, these two 'azulene' states are bracketing a dipoleallowed TAPP excited-state, which means that the energetic gap between the excited-states is now small and one can reasonably expect Kasha's rule to be obeyed in both 7a and 7b. We therefore optimized geometry of the two (very close) lowest-lying singlet excited-states and determined the theoretical emission energies. The results are displayed in Table 2. As can be seen the relaxation leads to moderate shifts of the energies and a slight weakening of the oscillator strengths. Following the energy gap law, emission from such low-lying states (< 2.0 eV) is very unlikely. In addition, these states are almost dark which is of course unfavorable for luminescence, which is probably why the emission is not seen here.

TD-DFT calculations have also been performed for the 2PA properties. The  $\sigma_2$  determined for the low-lying azulene-like excited-state is very small in both dyes: 2.3 GM for **7a** and 0.3 GM for **7b**, whereas for the TAPP-centered excited-state, a much higher response is computed: 315 GM for **7a** and 762 GM for **7b**, the relative intensities and magnitudes being in reasonable agreement with the experimental values (see Figure 6), though we do not include vibronic effects here. The calculations therefore indicate that the origin of 2PA is the TAPP moiety, the azulene states providing very small contributions.

	7a			7b			molety, the azulene states providing very small contributions.						
State		λ (nm)	f		λ (nm)	f							
S1	Au	555	0.08	$A_g$	532	0.00	Table 2: Vertical emission wavelength (in nm) and oscillator strengths for the two						
<b>S</b> <sub>2</sub>	$A_g$	551	0.00	Au	532	0.02	iowest states		u <b>75</b> .				
S₃	Au	389	1.09	Au	445	1.68		Meta Para					
		7a + H⁺			7b + H⁺		State		λ <sub>em</sub> (nm)	f		$\lambda_{em}$ (nm)	f
State		λ (nm)	f		λ (nm)	f	<b>S</b> 1	Au	637	0.07	$A_{g}$	626	0.00
<i>S</i> <sub>1</sub>	Α	550	0.77	Α	555	0.01	<b>S</b> <sub>2</sub>	$A_{g}$	632	0.00	Au	626	0.01
<b>S</b> <sub>2</sub>	Α	521	0.58	Α	523	1.52							
C.	Δ	161	0.01	Δ	151	0.08							

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#### Conclusions

We have proved that it is possible to transform 2,5di(pyridyl)pyrrolo[3,2-b]pyrroles into pyrrolo[3,2-b]pyrroles possessing two azulene moieties, using Schweiger strategy. Both regioisomeric 2,5-bis(azulenyl)-pyrrolo[3,2-b]pyrroles behave like acceptor-donor-acceptor quadrupolar dyes. Linking heterocyclic core with azulene at position 6 leads to compound with much stronger conjugation, which leads to bathochromically shifted absorption band. In contrast, linkage at position 5 gives almost no shift as compared with 1,2,4,5tetraphenyl-pyrrolo[3,2-b]pyrrole. This intriguing difference, as proven by computational results is not caused by dihedral angle which is almost the same in both cases. Instead it is the stronger charge-transfer between the azulene moieties and the central pyrrolo[3,2-b]pyrrole in the former cases that induces this large redshift. The difference in the position of the main absorption band of the two dyes can be significantly decreased by protonation. The lack of fluorescence can be rationalized by the presence of low-lying azulene dark states.

#### Experimental

#### Materials

All chemicals were used as received unless otherwise noted. Reagent grade CH<sub>2</sub>Cl<sub>2</sub> was distilled prior to use. All reported <sup>1</sup>H NMR spectra were collected using 500 and 600 MHz spectrometers. Chemical shifts ( $\delta$  ppm) were determined with TMS as the internal reference; J values are given in Hz. Chromatography was performed on silicagel (200-400 mesh). The mass spectra were obtained via electrospray ionization (ESI-MS). Absorption spectra were recorded with PerkinElmer Lambda 25 UV/Vis spectrophotometer. For two-photon absorption measurements the samples of the investigated compounds were dissolved in CH<sub>2</sub>Cl<sub>2</sub> at concentration 0.1 and 0.5% (w/w), respectively, and the solutions were placed in 1 mm path length optical glass cells. The measurements were carried out in a relative manner, calibrating all the data against Z-scans carried out on a fused silica plate and taking into account the nonlinear signals obtained on a cell containing pure solvent.

The tunable excitation was achieved by directing the beam from a Quantronix Integra Ti:Sapphire regenerative amplifier (output wavelength 800 nm, pulse duration 130 fs, repetition rate 1 kHz) to an optical parametric amplifier (OPA, a Quantronix Palitra). The output beam was attenuated using a set of neutral density filters, so that the energy per pulse was on the order of 1  $\mu$ J. The reference, open and close aperture signals were detected by InGaAs detectors, recorded with a digital oscilloscope and transferred to a computer using custom-written LabView software.

#### Theory

All (TD-)DFT calculations have been performed using the Gaussian 09.D01 program,<sup>30</sup> but the 2PA calculations that were performed with the Dalton code.<sup>31</sup> For the Gaussian calculations, we used tightened self-consistent field (10<sup>-10</sup> a.u.)

#### and geometry optimization (10<sup>-5</sup> a.u.) convergence thresholds, and a large DFT integration grid (so-called ultrafine grid, 6a pruned 99,590 grid). The linear optical spectra (TD-)DFT calculations relied on the M06-2X hybrid functional.<sup>32</sup> This functional is known to provide slightly too large transition energies but consistent data (high correlation) with experiment. Following the basis set combination approach proposed elsewhere,<sup>33</sup> we used the 6-31G(d) atomic basis set for determining the geometrical and vibrational parameters whereas the transition energies have been computed with 6-311+G(2d,p). The nature of the ground-state stationary points was confirmed by analytical Hessian calculations that returned 0 (minima) imaginary vibrational modes. Environmental effects (here, dichloromethane) have been accounted for using the linear response (LR) variant of polarizable continuum model (PCM),<sup>34</sup> in its *non-equilibrium* limit for the vertical absorption. For the emission wavelengths, the excited-state structures have been optimized with the LR-PCM in its equilibrium limit, whereas the emission energies have been computed with the corrected LR (cLR)<sup>35</sup> PCM model in its non-equilibrium limit. Excited-states have been represented using density difference plots, in which the excited-state density were determined at the TD-DFT level using the Z-vector approach. In these plots blue and red regions respectively indicate decrease and increase of electron density upon photon absorption. The 2PA calculations have been performed in gas-phase using the rangeseparated CAM-B3LYP functional,<sup>36</sup> that is suited for non-linear optical calculations. We have applied the large 6-311++G(2d,2p) basis set for the 2PA simulations. For more details about the 2PA calculations, we redirect the reader to our previous work.15a

#### Synthetic procedures

#### 2,5-Di(pyridin-3-yl)-1,4-di-*p*-tolyl-1,4-dihydropyrrolo[3,2*b*]pyrrole, 4a

A solution of butane-2,3-dione (0.69 g, 0.7 mL, 8 mmol) in 10 mL of acetic acid was added dropwise to a solution of compound **3a** (3.15 g, 16 mmol) (quantitatively obtained by heating of equimolar amounts of 3-pyridinecarbaldehyde and 4-methylaniline at 120-130°C for 2.5 hours) and dry *p*-toluenesulfonic acid (0.28 g, 1.6 mmol) in 20 mL of acetic acid at 85-90°C. The resulting mixture was heated for additional 3 hours. On cooling the mixture was poured into 200-300 mL of ice-water and the acetic acid was neutralized with NaHCO<sub>3</sub> solution. The crude product was extracted with methylene chloride and the organic phase was dried over MgSO<sub>4</sub>. After evaporation the residue was treated with acetonitrile and compound **4a** was filtered off (0.66 g, yield 19%). The spectral data is identical to the previously described.<sup>19</sup>

#### 2,5-Di(pyridin-4-yl)-1,4-di-*p*-tolyl-1,4-dihydropyrrolo[3,2*b*]pyrrole, 4b

A solution of butane-2,3-dione (0.73 g, 0.75 mL, 8.5 mmol) in 10 mL of acetic acid was added dropwise to a solution of compound **3b** (3.34 g, 17 mmol) (obtained similarly as for **3a**) and dry *p*-toluenesulfonic acid (0.29 g, 1.7 mmol) in 20 mL of acetic acid at 85-90°C. The resulting mixture was heated for

additional 3 hours. On cooling the mixture was poured into 200-300 mL of ice-water and the acetic acid was neutralized with NaHCO<sub>3</sub> solution. The crude product was extracted with methylene chloride and the organic phase was dried over MgSO<sub>4</sub>. After evaporation the residue was treated with diethyl ether and the solid material was filtered off. Crystals were washed with acetonitrile and according to <sup>1</sup>H NMR and ESI-MS spectra the solid material is the mixture consisting of the target product **4b** and its reduced form **4bb** in approximately 1:1 ratio. Compounds **4b** and **4bb** were separated by column chromatography (SiO<sub>2</sub>, eluent: CH<sub>2</sub>Cl<sub>2</sub> (90%)-CH<sub>3</sub>OH (8%)– CH<sub>3</sub>COOH (2%)) to give 0.55 g (yield 15%) of **4b** and 0.42 g (yield 11%) of **4bb**. Chemically pure compound **4bbb** was crystallized from the acetonitrile filtrate during staying in a closed vessel for 3 days (0.25 g, yield 6%).

Characterization data for **4b**: Mp. 306-307°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25°C, TMS): 8.39 (dd, <sup>3</sup>J(H,H) = 4.6 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 4H), 7.23 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 4H), 7.18 (d, <sup>3</sup>J(H,H) = 8.4 Hz, 4H), 7.06 (dd, <sup>3</sup>J(H,H) = 4.6 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 4H), 6.51 (s, 2H), 2.42 ppm (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 149.5, 140.6, 136.8, 136.7, 134.2, 133.6, 130.2, 125.3, 121.6, 95.9, 21.1; HRMS (ESI-TOF): *m/z* calcd for C<sub>30</sub>H<sub>25</sub>N<sub>4</sub>: 441.2079 [MH]<sup>+</sup>; found: 441.2072.

Characterization data for **4bb**: Mp. 252-253°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 8.40 (d, <sup>3</sup>*J*(H,H) = 4.9 Hz, 2H), 8.35 (d, <sup>3</sup>*J*(H,H) = 5.3 Hz, 2H), 7.29 (d, <sup>3</sup>*J*(H,H) = 8.0 Hz, 2H), 7.15 (d, <sup>3</sup>*J*(H,H) = 8.0 Hz, 2H), 7.08 (d, <sup>3</sup>*J*(H,H) = 8.1 Hz, 2H), 6.98 (d, <sup>3</sup>*J*(H,H) = 5.4 Hz, 2H), 6.92-6.86 (m, 5H), 6.69-6.65 (m, 2H), 5.33 (s, 1H), 2.48 (s, 3H), 2.30 ppm (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 149.7, 149.5, 145.6, 142.8, 139.3, 139.0, 135.1, 132.1, 130.31, 130.29, 129.9, 129.0, 128.7, 126.5, 123.5, 121.4, 120.9, 120.0, 115.6, 107.7, 21.3, 20.5 ppm; HRMS (ESI-TOF): *m/z* calcd for C<sub>30</sub>H<sub>27</sub>N<sub>4</sub>: 443.2236 [MH]<sup>+</sup>; found: 443.2228.

Characterization data for **4bbb**: Mp. 177-178°C (dec); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 9.83 (br.s, 2H), 8.65 (dd, <sup>3</sup>*J*(H,H) = 4.4 Hz, <sup>4</sup>*J*(H,H) = 1.5 Hz, 2H), 8.63 (dd, <sup>3</sup>*J*(H,H) = 4.4 Hz, <sup>4</sup>*J*(H,H) = 1.5 Hz, 2H), 7.91 (dd, <sup>3</sup>*J*(H,H) = 4.4 Hz, <sup>4</sup>*J*(H,H) = 1.5 Hz, 2H), 7.91 (dd, <sup>3</sup>*J*(H,H) = 4.4 Hz, <sup>4</sup>*J*(H,H) = 1.5 Hz, 2H), 7.39 (d, <sup>3</sup>*J*(H,H) = 8.3 Hz, 2H), 7.27 (d, <sup>3</sup>*J*(H,H) = 8.2 Hz, 2H), 7.21 (dd, <sup>3</sup>*J*(H,H) = 4.4 Hz, <sup>4</sup>*J*(H,H) = 1.7 Hz, 2H), 7.13 (s, 4H), 5.94 (s, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 1.80 ppm (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 178.1, 171.3, 170.3, 150.5, 149.7, 144,2, 139.2, 137.3, 137.1, 136.9, 132.6, 130.2, 130.1, 127.9, 123.6, 122.6, 122.4, 97.0, 91.1, 24.5, 21.2, 21.1 ppm; HRMS (ESI-TOF): *m/z* calcd for C<sub>24</sub>H<sub>24</sub>N<sub>3</sub>O: 370.1919 [MH]<sup>+</sup>; found: 370.1911; Anal. Calcd. for C<sub>24</sub>H<sub>23</sub>N<sub>3</sub>O×C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (491.58): C, 73.15; H, 5.73; N, 11.37; Found: C, 73.16; H, 5.71; N, 11.40.

#### 3,3'-(1,4-Di-*p*-tolyl-1,4-dihydropyrrolo[3,2-*b*]pyrrole-2,5diyl)bis(1-(2,4-dinitrophenyl)pyridin-1-ium) dichloride, 5a

Compound **4a** (0.66 g, 1.5 mmol) and 2,4-dinitrochlorobenzene (3.04 g, 15 mmol) were heated at 130-140°C for 3 hours. On cooling the product was solidified with CH<sub>2</sub>Cl<sub>2</sub> to give 1.15 g (90%) of pure product. Mp. 232-233°C; <sup>1</sup>H NMR (500 MHz, CF<sub>3</sub>COOD, 25°C, TMS):  $\delta$  = 9.23 (s, 2H), 8.78 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 2H), 8.62 (br.s, 2H), 8.55 (d, <sup>3</sup>J(H,H) = 4.0 Hz, 2H), 8.42 (dd, <sup>3</sup>J(H,H) = 9.0 Hz, <sup>4</sup>J(H,H) = 2.5 Hz, 2H), 8.12-8.02 (m, 4H), 7.34 (d, <sup>3</sup>J(H,H) = 6.5 Hz, 4H), 7.23 (br.s, 4H), 2.43 ppm (s, 6H); <sup>13</sup>C NMR (125 MHz, CF<sub>3</sub>COOD, 25°C, TMS):  $\delta$  = 152.3, 146.9, 145.2, 143.9,

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## 142.7, 142.0, 141.0, 138.4, 137.7, 136.7, 135.5, $133_{A_{icl}} 3_{A_{icl}} 3$

4,4'-(1,4-Di-*p*-tolyl-1,4-dihydropyrrolo[3,2-*b*]pyrrole-2,5diyl)bis(1-(2,4-dinitrophenyl)pyridin-1-ium) dichloride, 5b

Compound **5b** was synthesized analogously to **5a** (yield 91%). The 1:1 mixture of compounds **4b** and **4bb** (preparation of **4b**) can be used in this method without separation. In this case the reaction yield of product **5b** decreases to 41%. Mp. 250°C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, 25°C, TMS):  $\delta$  = 9.09 (d, <sup>3</sup>*J*(H,H) = 2.5 Hz, 2H), 9.03 (d, <sup>3</sup>*J*(H,H) = 7.2 Hz, 4H), 8.93 (dd, <sup>3</sup>*J*(H,H) = 8.7 Hz, <sup>4</sup>*J*(H,H) = 2.5 Hz, 2H), 8.38 (d, <sup>3</sup>*J*(H,H) = 8.7 Hz, 2H), 7.97 (d, <sup>3</sup>*J*(H,H) = 7.1 Hz, 4H), 7.62 (s, 2H), 7.48 (s, 8H), 2.45 ppm (s, 6H); <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, 25°C, TMS):  $\delta$  = 148.8, 147.8, 144.3, 143.2, 138.8, 138.4, 138.2, 135.2, 135.0, 131.9, 130.9, 130.1, 125.8, 122.2, 121.5, 102.7, 20.6 ppm; HRMS (ESI-TOF): *m/z* calcd for C<sub>42</sub>H<sub>30</sub>N<sub>8</sub>O<sub>8</sub><sup>2+</sup>: 387.1088 [M]<sup>2+</sup>; found: 387.1098. *N*,N'-((2,2',4,4')-(1,4-Di-*p*-tolyl-1,4-dihydropyrrolo[3,2-

### *b*]pyrrole-2,5-diyl)bis(5-(dimethylamino)penta-2,4-dien-2-yl-1-ylidene))bis(*N*-methylmethanaminium)

dihexafluorophosphate, 6a

A solution of dimethylamine in methanol (2M, 3 mL, 6 mmol) was added to the suspension of compound **5b** (0.85 g, 1 mmol) in 25 mL of methanol (HPLC grade) and the mixture was stirred at ambient temperature for 3 hours in a closed flask. After the evaporation of methanol and dimethylamine the residue was dissolved in ethanol, the solid material was removed by the filtration. Ethanol solution containing 500 mg of NH<sub>4</sub>PF<sub>6</sub> and 2 mL of water was added to the filtrate to precipitate of compound **6a** in a form of dihexafluorophosphate (0.57 g, 65%). Mp. 180°C; HRMS (ESI-TOF): m/z calcd for C<sub>38</sub>H<sub>48</sub>N<sub>6</sub><sup>2+</sup>: 294.1965 [M]<sup>2+</sup>; found: 294.1974.

#### N,N'-((2,2',4,4')-(1,4-Di-*p*-tolyl-1,4-dihydropyrrolo[3,2b]pyrrole-2,5-diyl)bis(5-(dimethylamino)penta-2,4-dien-3-yl-

1-ylidene))bis(N-methylmethanaminium) diperchlorate, 6b A solution of dimethylamine in methanol (2M, 0.57 mL, 1.13 mmol) was added to the suspension of compound 5b (0.16 g, 0.19 mmol) in 25 mL of methanol (HPLC grade) and the mixture was stirred at ambient temperature for 3 hours in a closed flask. The solvent was evaporated and the crude product was solidified with water and filtered off. The solid material was dissolved in ethanol and the pure product was precipitated by the addition of the ethanol solution containing 170 mg of NaClO<sub>4</sub>×H<sub>2</sub>O. Yield 0.072 g (48%). Mp. 280°C (dec); <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, 80°C, TMS):  $\delta$  = 7.56 (d, <sup>3</sup>J(H,H) = 11.6 Hz, 4H), 7.28 (d, <sup>3</sup>J(H,H) = 8.6 Hz, 4H), 7.26 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 4H), 6.58 (s, 2H), 5.68 (d, <sup>3</sup>J(H,H) = 11.9 Hz, 4H), 3.3-2.9 (m, 18H), 2.36 (s, 6H), 1.90 ppm (s, 6H); <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, 80°C, TMS):  $\delta$  = 171.0, 157.7, 157.1, 135.9, 135.8, 133.2, 129.3, 123.9, 100.1, 20.3, 20.0 ppm; HRMS (ESI-TOF): m/z calcd for C<sub>38</sub>H<sub>48</sub>N<sub>6</sub>: 294.1965 [M]<sup>2+</sup>; found: 294.1974.

#### 2,5-Di(azulen-5-yl)-1,4-di-*p*-tolyl-1,4-dihydropyrrolo[3,2*b*]pyrrole, 7a

Compound **6a** (0.88 g, 1 mmol), cyclopentadiene (0.26 g, 4 mmol) and sodium *tert*-butoxide (0.19 g, 2 mmol) in 5 mL of dry pyridine was stirred at RT overnight. After that, the mixture was

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heated at 80°C for additional 3 hours. The solvent was evaporated and the residue was eluted through the silica column (CH<sub>2</sub>Cl<sub>2</sub>-cyclohexane 1:1) to yield 0.026 g (5%) of the title compound. Mp. 296-297°C (dec); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 8.50 (d, <sup>4</sup>/(H,H) = 1.1 Hz, 2H), 8.19 (d, <sup>3</sup>/(H,H) = 9.5 Hz, 2H), 7.84 (t, <sup>3</sup>/(H,H) = 3.7 Hz, 2H), 7.58 (br.d, 2H), 7.31 (d, <sup>3</sup>/(H,H) = 3.4 Hz, 2H), 7.24-7.20 (m, 6H), 7.13 (d, <sup>3</sup>/(H,H) = 8.2 Hz, 4H), 6.99 (t, <sup>3</sup>/(H,H) = 10.0 Hz, 2H), 6.52 (s, 2H), 2.34 ppm (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 140.0, 139.3, 138.9, 138.0, 137.9, 137.3, 135.4, 135.1, 131.8, 129.9, 128.2, 125.0, 121.9, 119.0, 117.8, 95.7, 21.0 ppm; HRMS (ESI-TOF): *m/z* calcd for C<sub>40</sub>H<sub>30</sub>N<sub>2</sub> (538.69): C, 89.19; H, 5.61; N, 5.20; Found: C, 89.19; H, 5.67; N, 5.07.

#### 2,5-Di(azulen-6-yl)-1,4-di-*p*-tolyl-1,4-dihydropyrrolo[3,2*b*]pyrrole, 7b

The product was synthesized analogously to compound **7a** in 40% yield. Mp. >350°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 8.14 (d, <sup>3</sup>J(H,H) = 10.6 Hz, 4H), 7.77 (t, <sup>3</sup>J(H,H) = 3.7 Hz, 2H), 7.27 (d, <sup>3</sup>J(H,H) = 3.7 Hz, 4H), 7.22-7.18 (m, 8H), 7.15 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 4H), 6.59 (s, 2H), 2.36 ppm (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 142.2, 140.5, 138.3, 137.2, 136.0, 135.7, 135.3, 133.7, 130.0, 125.0, 123.6, 118.2, 97.6, 21.0 ppm; HRMS (ESI-TOF): *m/z* calcd for C<sub>40</sub>H<sub>31</sub>N<sub>2</sub>: 539.2487 [MH]<sup>+</sup>; found: 539.2484; Anal. Calcd. for C<sub>40</sub>H<sub>30</sub>N<sub>2</sub> (538.69): C, 89.19; H, 5.61; N, 5.20; Found: C, 89.06; H, 5.48; N, 5.06.

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### Notes and references

**‡** X-ray crystallographic data for **4bbb**. CCDC 1496153. Formula: C<sub>24</sub>H<sub>23</sub>N<sub>3</sub>O×C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>,  $M_w$  = 492.56; monoclinic, P 2<sub>1</sub>/c; *a* = 9.7023(13) Å, *b* = 19.694(3) Å, *c* = 13.7791(18) Å; *V* = 2576.3(6), Å<sup>3</sup>, *Z* = 4; *D<sub>c</sub>* = 1.270 g cm<sup>-3</sup>; *R*<sub>1</sub> = 0.0975 (*I* > 2*σ*(*I*)), *wR*<sub>2</sub> = 0.1746 (all data), GOF = 0.989.

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#### Table on contents graphic:

Linking pyrrole[3,2-b]pyrrole core with azulene moieties leads to dyes possessing strong absorption of visible light, no emission and reach two-photon absorption spectra.

сно Ar 5 steps N Ν Ar/  $\lambda_{max}$  = 504 nm

 $\lambda_{2PA} = 875 \text{ nm} (500 \text{ GM})$