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## SYNTHESIS AND OPTICAL PROPERTIES OF SUBSTITUTED 5,6,7,8-TETRAAZA-AZULENO[1,8-*b,c*]FLUORENES, SMALL ORGANIC MOLECULES OF UNUSUAL TOPOLOGY DESIGNED FOR CIRCULARLY POLARIZED LUMINESCENCE

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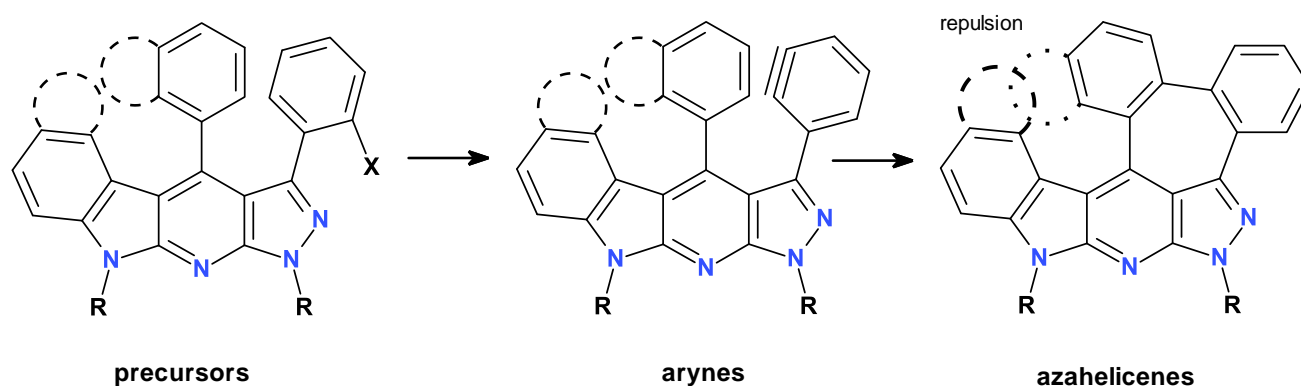
Dedicated to Professor Herbert Mayr on the occasion of his 75th birthday

**Abstract** – Helical photoluminescent substituted 5,6,7,8-tetraaza-azuleno[1,8-*b,c*]fluorenes were obtained as racemates. The compounds have been designed for circularly polarized luminescence. Some of the compounds were separated on to enantiomers with chiral HPLC column and showed Cotton effects in absorption and emission spectra. The experimental results were compared with DFT calculations, which led us to assess the chirality to structure.

### INTRODUCTION

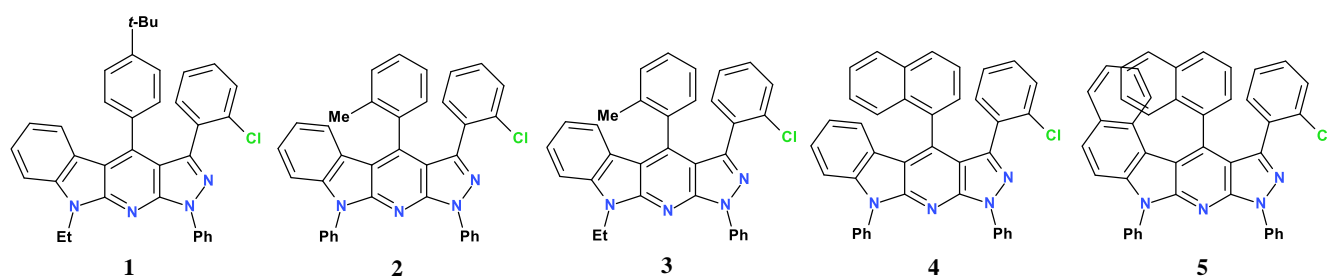
Circularly polarized light (CPL) is of great importance in science and photonic technologies.<sup>1</sup> There are two main methods to generate a polarized light output from OLED, either from chiral polymers being the active layer or via a chiral small-molecule dopant.<sup>2</sup> Recently the 4f-based metal complexes with strong CPL emission have been recognized as candidates for potential technological applications. However the difficulties with obtaining of highly pure samples and significant production costs stunt progress in this case.<sup>3</sup> Thus chiral luminescence organic molecules are essential for development in advance photonic technology. In comparison to a plethora of available OLED candidates,<sup>4</sup> the number of the circularly

polarized light emitting compounds, thermally and chemically stable, is still not outstanding. In former works we described the synthesis and spectral properties of azafluoranthene and heteroazulene derivatives.<sup>5</sup> Specially, the second group of compounds has focused our attention, as they contained helical arrangements of four *ortho*-fused rings. Their helicity is the result of steric repulsion between hydrogen atoms in “fiord” regions as well as the demanding geometry imposed by the seven-membered ring embedded in the main framework of the molecules. Additionally, conjugated polycyclic hydrocarbons containing seven-membered rings have been rarely explored, this has prompted us to focus our effort on the synthesis of azulene-fluorene-like helical structures. It is worth to admit, merging of seven-membered rings in terms of the application of carbon materials to organic electronics, may become a key factor.<sup>6</sup> The advantage of being intrinsically helical and the choice between their right-handed and left-handed enantiomeric forms, make azahelicenes attractive candidates in CPL technology. To fulfil the criteria of satisfying operational parameters must be considered sufficient high racemisation barrier when designing the active molecule. Our earlier findings delivered helicenes of a low racemisation barrier,<sup>7</sup> thus excluding them from the construction of CPL emitting devices. Therefore we decided to hinder the quick inversion of enantiomers either by introducing an additional fused ring or a bulky group. In this study we describe the synthesis of racemic mixtures and their separation into enantiomers, as well as the optical properties of novel heterocycles - substituted 5,6,7,8-tetraaza-azuleno[1,8-*b,c*]fluorenes, helical compounds – of unusual topology. The precursors are derived from substituted pyrazolo[3,4-*b*]pyridines. The idea is that an aryne generated during elimination/addition reaction of halogens attacks the intramolecular neighbouring ring to form aza[5 or higher]helicenes. In this study we present preliminary results in helical tetraaza-azuleno-fluorenes investigations and, have focused our attention on  $\alpha$ -carbolins as the starting compounds, which were obtained in a one-pot, three component cascade reaction.<sup>8</sup>

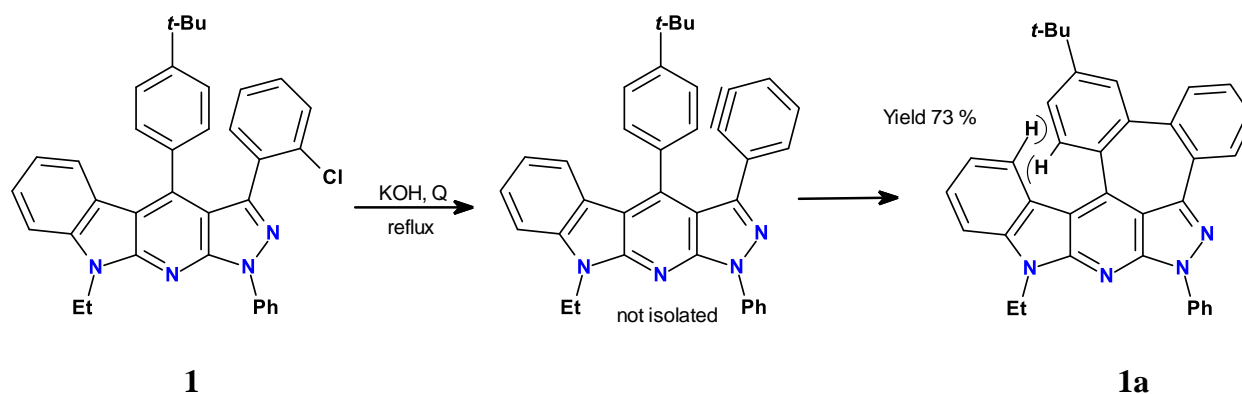


## RESULTS AND DISCUSSION

The  $\alpha$ -carbolines **1-5** with the structures drawn below as precursors for the synthesis of tetraaza-azulene-fluorenes **1a-5a**, were obtained in a one-pot, three component cascade reaction from appropriate substituted indolinone, arylaldehyde and 5-(2-chlorophenyl)-2-phenylpyrazol-3-amine in ionic liquid Br [Bmim] as the solvent and *para*-toluenesulfonic acid as catalyst at 140 °C, as described by Bazgir *et al.*<sup>8</sup> Many examples of application of this reaction in more multicomponent variations can be found in ref 8b. (see also Supp. Inf. for more details)



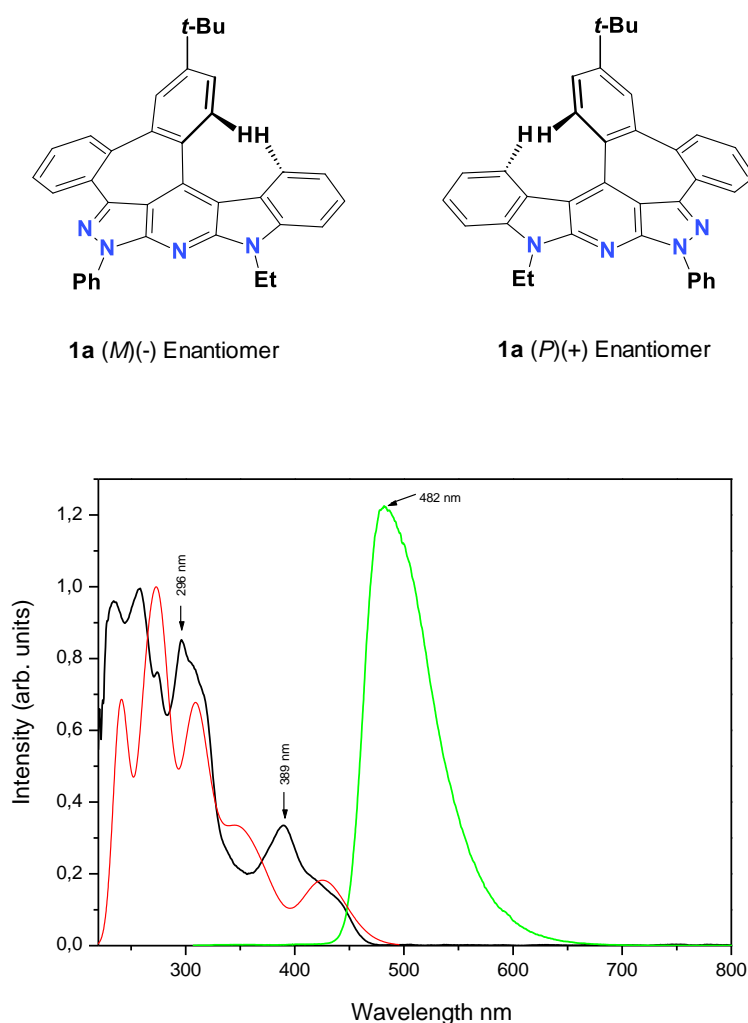
Thus, the compound **1a** (*M*)(*P*)( $\pm$ )-15-*tert*-butyl-8-ethyl-6,8-dihydro-6-phenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b,c*]fluorene obtained from the precursor **1** (Scheme 1) does not show diastereotopic differentiation at CH<sub>2</sub> protons of the ethyl group in <sup>1</sup>H-NMR spectrum. The compound shows absorption in UV-Vis spectrum at  $\lambda_{\max}$  = 389 nm and emission (PL) at  $\lambda_{\max}$  = 482 nm (Figure 1).



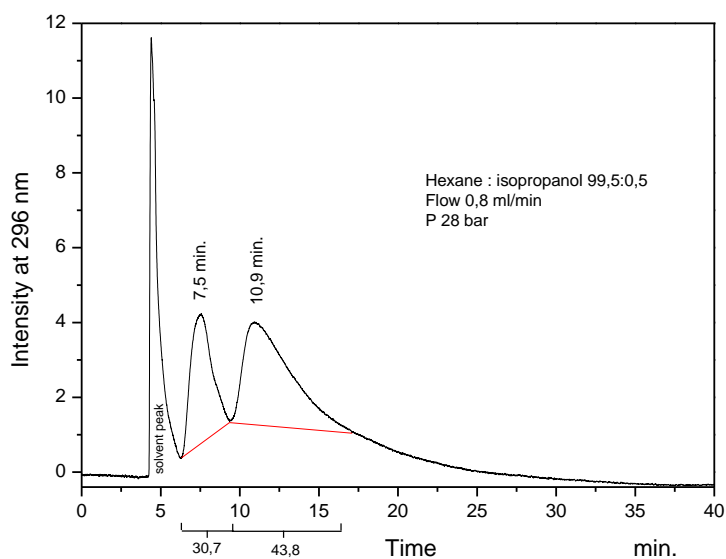
**Scheme 1.** Synthesis of (*M*)(*P*)( $\pm$ )-15-*tert*-butyl-8-ethyl-6,8-dihydro-6-phenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b,c*]fluorene

Calculated UV-Vis spectrum gave absorption maxima at  $\lambda_{\max}$  = 425 nm and  $\lambda_{\max}$  = 347 nm, and correspondingly, PL at  $\lambda_{\max}$  = 526 nm. The racemic mixture could be possibly separated on two fractions (Figure 2) with HPLC OD-H chiral column with approximated ratio 1:1, but the fractions devoid of optical rotation measured next day. We assume that this compound possesses a low racemisation barrier and racemised after resolution overnight. That was consecutively confirmed by the calculated racemisation barrier value of  $\Delta G$  6-31G(d) at 298.15 K 99.0 kJ/mol, and half-life time (calculated time after which the

mixture contains both enantiomers in 3:1 ratio) at 298.15 K is 207 minutes, which explains the disappearance of the optical activity of **1a**. Calculated specific optical rotation for enantiomer (*M*)  $[\alpha]_D = -170^\circ$  suggests the configuration (*M*)(-) and (*P*)(+) for enantiomers of **1a**. Calculations were carried out with the GAUSSIAN 09W rev. A.02 program for *M* enantiomers. Preliminary geometry optimizations were done semiempirically at AM1 level. Final structure optimizations were accomplished with the use of DFT B3LYP functional and 6-31G(d) basis set including the polarisable continuum model (PCM) for modelling molecules in solution ( $\text{CH}_2\text{Cl}_2$ ), (for more details see Supp. Inf.).

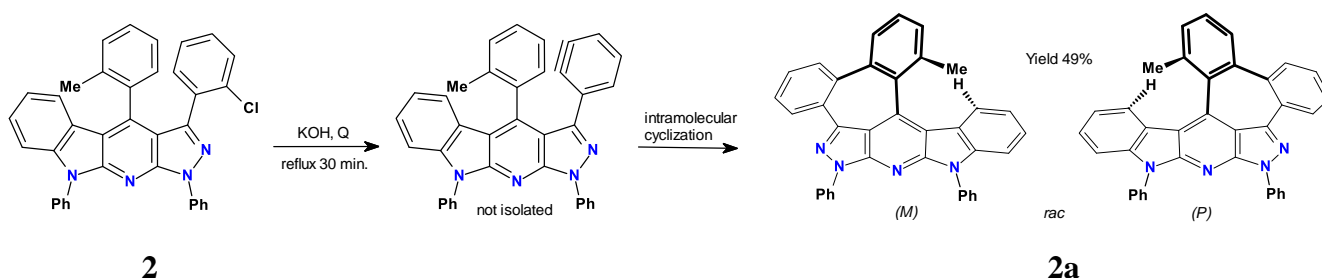


**Figure 1.** UV absorption (black line), calculated absorption spectrum (red line) and emission spectrum (green line) of **1a**, in  $\text{CH}_2\text{Cl}_2$ . Excitation at 296 nm



**Figure 2.** Separation of **1a** on to enantiomers on HPLC ODH column with hexane-isopropanol eluent

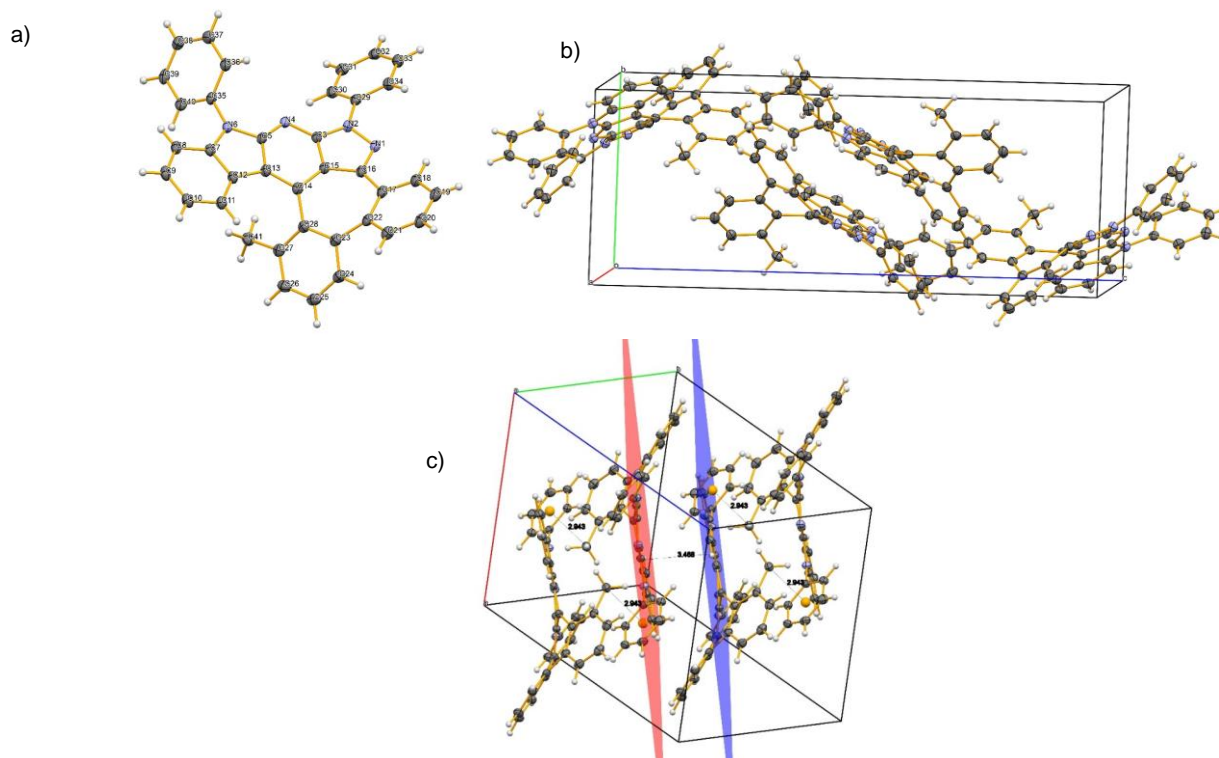
Next compound with the methyl group at the sterically crowded position 13 is (*M*)(*P*)(±)-6,8-dihydro-13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b,c*]fluorene **2a** (Scheme 2).



**Scheme 2.** Synthesis of (*M*)(*P*)(±)-6,8-dihydro-13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b,c*]fluorene

For three compounds **2a**, **3a** and **4a** it was possible to obtain single crystals suitable to X-ray diffraction data collection. Compound **2a** crystallize in  $P2_1/c$  space group. Uneven and helically twisted molecules of them preclude the regular  $\pi$ - $\pi$  stacking, however numerous interactions with  $\pi$  electron systems are observed in the crystal structure (Figure 3). Three of the them should be mentioned as the interactions which significantly determines the crystal packing. Atoms N1 - C16 which forms approximately flat system of four aromatic rings in central part of molecule, interacts with their counterparts in molecule related by inversion located at  $(1/2, 1/2, 1/2)$ . This  $\pi$ - $\pi$  interaction, with 3.468 Å distance between planes

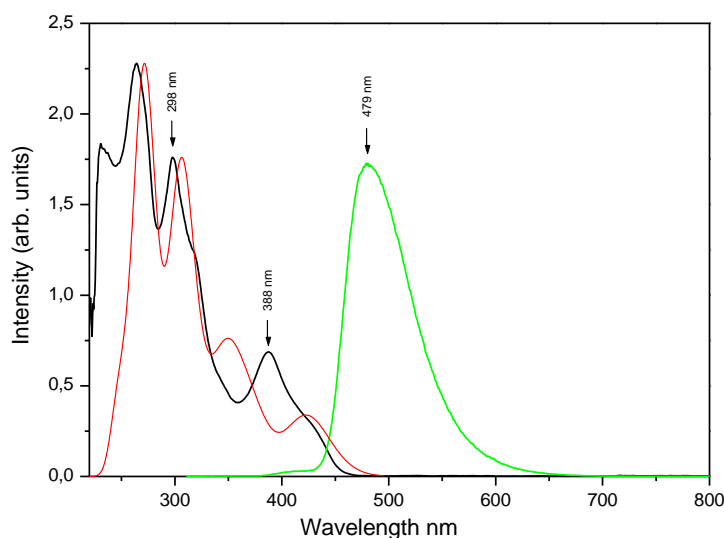
forms a kind of dimers of (*P*) and (*M*) enantiomers. Hydrogen atom joined to atom C41 is in the 2.943 Å distance to centre of phenyl ring formed by atoms C35 - C40 related also by inversion, but in position (0, 1/2, 1/2). Geometry of this interaction indicates the C-H -  $\pi$  interaction type III.<sup>9</sup> These pair of symmetry related C-H -  $\pi$  interactions are joining mentioned above  $\pi$ - $\pi$  dimers in supramolecular chain along direction [0 1 0] in lattice (Figure 3). "The "edge to face" interaction between phenyl rings formed by atoms C23 - C28 and C29 - C34 transformed by gliding mirror plane located at (x, 1/4, z), is also noticeable. This contact is responsible for bindings between mentioned chains perpendicularly to their axes.



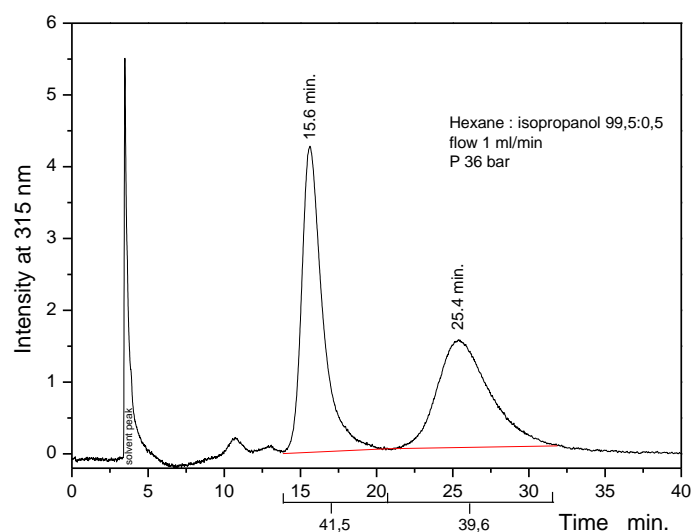
**Figure 3.** X-Ray structure of the compound **2a**: a) single molecule; b) crystal packing approximately towards [1 0 0] direction; c)  $\pi$ - $\pi$  and C-H -  $\pi$  interactions

Compound **2a** shows absorption in UV-Vis spectrum at  $\lambda_{\max} = 388$  nm and emission peak (PL) at  $\lambda_{\max} = 479$  nm (Figure 4). Calculated UV-Vis spectrum shows absorption maxima at  $\lambda_{\max} = 422$  nm and  $\lambda_{\max} = 350$  nm. The racemic mixture can be separated on two fractions (Figure 5) on OD-H chiral column with hexane-isopropanol eluent. The CD-spectrum of the first fraction (retention time 15.6 min.) shows weak positive Cottons effect with  $\lambda_{\max} = 320$  nm, and stronger negative at  $\lambda_{\max} = 290$  nm (Figure 6). Comparison with calculated CD-spectra and measured specific optical rotation  $[\alpha]_D^{20} = +869^\circ (\pm 143^\circ)$  ( $\text{CH}_2\text{Cl}_2$ ) leads to assessment the configuration for the first fraction compound as (*M*)(+)-6,8-dihydro-

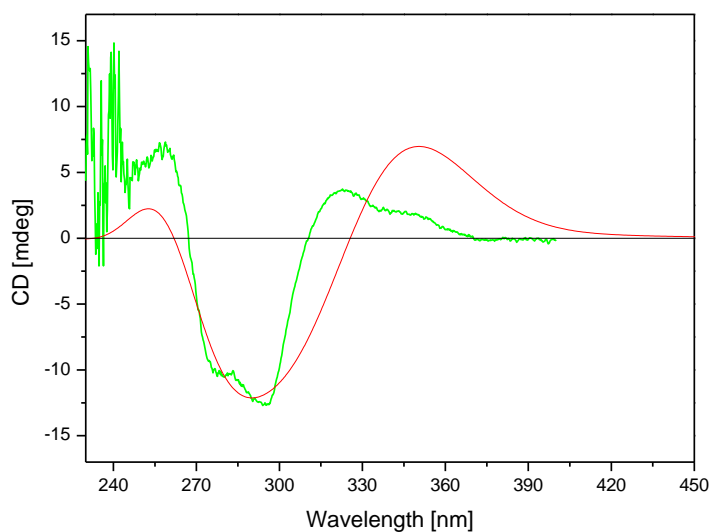
13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*bc*]fluorene. Calculated specific optical rotation for enantiomer (*M*)  $[\alpha]_D = +150^\circ$  confirms the configuration (*M*)(+) for this enantiomer of compound **2a**. The second fraction from HPLC (retention time 25.4 min.) shows opposite effect, weak negative Cottons effect with  $\lambda_{\max} = 320$  nm, and stronger positive at  $\lambda_{\max} = 290$  nm (Figure 1 in Supp. Inf.) and the measured optical rotation  $[\alpha]_D^{20} = -926^\circ (\pm 187^\circ)$  ( $\text{CH}_2\text{Cl}_2$ ) confirms the configuration (*P*)(-) for this enantiomer of the compound **2a**. Comparison of the measured CD spectra for both fraction from chiral HPLC column shows exact opposite Cottons effects as expected for separated enantiomers of **2a** (Figure 7). Calculated racemisation barrier  $\Delta G$  6-31G(d) at 298.15 K is 157 kJ/mol, and half-life time at 298.15 K is longer than 5 400 000 years, what excludes quick racemisation of the **2a** enantiomers. Fluorescence detected circular dichroism (FDCD spectrum) of **2a** fraction (15.6 min.) (*M*)(+)-6,8-dihydro-13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b,c*]fluorene shows weak positive Cottons effect at 325 nm and strong negative Cottons effect at 290 nm (Figure 2 in Supp. Inf.). FDCD spectrum of **2a** fraction with retention time 25.4 min. (*P*)(-)-6,8-Dihydro-13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b,c*]fluorene shows weak negative Cottons effects at 325 nm and strong positive Cottons at 290 nm (Figure 3 in Supp. Inf.). Comparison of both enantiomers FDCD spectra with mirror Cottons effects shows Figure 8.



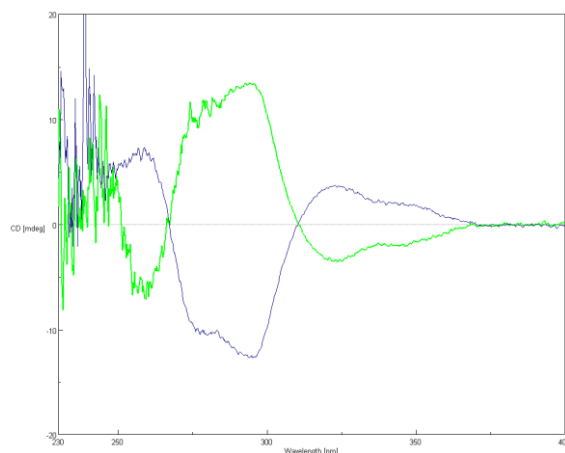
**Figure 4.** UV absorption (black line), calculated absorption spectrum (red line) and emission spectrum (green line) of **2a** in  $\text{CH}_2\text{Cl}_2$ . Excitation at 298 nm



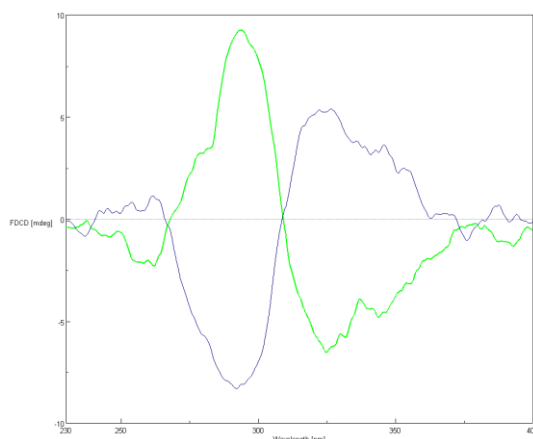
**Figure 5.** Separation of **2a** on to enantiomers on HPLC OD-H column with hexane-isopropanol eluent



**Figure 6.** Comparison of the measured CD spectrum of (*M*)(+)-6,8-dihydro-13-methyl-6,8-diphenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b,c*]fluorene **2a** (green line, CH<sub>2</sub>Cl<sub>2</sub>) - the first fraction from HPLC with retention time 15.6 min with calculated CD-spectrum (red line), measured specific optical rotation  $[\alpha]_D^{20} = +869^\circ (\pm 143^\circ)$  (CH<sub>2</sub>Cl<sub>2</sub>)

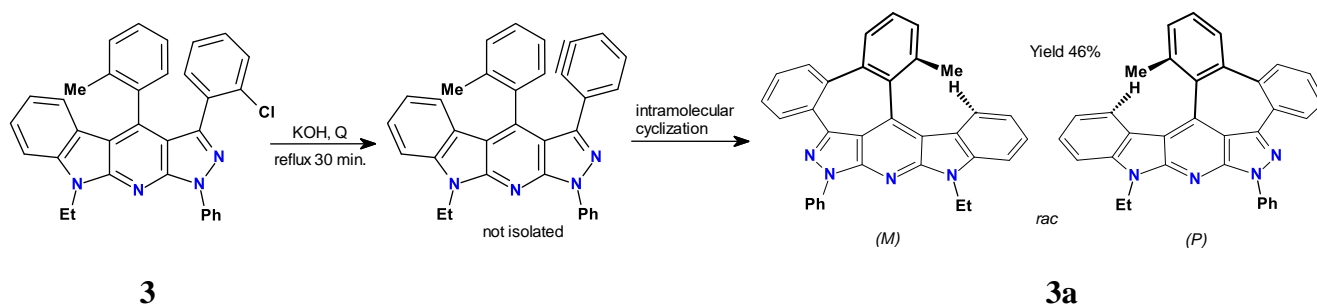


**Figure 7.** Comparison of the measured CD spectra for separated fractions of **2a**. The first fraction from HPLC 15,6 min. (blue line) (*M*)(+)-**2a**, and second fraction 25,4 min. (green line) (*P*)(-)-**2a**, (CH<sub>2</sub>Cl<sub>2</sub>).



**Figure 8.** Comparison of the measured fluorescence detected circular dichroism (FDCD spectra) of **2a** enantiomers. (*M*)(+)-**2a** (blue line) and (*P*)(-)-**2a** (green line) (solvent CH<sub>2</sub>Cl<sub>2</sub>).

Compound **3a** with methyl group at the sterically crowded position 13 and ethyl group with diastereotopic CH<sub>2</sub> protons at the nitrogen in position 8 (Scheme 3).

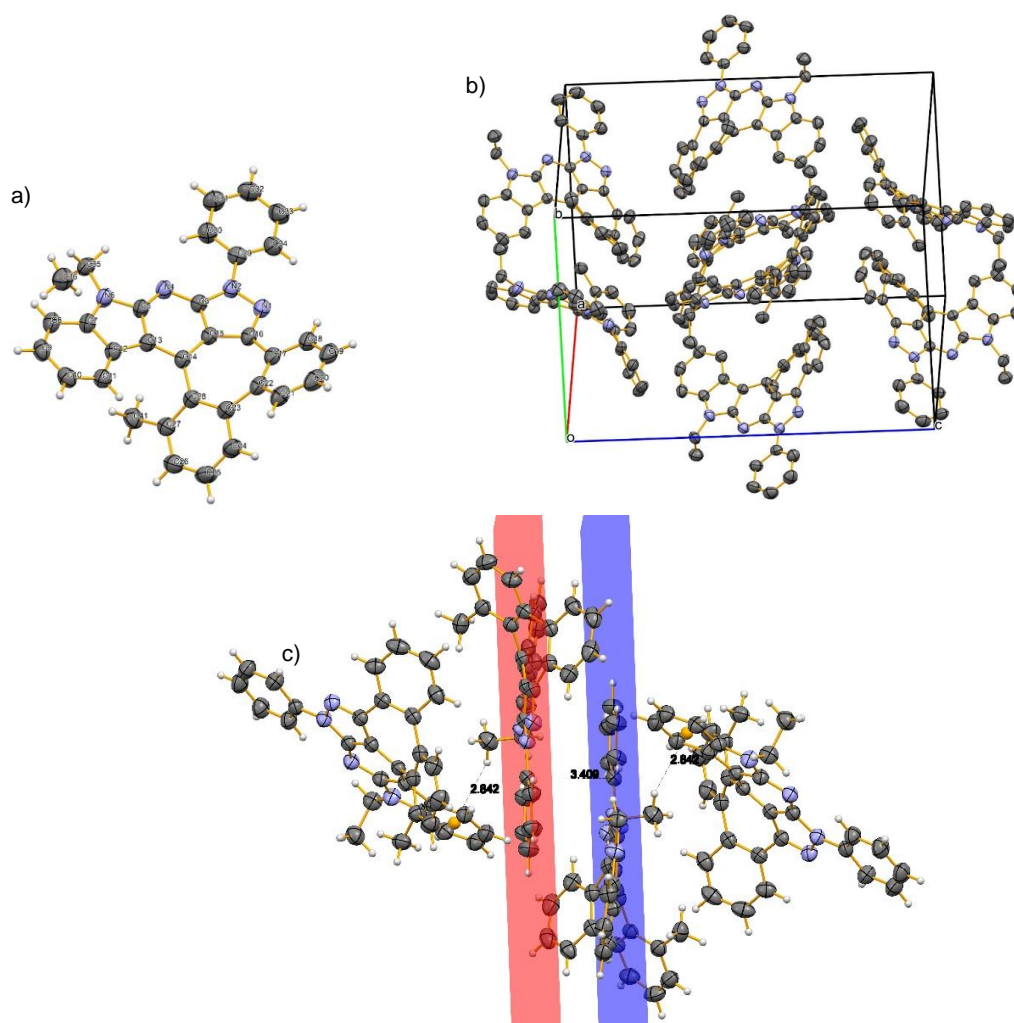


**Scheme 3.** Synthesis of (*M*)(*P*)(±)-8-ethyl-6,8-dihydro-13-methyl-6-phenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*bc*]fluorene

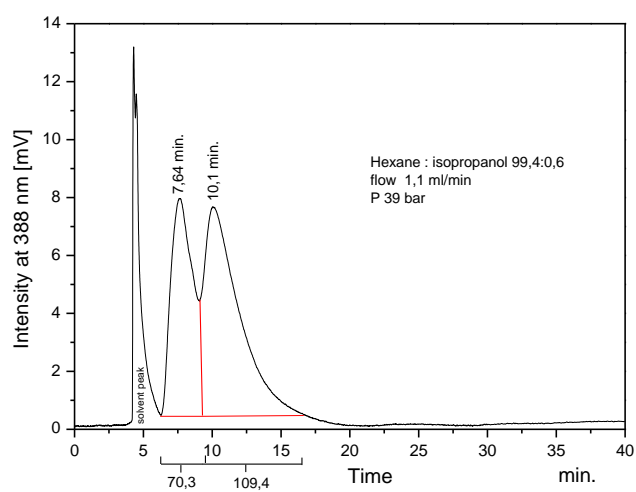
(*M*)(*P*)(±)-8-Ethyl-6,8-dihydro-13-methyl-6-phenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b,c*]fluorene **3a**, <sup>1</sup>H-NMR spectrum of this compound shows diastereotopic differentiation at CH<sub>2</sub> protons of the ethyl group with  $\delta_{\text{H}}$  4.55 (1 H, dq,  $J^2$  14.4 Hz,  $J^3$  7.19 Hz), 4.62 (1 H dq,  $J^2$  14.5 Hz,  $J^3$  7.26 Hz), a clear confirmation of the chiral vicinity (Figure 9). Compound **3a** shows absorption in UV-Vis spectrum at  $\lambda_{\text{max}} = 388$  nm and emission at  $\lambda_{\text{max}} = 480$  nm (Figure 10). Calculated UV-Vis spectrum shows absorption maxima at  $\lambda_{\text{max}} = 421$  nm, and  $\lambda_{\text{max}} = 307$  nm. Compound **3a** shows the lattice symmetry consistent with the Pbc<sub>a</sub> space group in crystal. Two interactions are worth the brief description. Atoms N1 - C5, C14 - C16 and C29 - C34 forms approximately flat system of three aromatic rings which engaged in  $\pi$ - $\pi$  contact with the same group of atoms, but related by inversion located at (0, 1/2, 0) in lattice. Note that unlike to compound **2a** this  $\pi$ - $\pi$  interaction characterise much less effective overlapping. It also to be important in terms of crystal packing seems the contact (with distance 2.842 Å) of hydrogen atom at C36 to center phenyl ring formed by atom C7-C12. It complies with the condition of C-H -  $\pi$  interactions type III (Figure 11).

The racemat can be separated on two fractions with HPLC on OD-H chiral column with hexane-isopropanol eluent (Figure 12). CD spectrum of the less polar fraction (retention time 7.64 min.) shows weak positive Cottons effect with  $\lambda_{\text{max}} = 325$  nm, and stronger negative at  $\lambda_{\text{max}} = 290$  nm (Figure 13). Comparison of measured CD spectrum with calculated spectrum lead us to assess the chirality as (*M*) enantiomer, and the measured specific optical rotation  $[\alpha]_D^{20} = +816^\circ (\pm 131^\circ)$  (CH<sub>2</sub>Cl<sub>2</sub>) gives finally configuration for this compound as *M*(+). Calculated specific optical rotation for enantiomer (*M*)  $[\alpha]_D = +205^\circ$ . The second fraction from HPLC (retention time 10.1 min) shows opposite effects, week negative Cottons effect with  $\lambda_{\text{max}} = 325$  nm, and stronger positive at  $\lambda_{\text{max}} = 290$  nm (Figure 4 in Supp. Inf.). Comparison measured CD spectrum with calculated one lead us to assess the chirality as (*P*) enantiomer, and measured specific optical rotation  $[\alpha]_D^{20} = -773^\circ (\pm 187^\circ)$  (CH<sub>2</sub>Cl<sub>2</sub>) gives finally configuration for this compound as *P*(-)-8-ethyl-6,8-dihydro-13-methyl-6-phenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*bc*]fluorene. Comparison of the measured CD spectra for both fraction from chiral HPLC column shows exact opposite Cottons effects as expected for separated enantiomers of compound **3a** (Figure 14). Calculated racemisation barrier  $\Delta G$  6-31G(d) at 298.15 K to be 156 kJ/mol, and half-life time at 298.15 K is longer than 4 100 000 years, what exclude quick racemisation of **3a**. Fluorescence detected circular dichroism - FDCD spectrum of *M*(+) enantiomer of **3a** (fraction from HPLC with retention time 7.64 min.) indicate weak positive Cottons effect at 320 nm and strong negative at 290 nm (Figure 5 in Supp. Inf.). FDCD spectrum of **3a** *P*(-) enantiomer, the HPLC fraction with retention time of 10.1 min. shows weak negative Cottons effects at 320 nm and strong positive Cottons effect at 290 nm (Figure 6 in Supp.

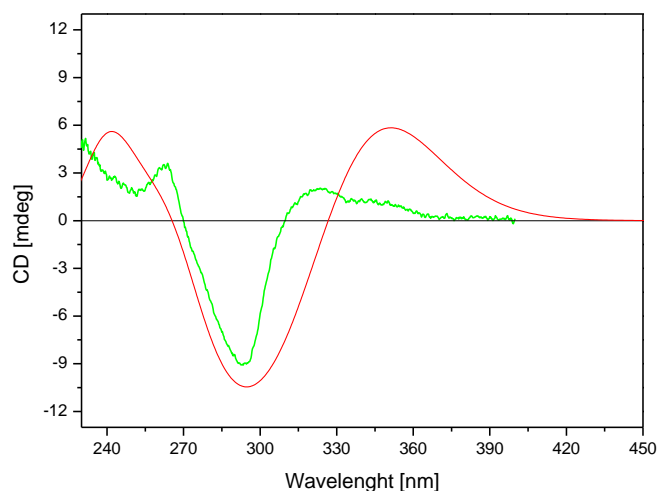




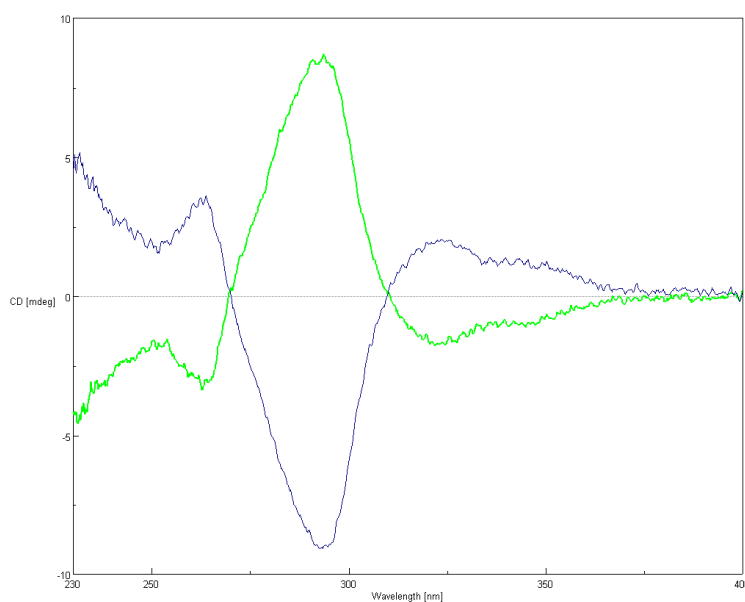
**Figure 11.** X-Ray structure of the compound **3a**: a) single molecule; b) crystal packing approximately towards [1 0 0] direction; c)  $\pi$ - $\pi$  and C-H  $\cdots$   $\pi$  interactions



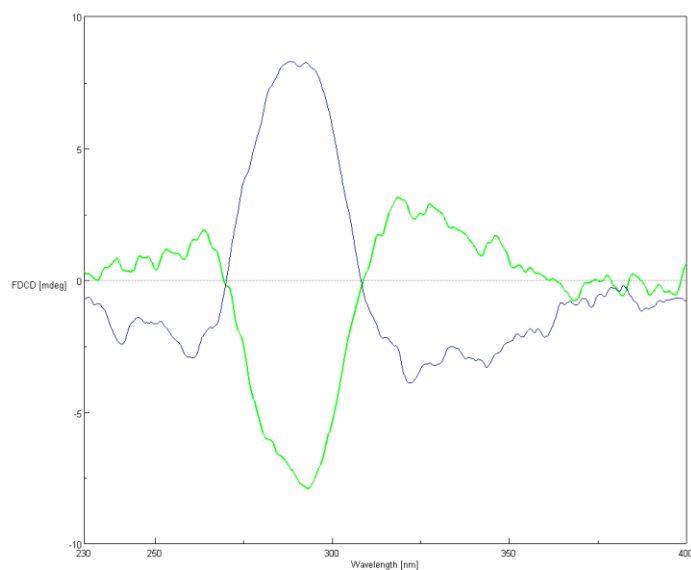
**Figure 12.** Separation of compound **3a** on to enantiomers on HPLC OD-H column with hexane-isopropanol eluent



**Figure 13.** Measured CD spectrum of **3a** (fraction from HPLC with retention time 7.64 min) *M*(+)-8-ethyl-6,8-dihydro-13-methyl-6-phenyl-5,6,7,8-tetraazadibenzo[4,5:6,7]azuleno[1,8-*b,c*]fluorene, (green line, CH<sub>2</sub>Cl<sub>2</sub>) and calculated CD spectrum (red line), measured specific optical rotation  $[\alpha]_D^{20} = +816^\circ (\pm 131^\circ)$  (CH<sub>2</sub>Cl<sub>2</sub>)

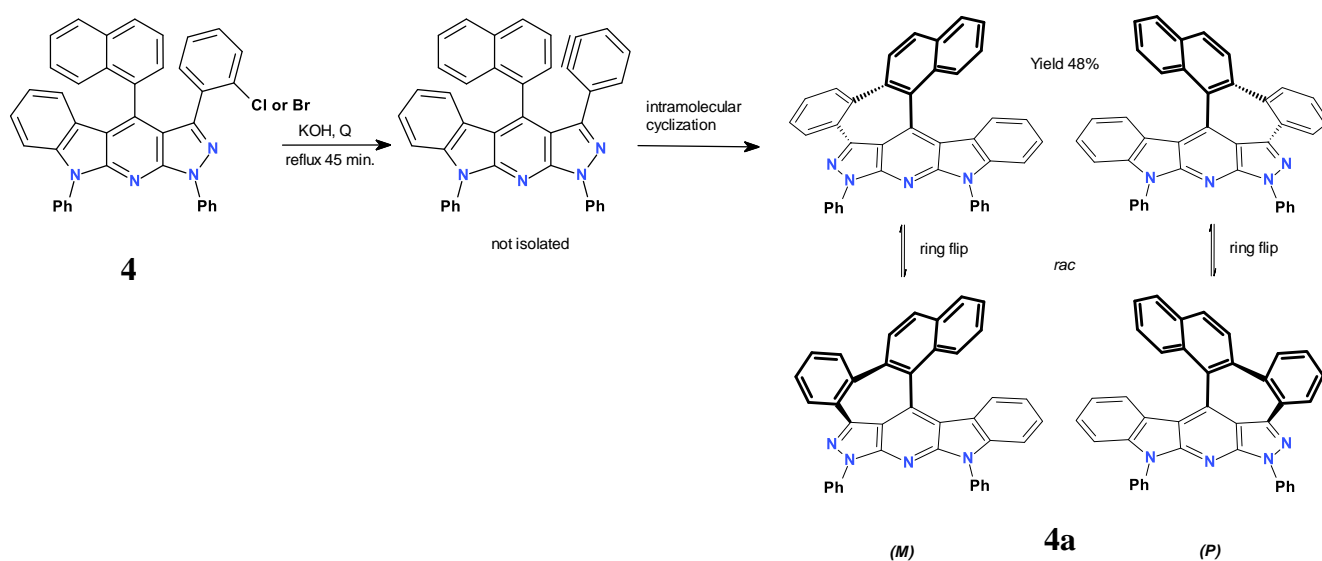


**Figure 14.** Comparison of the measured CD spectra for separated by HPLC fractions of **3a**. The first HPLC fraction 7.64 min (*M*)(+) enantiomer (blue line), and second fraction 10.1 min (*P*)(-) enantiomer (CH<sub>2</sub>Cl<sub>2</sub>)



**Figure 15.** Comparison of the measured fluorescence detected circular dichroism (FDCD spectra) of **3a** enantiomers. (*M*)(+)-**3a** (green line) and (*P*)(-)-**3a** (blue line). ( $\text{CH}_2\text{Cl}_2$ ) filter L-42

In compound **4a** we have enlarged the helically arranged rings with further benzo ring (Scheme 4).



**Scheme 4.** Synthesis of (*M*)(*P*)( $\pm$ )-6,8-dihydro-6,8-diphenyl-5,6,7,8-tetraaza-benzo[4,5]naphtho[2',1':6,7]azuleno[1,8-*b,c*]fluorene

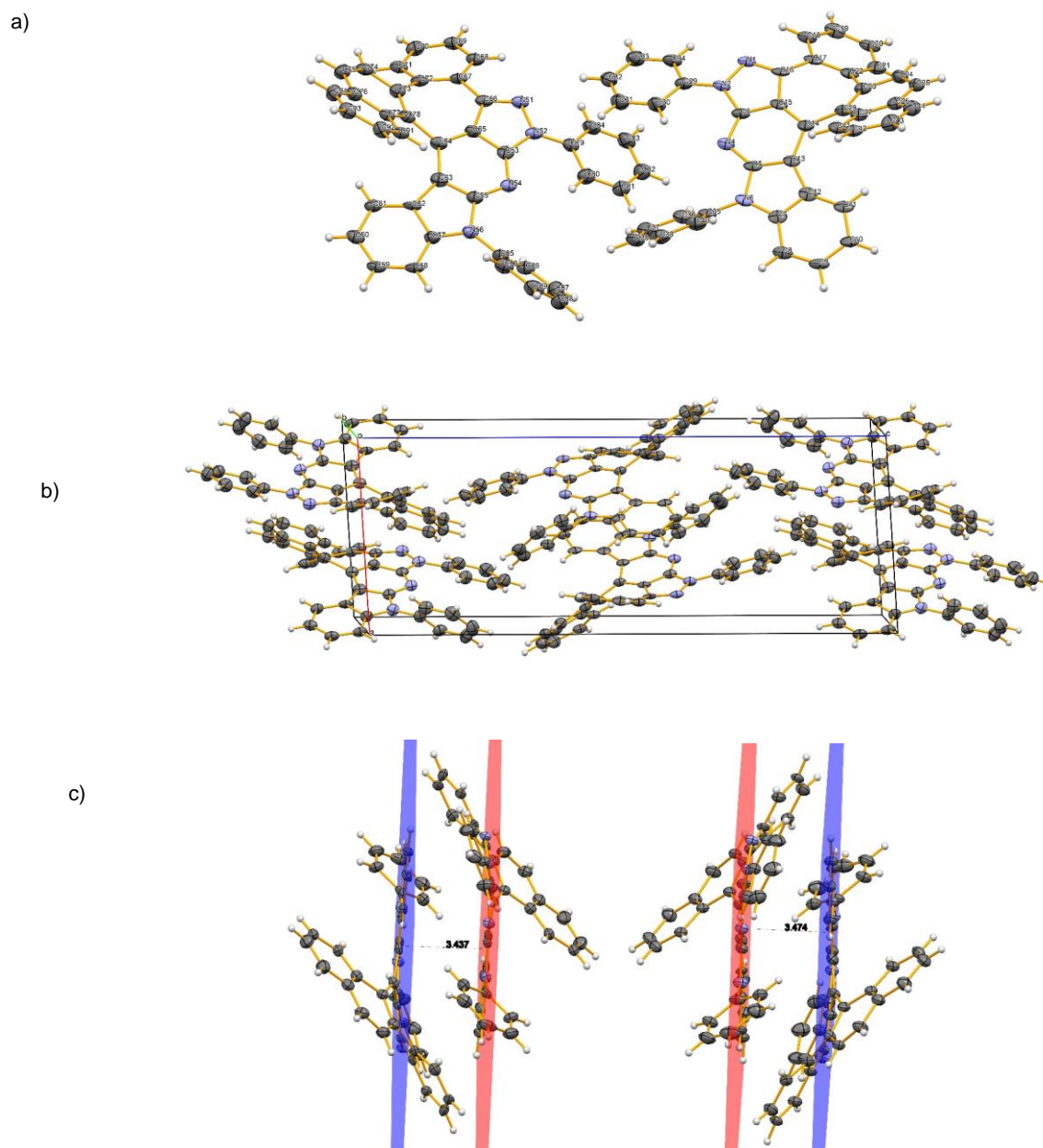
(*M*)(*P*)( $\pm$ )-6,8-Dihydro-6,8-diphenyl-5,6,7,8-tetraaza-benzo[4,5]naphtho[2',1':6,7]azuleno[1,8-*b,c*]fluorene **4a**, dark yellow solid, crystallize with cell symmetry consistent with the **P**-1 space group in triclinic crystal system. Unlike the previously discussed compounds **2a** and **3a** the asymmetric part of the unit cell contain both (*P*) and (*M*) enantiomers. It is worth noticing that although compounds **2a** and **4a** crystallize

in different types lattices, which shows completely different symmetry, their molecules forms locally very similar  $\pi$ - $\pi$  complexes. For first molecule, of enantiomer (*P*), atoms N1 - C16 forms approximately flat system of four aromatic rings in central part of molecule, which is in  $\pi$ - $\pi$  interaction, with their counterparts in molecule related by inversion located at (1/2, 1/2, 1/2), with 3.437 Å distance between planes. Similarly, atoms N51 - C66 in second molecule, of enantiomer (*M*), interacts with their analogue related by inversion at (1, 1/2, 0) and forms  $\pi$ - $\pi$  complex, with 3.474 Å distance between planes. In both cases we have P...M and M...P dimers of enantiomers, respectively, because the molecules on  $\pi$ - $\pi$  complexes are in the inversion relationship. Compound **4a** has no any methyl or methylene residues, so the C-H -  $\pi$  interactions are absent. It is also difficult to recognize other interaction with  $\pi$  electrons, but looking along direction [0 1 0], one can see how the molecules interlock to form a slider-like structure. It seems to be obvious that unclassified types of  $\pi$ - $\pi$  interactions are present here.

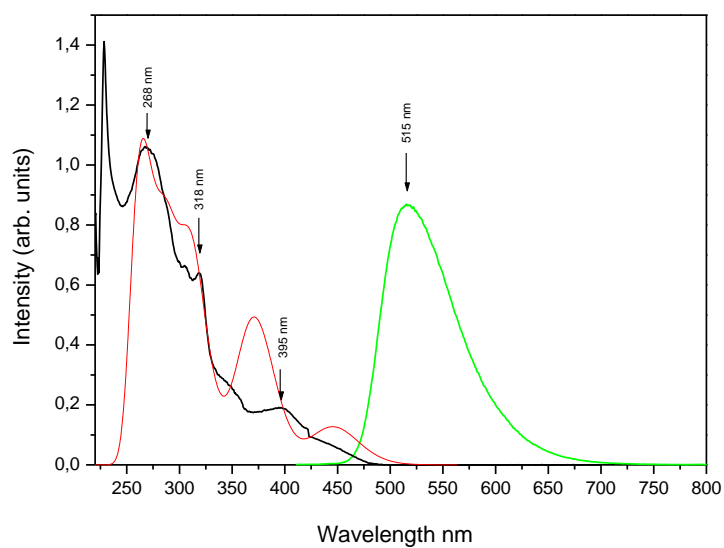
The comparison of the crystal structures of the compounds for which they were determined *i.e.* **2a**, **3a** and **4a**, shows the obvious differences in the crystal packing and the symmetry of the lattice. They result from the presence of various substituents responsible for contacts with neighbouring molecules and minor differences in the geometry of the same molecule fragments for all three compounds. There are also some similarities. The most important of these is the tendency to form some kinds of dimers joined by  $\pi$ - $\pi$  interactions. The molecules in these dimers are symmetric by inversion, so each dimer contain enantiomers P and M (Figure 16).

Compound **4a** possess absorption maxima in UV spectrum at  $\lambda_{\max} = 395$  nm and emission maxima at  $\lambda_{\max} = 515$  nm (Figure 17). Calculated UV-Vis spectrum shows absorption maxima at  $\lambda_{\max} = 445$  nm, and  $\lambda_{\max} = 411$  nm. The **4a** racemate can be separated with HPLC chiral column OD-H on two fraction (Figure 18), but those did not show optical rotation measured a few days after HPLC separation. We suppose that this compound exists in two conformational diastereoisomeric forms in an ratio near to 1:1. These diastereoisomeric forms arise probably from conformational 7-member ring flip, as shows on Scheme 4. Conformational ring flip is slow enough in NMR scale time to allow detection of both diastereoisomers, thus NMR spectra shows duplicate signals both in  $^1\text{H}$  and  $^{13}\text{C}$  spectres (see Figure 7 in Supp. Inf.). Similar behaviour in helicaly arranged rings involved also 7-member ring in propeller-shaped polycyclic aromatic hydrocarbon has been observed by Segawa, Itami *et al.*<sup>10</sup> In case of the compound **4a** the separation on HPLC leads possibly to a pair of enantiomers (*M*)(*P*) and (*M'*)(*P'*) which are not optically active as they are conformational diastereoisomers mixtures and still racemates. Calculated racemisation barrier  $\Delta G$  6-31G(d) at 298.15 K to be 141 kJ/mol, and half-life time at 298.15 K to be 7782 years, what rather excludes quick racemisation of **4a** enantiomers (CD measurements were performed a few weeks

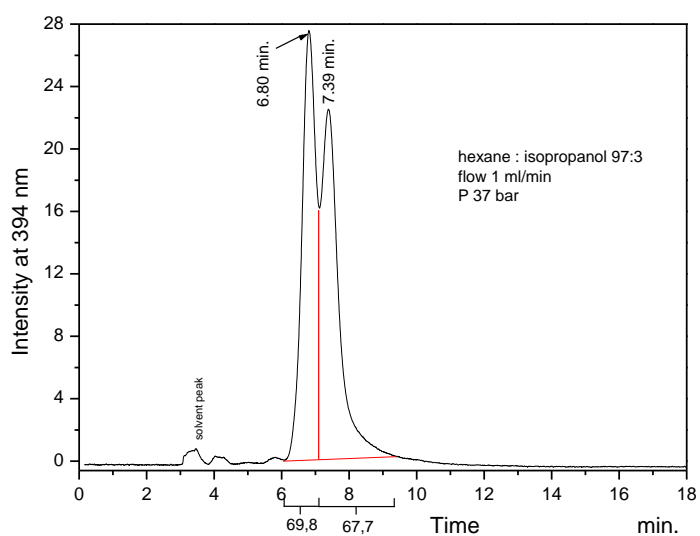
after HPLC separation), astonishingly, the calculated racemisation barrier is notably lower than in compounds of **2a** and **3a**. Calculated specific optical rotation for enantiomer (*M*)  $[\alpha]_D = +30^\circ$  suggests the (*M*)(+) and (*P*)(-) configurations for enantiomers of compound **4a**, however those possess additional chiral surface by meaning of side rings and shell be analysed as such with at least two surface chirality inclined events, what additional complicated analyses (see Figure 8 and Movie 1 in Supp. Inf.).



**Figure 16.** X-Ray structure of the compound **4a**: a) asymmetric unit containing enantiomers (*P*) and (*M*), with labels; b) crystal packing towards [0 1 0] direction; c)  $\pi$ -complexes of **4a** compound, complexes were separated for clarity

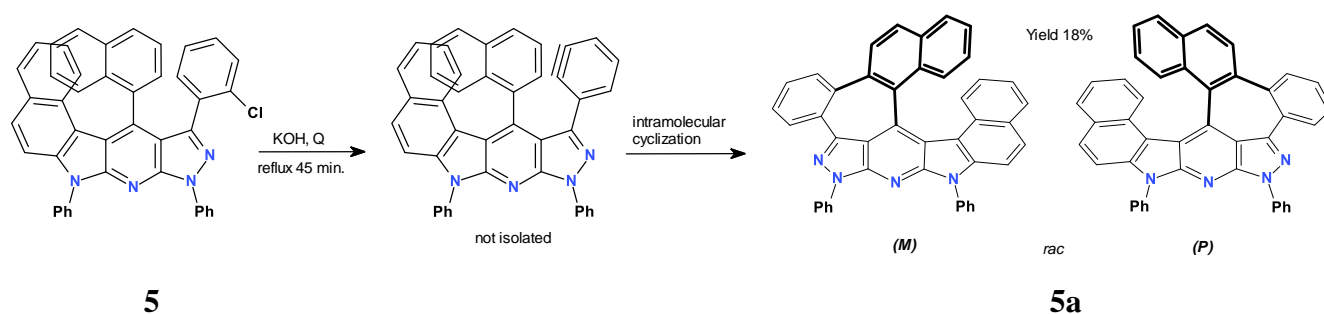


**Figure 17.** UV absorption (black line – measured spectrum, red line – calculated spectrum) and emission spectrum (green line) of **4a** in  $\text{CH}_2\text{Cl}_2$ . Excitation at 395 nm



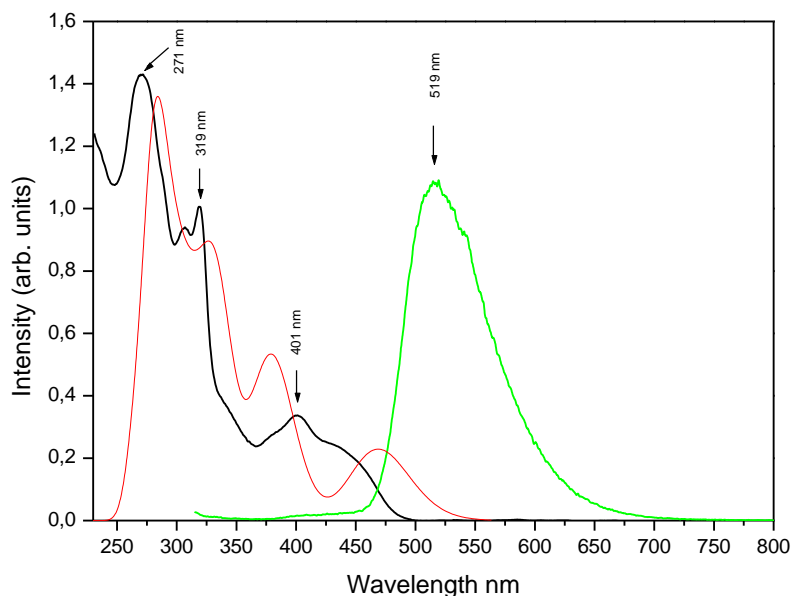
**Figure 18.** Separation of **4a** on HPLC OD-H column on two fraction with hexane-isopropanol eluent

In compound **5a** we have annulated the helically arranged rings with further benzo ring at the opposite side of helical surface.



**Scheme 5.** Synthesis of **5a** (*M*)(*P*)(±)-6,8-dihydro-6,8-diphenyl-5,6,7,8-tetraazabenzog[*g*]benzo[6,5]naphtho[2',1':6,7]azuleno[1,8-*b,c*]fluorene

(*M*)(*P*)(±)-6,8-Dihydro-6,8-diphenyl-5,6,7,8-tetraazabenzog[*g*]benzo[6,5]naphtho[2',1':6,7]azuleno[1,8-*b,c*]fluorene **5a** - isolated as orange solid, with absorption maxima at  $\lambda_{\max} = 401$  nm and  $\lambda_{\max} = 319$  nm, and emission at  $\lambda_{\max} = 519$  nm (Figure 19). Calculated UV-Vis spectrum shows absorption maxima at  $\lambda_{\max} = 470$  nm, and  $\lambda_{\max} = 379$  nm, and  $\lambda_{\max} = 327$  nm. The attempt to separate compound **5a** on to enantiomers failed. Unfortunately we were not able to find the conditions for HPLC separation of **5a** racemate to enantiomers, neither with OD-H column nor with other columns like AS-H and OJ-H. Calculated racemisation barrier  $\Delta G$  6-31G(d) is 193 kJ/mol at 298.15 K, and the half-life time at 298.15 K is  $1.35 \times 10^{13}$  years, what excludes racemisation of **5a** enantiomers.



**Figure 19.** UV absorption (black line), calculated absorption spectrum (red line) and, emission spectrum (green line) of **5a** in  $\text{CH}_2\text{Cl}_2$ . Excitation at 271 nm

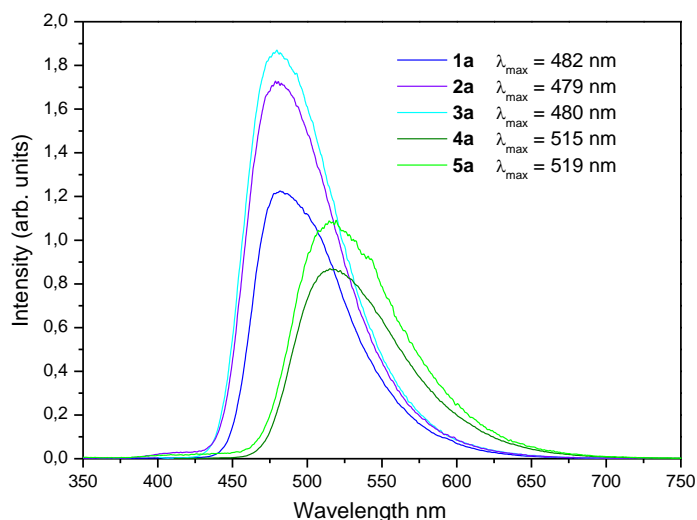
**Table 1.** Substituted 5,6,7,8-tetraaza-azuleno[1,8-*b,c*]fluorenes synthesis and properties

Substrate	Reaction time [min.]	Product	Yield (%)	Mp °C	$\lambda_{\text{abs}}$ [nm]	$\lambda_{\text{fl}}$ [nm]
<b>1</b>	30	<b>1a</b>	73	319-321 CHCl <sub>3</sub> /MeOH	389	482
<b>2</b>	30	<b>2a</b>	49	270-274 CH <sub>2</sub> Cl <sub>2</sub> /MeOH	388	479
<b>3</b>	30	<b>3a</b>	46	265-269 toluene/MeOH	388	480
<b>4</b>	45	<b>4a</b>	48	278-282 CH <sub>2</sub> Cl <sub>2</sub> /acetone	394	515
<b>5</b>	60	<b>5a</b>	18	303-306 CH <sub>2</sub> Cl <sub>2</sub> /acetone	401	519

## CONCLUSIONS

*Reaction.* The reaction conditions are very harsh (melted KOH, quinoline reflux, ca. 237 °C), and reaction time increase with increasing of the steric hindrance in the substrate. The yields decrease with longer reaction time because decomposition reactions occur. Increased yields were reached if higher dilution and heating attenuation were applied. Palladium catalysed cyclization the bromo analogues compounds **1-5** to **1a-5a** can be performed in DMF at 140 °C, however the reaction time over 24 hours is necessary, and the yields are not much higher as in quinoline reflux. We have also attempt to synthesised homologs to compounds **1-5** possessing electron donor substituents at the benzo rings side, but the three component reaction described by Bazgir *et al.*<sup>8</sup> used for synthesis of the starting compounds does not work well in this case, so we isolated only traces of the products.

*Photoluminescence.* All studied substituted 5,6,7,8-tetraaza-azuleno[1,8-*b,c*]fluorenes show intense yellow-green luminescence in solution and in steady state, a prerequisite to be the candidate in OLED technology. Additionally, the robust to high temperature and high racemisation barrier are another requirement to make some of these compounds amenable in OLEDs with circularly polarised luminescence. The shift of the photoluminescence maxima from  $\lambda_{\text{max}} = 479$  nm for **2a** to  $\lambda_{\text{max}} = 519$  nm for **5a** resulted of the bathochromic effect of the additional benzene rings in chromophore (Table 1, Figure 20). The photoluminescence maxima wavelength were independent of the excitation wavelength.



**Figure 20.** Comparison of the UV emission spectra of substituted 5,6,7,8-tetraaza-azuleno[1,8-*b,c*]fluorenes **1a-5a** in CH<sub>2</sub>Cl<sub>2</sub> (different concentrations)

## EXPERIMENTAL

*Substituted 5,6,7,8-tetraaza-azuleno[1,8-*b,c*]fluorenes 1a-5a synthesis, a general procedure.* In quartz glass vessel the precursor of tetraaza-azuleno[1,8-*b,c*]fluorene (**1-5**) was dissolved in dry, freshly distilled quinoline, powdered KOH was added in 4 fold excess. Then the mixture was refluxed under nitrogen for 15-60 min depending on the substrate (Table 1). The conversion of the substrate to product was monitored in UV light, by changes of the solutions colour from blue to yellow-green. The reaction was cooled to rt, washed with water, treated with 4M HCl and extracted with toluene. The organic layer was washed with 5% aqueous NaHCO<sub>3</sub> and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed *in vacuo* and residue was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, CH<sub>2</sub>Cl<sub>2</sub>/acetone or toluene/MeOH, alternatively it was purified by column chromatography on Al<sub>2</sub>O<sub>3</sub> with toluene-hexane eluent. Supporting information with furthermore experimental details for this article is given.

## FOUNDING

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