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## **Polycyclic Heteroaromatic Hydrocarbons Containing a Benzoisoindole Core**

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# Polycyclic Heteroaromatic Hydrocarbons Containing a Benzoisindole Core

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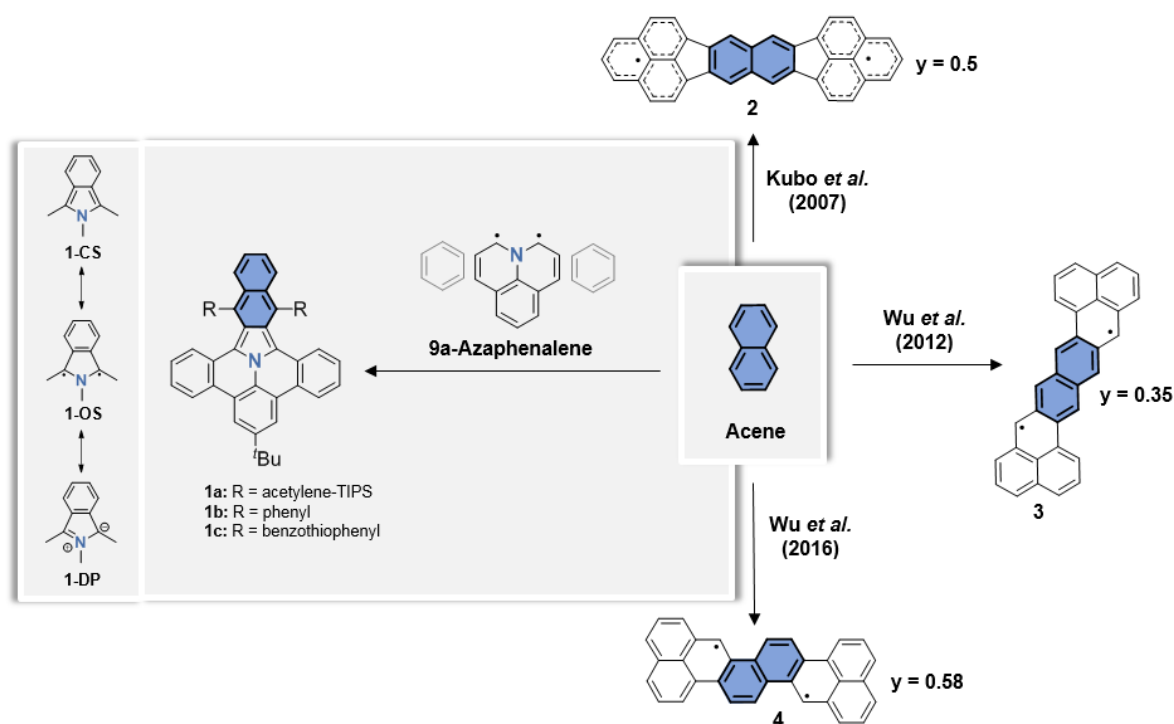
† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

**Abstract:** By the combination of 9a-azaphenalene and a perpendicularly oriented acene, we have synthesized three derivatives of a series of novel, fully-conjugated nitrogen-containing polycyclic aromatic hydrocarbons (PAHs), namely [7,8]naphtho[2',3':1,2]indolizino[6,5,4,3-def]phenanthridine, with an acetylene triisopropylsilyl (TIPS), phenyl or benzothiophenyl substituent. Their optoelectronic properties were studied via UV-Vis-NIR absorption, fluorescence spectroscopy and cyclic voltammetry. In addition, in situ spectroelectrochemistry was performed to investigate the optical and magnetic properties of the mono-radical cation and anion by quasi-reversible oxidation and reduction of 11-(*tert*-butyl)-5,17-is((triisopropylsilyl)ethynyl)[7,8]naphtho[2',3':1,2]indolizino[6,5,4,3 def]phenanthridine (**1a**). Theoretic modelling confirmed predominately closed-shell electronic ground state with a weak diradical character depending on the geometry.

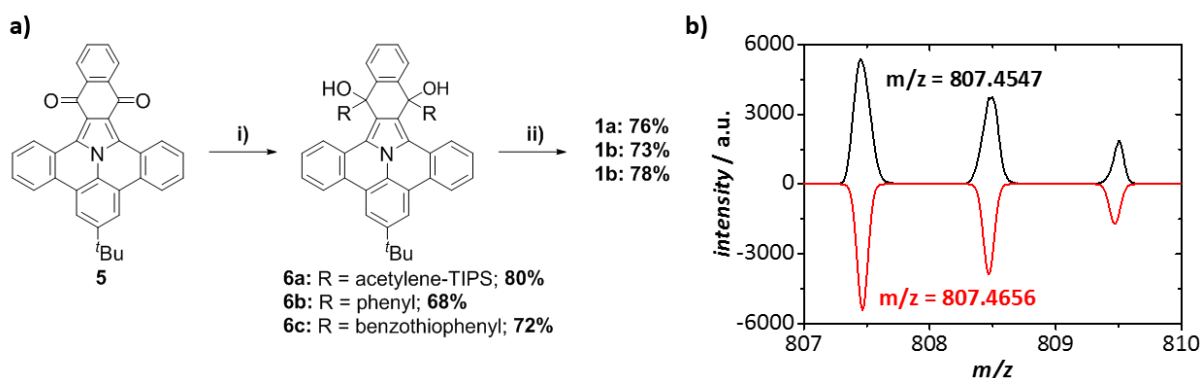
## Introduction

Polycyclic hydrocarbons (PHs) can be divided according to the aromaticity of their ground state into fully benzenoid polycyclic aromatic hydrocarbons (PAHs), such as hexa-*peri*-hexa-benzocoronene, and other non-benzenoid PHs, in which their electronic ground state can possess a mixed closed-shell (CS) and open-shell (OS) state (proaromatic) or pure OS ground state. This can be quantified by the diradical character  $y$ , which is defined as twice the weight of the double excitation configuration in the singlet ground state within the multiconfigurational self-consistent-field theory.<sup>1-4</sup> The diradical character can have values between 0 (pure CS) and 1 (pure OS).<sup>5, 6</sup> In any OS state exists at least one unpaired electron.<sup>7-10</sup> PHs with an dominant participation of an OS state are attracting an increased attention due to unique properties such as responsive spin structure, two-photon-absorption or small band gap.<sup>5, 6, 11-16</sup> These materials hold great promise for organic electronics, nonlinear optics or organic spintronic applications.<sup>17, 18</sup> From the molecular perspective, the aromaticity and the electronic structure of PHs are strongly influenced by their shape, periphery, and geometry. For example, the electronic ground state of an acene or a heteroatom-containing homologue - called heteroacene - strongly depends on its lateral extension. The handling of higher homologues in the acene series becomes difficult,<sup>19-23</sup> because of the increasing participation of an OS diradical ground state leading to oxidation or dimerization reactions.<sup>24-27</sup> The introduction of nitrogen atoms into an acene changes the electronic structure and can help to improve the ambient stability.<sup>21, 28-33</sup> A famous representative of PHs with an OS ground state is the phenalenyl radical, which possesses an odd number of thirteen carbon atoms and electrons.<sup>34, 35</sup> As a result, one electron is unpaired and the overall magnetic moment of the phenalenyl radical is paramagnetic.<sup>36-38</sup> Several derivatives of the phenalenyl radical with steric and electronic perturbation have been

isolated.<sup>35, 39-44</sup> Recently, we presented the synthesis of a 9a-azaphenalene with dibenzo-elongated zigzag edge (Figure 1), which is a diradical stabilized in a zwitterionic structure.<sup>45-48</sup> Kubo, Wu and others demonstrated the phenalenyl moiety as versatile building block for the synthesis of novel OS materials.<sup>8, 26, 36</sup> The combination of two phenalenyl moieties via an acene as spacer influences the diradical character  $y$  depending on the connection motif ranging from phenalenyl-based Kekulé PH **2** ( $y = 0.5$ ) to octazethrene **3** ( $y = 0.35$ ) to the 1,5-naphthoquinodimethane (NQDM) derivative **4** ( $y = 0.58$ ) as summarized in Figure 1.<sup>49-51</sup> In this work, we explore the effect on the electronic ground state of 9a-azaphenalene when fused with an acene represented by naphthalene (Figure 1). To the best of our knowledge, a similar fusion of phenalene and acene is so far not synthetically achieved for neither the pristine nor other heteroatom containing case. In contrast to NQDMs **2-4**, the diradical resonance structure of **1a-c** represented by **1-OS** is masked in two closed shell forms **1-CS** and **1-DP** (see figure 1). Towards this end, we synthesized a novel class of internally nitrogen-containing PHs represented by 11-(*tert*-butyl)-5,17-bis((triisopropylsilyl)ethynyl)[7,8]naphtho[2',3':1,2]indolizino[6,5,4,3-def]phenanthridine (**1a**), 11-(*tert*-butyl)[7,8]-5,17-diphenylnaphtho[2',3':1,2]indolizino[6,5,4,3-def]phenanthridine (**1b**) and 5,17-bis(benzo[*b*]thiophen-2-yl)-11-(*tert*-butyl)[7,8]naphtho[2',3':1,2]indolizino[6,5,4,3-def]phenanthridine (**1c**). We further investigated the electronic structure in solution by UV-Vis as well as by theoretic modelling by DFT-calculations. The formation of radical cations of **1a-c** was unambiguously elucidated by UV-Vis absorption and in situ spectroelectrochemistry.



**Figure 1.** Conceptual route of the novel N-containing PHs **1a-c** by naphthalene and 9a-azaphenalene fusion in comparison to the previous synthesis work of OS PHs from Kubo and Wu *et al.* In addition, benzoannulation stabilizes the azaphenalene core with acetylene-TIPS substituents **1a** or aryl substituents (**1b-c**) in the 5, 17-positions. A possible diradical character of **1a-c** represented by the resonance structure **1-OS** is masked in two closed shell forms **1-CS** and **1-DP**.



**Figure 2.** a) Synthesis scheme of target compounds **1a-1c**: i) for **6a**: *n*-butyl lithium, triisopropylsilylacetylene, THF, 0°C to r.t., 3 days, 80%; for **6b**: phenyllithium, THF, r.t., 3 days, 68%; for **6c**: *n*-butyl lithium, 2-bromobenzo[*b*]thiophene, THF, -78°C to r.t., 3 days, 72%; ii) SnCl<sub>2</sub>, DCM, r.t., 3 days. b) The HR-MALDI-TOF spectrum of **1a** (black line) is in perfect agreement to the expected isotopic distribution pattern (red line).

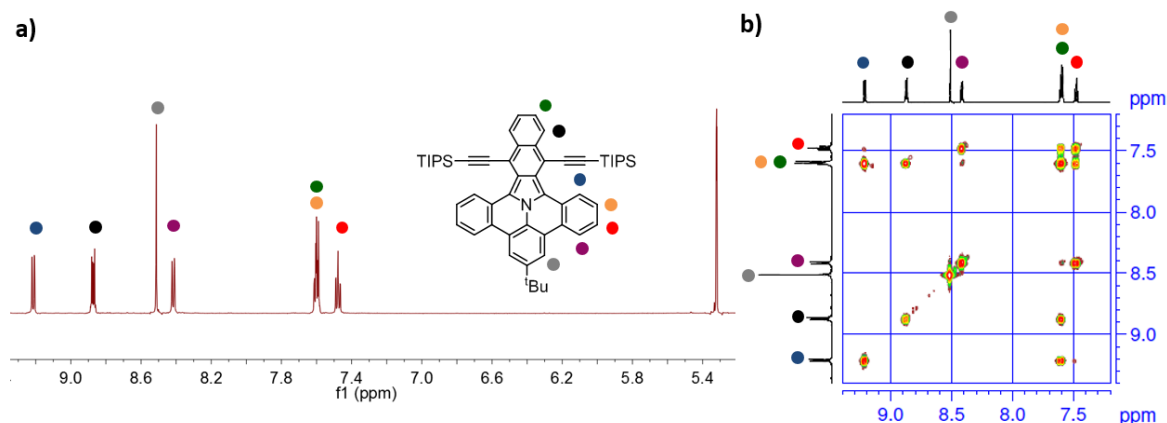
## Results and Discussion

### Synthesis

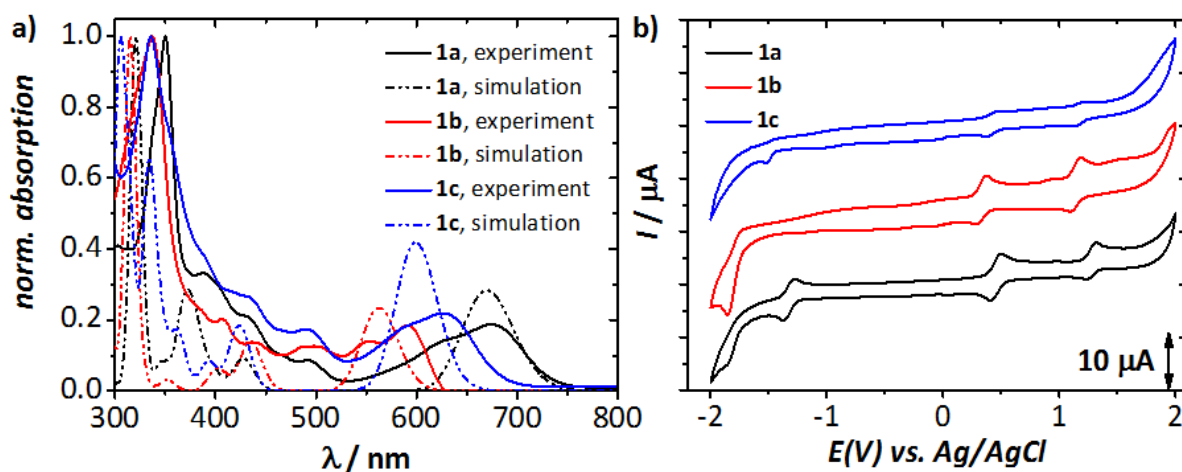
The target compounds **1a-c** were synthesized in two steps from 8-(*tert*-butyl)dibenzo[*d,k*]naphtha[*a*]ullazine-1,6-dione (**5**).<sup>47</sup> Nucleophilic addition of lithium triisopropylsilylacetylenide, phenyllithium and benzo[*b*]thiophen-2-yl lithium to **5** over a period of 24 hours gave diols 11-(*tert*-butyl)-5,17-bis((triisopropylsilyl)ethynyl)-5,17-dihydrobenzo[7,8]naphtho[2',3':1,2]indolizino[6,5,4,3-*def*]phenanthridine-5,17-diol (**6a**), 11-(*tert*-butyl)-5,17-diphenyl-5,17-dihydrobenzo[7,8]naphtho[2',3':1,2]indolizino[6,5,4,3-*def*]phenanthridine-5,17-diol (**6b**) and 5,17-bis(benzo[*b*]thiophen-2-yl)-11-(*tert*-butyl)-5,17-dihydrobenzo[7,8]naphtho[2',3':1,2]indolizino[6,5,4,3-*def*]phenanthridine-5,17-diol (**6c**) in yields of 68 %, 80 % and 72 %, respectively. Subsequent treatment of the diols **6a-c** with anhydrous SnCl<sub>2</sub> provided the target compounds **1a-c** after three days in yields of 76 %, 73 % and 78 % respectively. The high reactivity of the final compounds towards oxygen requested careful purification by precipitation in methanol in the glovebox. The intermediates **6a-c** were characterized by NMR-spectroscopy and high resolution matrix-assisted laser desorption/ionization time of flight (HR-MALDI-TOF) mass spectrometry (MS) (ESI Figure S17, S19 and S21). Partial fragmentation of the hydroxyl groups during MALDI-TOF MS could not be suppressed. The NMR spectra were measured in *d*<sub>2</sub>-dichloromethane (for **1a** and **1b**) or *d*<sub>2</sub>-tetrachloroethane (**1c**) (SI). All protons were assigned to the expected chemical structure by the assistance of two-dimensional NMR correlation spectroscopy (COSY) exemplified for **1a** in Figure 3. The exact molecular weight of **1a-c** was detected by HR-MALDI-TOF MS (Figure S18, S20 and S22). Furthermore, HR-MALDI-TOF MS showed an additional small peak in the interval of *m/z* = 17 for all target molecules, which can be attributed to the oxygen addition during the measurement or sample preparation. The isotopic distributions observed for **1a-c** were in perfect agreement with the simulated pattern (Figure 2b and ESI).

### Optical Properties

Compounds **1a-c** were characterized via UV-Vis absorption (Figure 4a) and fluorescence spectroscopy. For all measurements, freshly prepared solutions of **1a-c** in anhydrous dichloromethane (DCM) were used. The absorption maximum ( $\lambda_{\text{abs}}$ ) for **1a** was observed at  $\lambda_{\text{abs}} = 675$  nm. In comparison to **1a**, the absorptions maxima of **1b** and **1c** showed a hypsochromic shift of 84 nm for **1b** (84 nm) and 48 nm for **1c**. The optical energy gap  $E_g$  was estimated based from the onsets of its UV/Vis absorption spectra. The  $E_g$  was determined with 1.84 eV (**1a**), 2.09 eV (**1b**) and 1.97 eV (**1c**). Fluorescence emission maximum was found at 742 nm for **1a**, at 638 nm for **1b** and at 695 nm for **1c**. The fluorescence emission spectra are shown in the ESI (Figure S9-11).



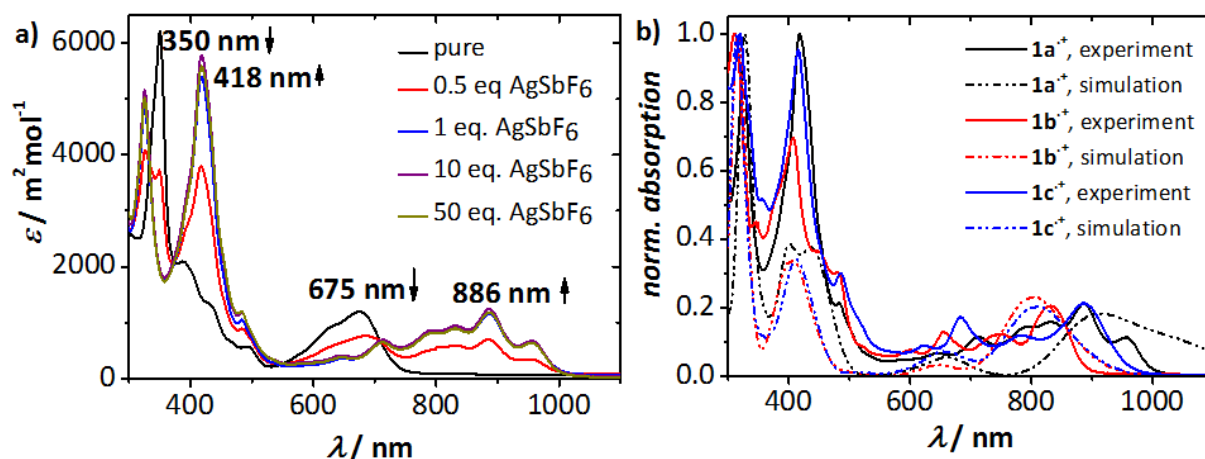
**Figure 3.** a) Aromatic range of the  $^1\text{H-NMR}$  from **1a** in  $\text{DCM-d}_2$  at r.t. after the addition of hydrazine. b) Aromatic range of the COESY spectrum from **1a** in  $\text{DCM-d}_2$  at r.t. with hydrazine.



**Figure 4.** a) Experimental UV-Vis absorption spectra of **1a-c** in comparison with simulation of the twisted conformation (see Figure S12 and S14). b) Cyclic voltammetry of **1a**, **1b** and **1c** in potential range of -2 to 2 V in dry DCM with 0.1 M  $n\text{-BuNPF}_6$  as supporting electrolyte.  $\text{Ag/AgCl}$  was used as reference electrode, platinum as a working electrode and a Pt-wire as a counter electrode. Cyclic voltammetry was performed at a scan rate of  $75 \text{ mVs}^{-1}$ .

### Electrochemical Properties

The electrochemical properties of **1a-c** were studied by cyclic voltammetry (CV) in DCM. As shown in Figure 4b, all compounds showed two quasi-reversible oxidations. The first oxidation potential ranges from 0.41 to 0.47 V for **1a-c**. The second oxidation was observed between 1.20 and 1.27 V. Also a quasi-irreversible reduction for **1a-c** was measured from -1.52 to -1.85 V. Furthermore, compound **1a** showed an additional quasi-reversible reduction at -1.33 V. Due to the poor solubility of **1c** in DCM, the peaks are weak in comparison to those of **1a** and **1b**. The highest occupied molecular orbital (HOMO) were thus estimated based on the onset potentials of the first reversible oxidation for **1a-c** and were determined to be -4.81 eV (**1a**), -4.83 eV (**1b**) and for **1c** at -4.77 eV. The lowest unoccupied molecular orbital (LUMO) was derived based on the onset potentials of the first reversible reduction for **1a**. Consequently, the electrochemical energy gap was calculated at 1.78 eV and agrees well with the optical band gap. The LUMO for **1b** and **1c** were calculated from the optical band gap and the HOMO of the first reversible oxidation. The calculated HOMO energy levels and LUMO energy levels are summarized together with the results from optical spectroscopy and theoretical calculation in Table 1.



**Figure 5.** a) UV-Vis absorption titration spectra using  $\text{AgSbF}_6$  as one-electron-oxidant of molecule **1a** at  $10^{-5}$  mol/l. b) UV-Vis spectra of **1a-c**<sup>•+</sup> in the comparison with the UV-Vis- spectra simulation of the twisted conformation.

**Table 1.** Comparison of photophysical, electrochemical and calculated results.

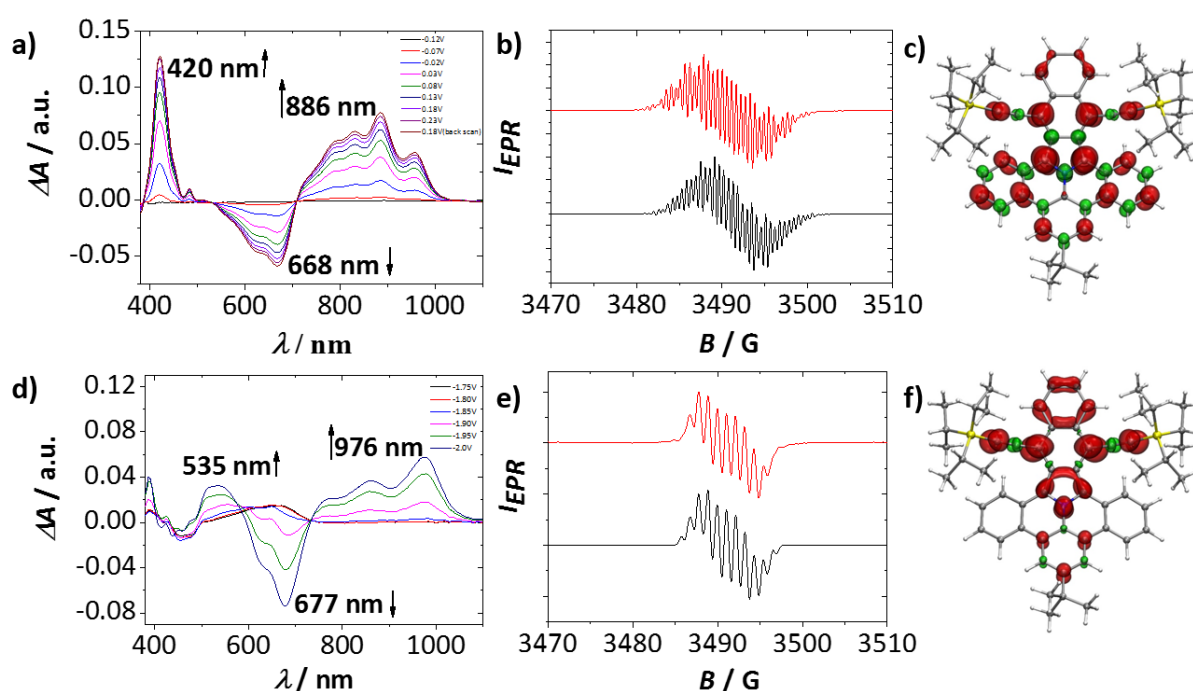
	<u>UV-Vis absorption</u>		<u>fluorescence</u>		<u>electrochemistry</u>		<u>DFT calculations</u>	
	$\lambda_{\text{abs}}^{\text{a}}$ [nm]	$\epsilon$ [m <sup>2</sup> /mol]	$E_{\text{g}}^{\text{b}}$ [eV]	$\lambda_{\text{max}}$ [nm]	$E_{\text{HOMO}}^{\text{c}}$ [eV]	$E_{\text{LUMO}}^{\text{d}}$ [eV]	$\text{IP}^{\text{e}}$ [eV]	$\text{EA}^{\text{e}}$ [eV]
<b>1a</b>	675	1211	1.84	742	-4.81	-3.03	4.66	2.6
<b>1b</b>	591	1559	2.09	638	-4.83	-2.74*	4.41	2.1
<b>1c</b>	627	1340	1.97	695	-4.77	-2.80*	4.53	2.4

a) Absorption at maximum wavelength. b) Estimated from the UV-Vis absorption maxima. c) HOMO was calculated from the onset of the first oxidation waves. d) LUMO was calculated from the onset of the first reduction/ (\*) LUMO was estimated according to  $E_{\text{LUMO}} = E_{\text{HOMO}} + \Delta E_{\text{g}}$  e) The polarization- and relaxation-corrected ionization potentials (IP) and electron affinities (EA) correspond to the HOMOs and LUMOs.

### Oxidation into Radical Cations

The reversible oxidation found for **1a-c** encouraged the investigation of the ability for the generation of the radical cation species. We first performed UV-Vis-oxidation titration of solutions of **1a-c** in anhydrous DCM with the one-electron-oxidant silver antimony hexafluoride ( $\text{AgSbF}_6$ ) into their respective radical cations **1a**<sup>•+</sup>, **1b**<sup>•+</sup> and **1c**<sup>•+</sup>. Addition of 0.5 – 1 equivalent (eq.) of  $\text{AgSbF}_6$  to solutions of **1a-c** in DCM induced a dramatic change in the near infrared region (Figure 5a and SI). The addition of an excess of 10 and 50 eq.  $\text{AgSbF}_6$  did not lead to further changed spectra. MALDI-TOF MS did not show any decomposition products (Figure S23-S25). The bathochromic shifts of absorption upon addition of one-electron-oxidant (Figure 5b) are attributed to the generation of the mono radical cation species which are further corroborated by theoretical calculations (see Figure 5b). A similar change in the absorption was also observed for the stronger oxidant antimony pentachloride ( $\text{SbCl}_5$ ). Nevertheless, addition of more than five equivalents of  $\text{SbCl}_5$  led to decomposition (Figure S8). Subsequently, the treatment of **1a-c** with  $\text{AgSbF}_6$  in a preparative scale provided access to the isolated radical cation species in the yields of 84% for **1a**<sup>•+</sup>, 79% for **1b**<sup>•+</sup> and 71% for **1c**<sup>•+</sup>. For more detailed preparation and analysis see ESI. To understand each charged state in more detail, we further performed in situ spectroelectrochemical (SEC) measurements for **1a** (Figure 6) and **1c**. For **1a**, at slow scan rates of 2.5 mV/s, the first reversible oxidation was observed close to 0.3 V. The UV-Vis spectrum showed a shift of the absorption maximum of 218 nm and is in agreement with absorption maxima of the UV-Vis spectrum after treatment with  $\text{AgSbF}_6$  (Figure 7a). The in situ EPR measurement for **1a**<sup>•+</sup> showed a broad signal with hyperfine structure and a g-factor of 2.0025 (Figure 6b). The spin density is localized over the full  $\pi$ -system (Figure 6c). The SEC

measurement was also performed for **1c** (Figure S16). The resulting radical cation **1c<sup>•+</sup>** species could be confirmed by UV-Vis with a bathochromic shift of the absorption maximum of 259 nm from 627 nm to 886 nm and the resulting EPR-signal with a g-factor of 2.0024. In contrast to the first reversible oxidation, the first reduction of **1a** measured at a slow scan rate was found to be irreversible. The UV-Vis spectrum after the first reduction showed a bathochromic shift of the absorption maxima from 677 nm to 976 nm (Figure 6d). The EPR spectrum of **1a<sup>•-</sup>** showed a broad signal with a hyperfine structure (Figure 6e). The g-factor was measured to be  $g = 2.0026$ . The observed EPR spectra are in good agreement with fitted values. Interestingly, the spin density of the radical cation is completely different compared to the radical anion (Figure 6c and 6f). The spin density is much more localized at the benzoisindole core and acetylene-TIPS substituent.



**Figure 6.** a) UV-Vis spectra of **1a** with the first oxidation. b) EPR signal of **1a<sup>•+</sup>** (black: measurement and red: simulation). c) DFT-computed spin density distribution in **1a<sup>•+</sup>** (red"+", green"-"). d) UV-Vis spectra from the first reduction of **1a**. e) EPR signal of **1a<sup>•-</sup>** (black: measurement and red: simulation). f) DFT-computed spin density distribution in **1a<sup>•-</sup>** (red"+", green"-").

### Computational analysis

To gain further insight in the characteristics of **1a-c**, DFT and time-dependent DFT (TD-DFT) calculations were performed using the spin-unrestricted UCAM-B3LYP functional in combination with the 6-311G\*\* (structure relaxations, absorption spectra)<sup>52, 53</sup> or the cc-pVTZ basis set (energy levels)<sup>54</sup> as implemented in the Gaussian09 suite.<sup>55</sup> At least a minimum of two stable conformers can be found for **1a-c** and are shown exemplified for the phenyl substituted derivative **1b** in Figure S12. The global energy minimum is thereof a conformer with a twisted backbone. Graphical representation of LUMOs and HOMOs of **1a-c** based on the geometry of the twisted conformation can be found in ESI (Figure S13). Similar results are observed for the ionic species again with the twisted conformer as the global energy minimum for all compounds. The presence of different conformers in solution even at room temperature is further supported by the experimental absorption spectra showing pronounced multi-peak structures which appear to go beyond simple vibrational features (Figure 4a, Figure 5b). Indeed, simulated absorption spectra obtained for the twisted and saddle conformer differ in a global bathochromic shift for compounds **1a-c** (Figure S14). Still, the bathochromic shift is relatively small and both conformers behave electronically similar. By applying empirical shifts accounting for polarization effects in DCM and systematic inconsistencies by TD-DFT,<sup>56, 57</sup> positions of absorption maxima can be accurately reproduced as shown in Figure 4a and 5b. The diradical character of the twisted conformer of

**1b**, reveals a very low open-shell character of  $y = 0.08$ , which is evaluated from CASSCF(2,2)/6-311G\*\* calculations indicating that **1b** exhibits a closed-shell singlet ground state. A more detailed discussion on the diradical character  $y$  of individual conformers is provided in ESI.

## Conclusions

In summary, we have demonstrated that fusion of dibenzo-elongated zigzag edges 9a-azaphenylene and naphthalene in orthogonal orientation led to novel N-PHs with a benzoisindole structure with a closed shell ground state. These N-PHs allow an easy access to higher oxidation states such as the radical cationic species, which can be monitored by UV-Vis absorption and in situ spectroelectrochemistry. Furthermore, in agreement with in situ spectroelectrochemistry, a radical anion species was observed by quasi-reversible reduction. Finally, these N-PHs can further be functionalized or extended in various ways giving access to an unprecedented family of molecules with stronger open-shell character with potential application in organic electronic devices.

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