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Pyrene-fused s-indacene

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Supporting Information Placeholder
**ABSTRACT:** One antiaromatic polycyclic hydrocarbon (PH) with and without solubilizing tert-butyl substituents, namely s-indaceno[2,1-a:6,5-a’]dipyrène (IDPs), has been synthesized by a four-step protocol. The IDPs represent the longitudinal, peri-extension of the indeno[1,2-b]fluorene skeleton towards a planar 40 π-electron system. Their structures were unambiguously confirmed by X-ray crystallographic analysis. The optoelectronic properties were studied by UV/Vis absorption spectroscopy and cyclic voltammetry. These studies revealed that peri-fusion renders the IDP derivatives with a narrow optical energy gap of 1.8 eV. The maximum absorption of IDPs is shifted by 160 nm compared to the parent indenofluorene. Two quasi-reversible oxidation as well as reduction steps indicate an excellent redox behavior attributed to the antiaromatic core. Formation of the radical cation and the dication was monitored by UV/Vis absorption spectroscopy during titration experiments. Notably, the fusion of s-indacene with two pyrene moieties lead to IDPs with absorption maxima approaching the Near Infrared (NIR) regime.

**INTRODUCTION**

Polycyclic hydrocarbons (PHs) featuring antiaromaticity have been in the focus of research for decades because of their unique electronic structure and the related magnetic, photophysical and electronic properties. In contrast to polycyclic aromatic hydrocarbons (PAHs) their absorption maxima are significantly bathochromically shifted as the energy difference of their frontier orbitals is significantly reduced and comparable to those of the acene series. The narrow optical energy gap renders antiaromatic PHs promising materials for application in optoelectronic devices. The most common way to obtain antiaromatic, π-conjugated structures is embedding a s-indacene moiety into the core of a π-conjugated framework in which a quinodimethane (QDM) subunit is found. This strategy has been widely used to synthesize antiaromatic but also proaromatic PHs with partial diradical character. Several ortho-, meta- and para-QDM structures have been synthesized in the past years by Wu, Toberi and Haley whereby m- and o-structures are considered as highly reactive due to their increased open-shell character compared to their p-analogues. Typical p-QDM representatives are diphenalenenes and octaethrenes which feature a biradical character at 0.68 eV. The 1,6-indeno[1,2-b]fluorenes (IF, red sub-structures in the formula displayed in Figure 1) which can be regarded as benzo-fused s-indacenes with an unusually insignificant biradical character. Therefore, IFs are considered as stable closed-shell systems. Moreover, indeno[1,2-b]fluorene shows notable resistance towards air, light and heat when protective substituents such as mesityl (Mes) at the reactive 6- and 12-positions are introduced.

![Figure 1: Representation of the different fusion-patterns for IF; in addition to ortho- and ortho-peri-extension in 2a-d and 3a,b we present peri-fusion by formally adding phenalene units to indeno[1,2-b]fluorene.](image_url)

The stability enables processibility for potential application in organic field-effect transistors (OFETs), photovoltaics (OPVs) and light-emitting diodes (OLEDs). To further tune their optoelectronic properties, several longitudinal extended indenofluorenes have been synthesized by Haley. As exemplified in Figure 1, in these derivatives, the benzene rings for 2a-d and also heteroatom containing analogs are fused in ortho-fashion to the parent IF. Recently, our group reported also lateral ortho-peri - along the “bay-position” -extended indeno[1,2-b]fluorenes 3a,b resulting in twisted geometries. In contrast to ortho- (2a-d) and ortho-peri-expansion (3a,b) whereby conjugation is extended only over two bonds (indicated by the dashed bonds in Figure 1), peri-fusion of PAHs extends the conjugation along three directions and, thus, a significant effect on the optoelectronic properties is expected.

**Scheme 1. Synthesis of 1a,b.**
In this work, we report a scalable four-step synthetic route to s-indacenodipyreries (IDPs), namely 8,18-dimethyld-s-indaceno[2,1-a:6,5-a’]dipyrene (1a) and 2,12-diter-butyl-8,18-dimethyld-s-indaceno[2,1-a:6,5-a’]dipyrene (1b). Formal peri-fusion causes a red shift of ~160 nm of the maximum absorption from 512 nm for parent IF to 676 nm for 1a and 682 nm for 1b, thus approaching the NIR region.14

The targeted IDPs 1a and 1b were synthesized starting from 4,4,5,5-tetramethyl-2-(pyren-2-yl)-1,3,2-dioxaborolane (4a) or 2-(7-(tert-butyl)pyren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b), which were both easily accessible by C-H borylation of pyrene developed by the group of Marder (Scheme 1).23 Suzuki reaction of 4a, b and 2,5-dibromoterpahaldehyde41 provided linear 2,5-diper(hyren-2-yl)tereophalaldehyde (5a) and 2,5-bis(7-(tert-butyl)pyren-2-yl)tereophalaldehyde (5b). Crude compounds 5a and 5b were suspended in THF and treated with mesityl magnesium bromide. Without further purification, Friedel-Crafts reaction induced by boron trifluoride diethyl etherate afforded the highly blue fluorescent precursor molecules, 8,18-dimethyld-8,18-dihydro-s-indaceno[2,1-a:6,5-a’]dipyrene (6a) and 2,12-diter-butyl-8,18-dimethyld-8,18-dihydro-s-indaceno[2,1-a:6,5-a’]dipyrene (6b) in a yield of 90% and 86% over two steps, respectively. In the final step, treatment of 6a and 6b with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in dry toluene afforded the desired products 1a and 1b as green solids in yields of 69% and 60%, respectively, after filtration over aluminum oxide and subsequent precipitation in methanol. Both targeted compounds showed reasonable solubility (1.3 mg/ml) in toluene and tetrachloroethane. Two-dimensional NMR spectroscopy (H/H-COSY/NOesy, see Supporting Information Figure S9-S12 and S16-S17) allowed a full proton assignment of 1a and 1b after the addition of hydrazine to remove trace radical impurities.35

RESULTS AND DISCUSSION

In this work, we report a scalable four-step synthetic route to s-indacenodipyreries (IDPs), namely 8,18-dimethyld-s-indaceno[2,1-a:6,5-a’]dipyrene (1a) and 2,12-diter-butyl-8,18-dimethyld-s-indaceno[2,1-a:6,5-a’]dipyrene (1b). Formal peri-fusion causes a red shift of ~160 nm of the maximum absorption from 512 nm for parent IF to 676 nm for 1a and 682 nm for 1b, thus approaching the NIR region.14

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Single crystals of 1a and 1b suitable for X-ray analysis were obtained by slow evaporation of their solutions in a CS$_2$/n-hexane mixture and their molecular arrangements were unambiguously confirmed. Both compounds 1a (Figure 2) and 1b (Supporting Information Figure S18) possess a planar $\pi$-conjugated carbon skeleton and a C$_3$ point symmetry. The central core possesses two short C(sp$^2$)-C(sp$^2$) bonds (1.356(2) and 1.357(2) Å for 1a and 1b) and four long C(sp$^2$)-C(sp$^2$) bonds (1.425(2)/1.457(2) Å for 1a and 1.432(2)/1.452(2) Å for 1b). These bond lengths are in agreement with known p-quinoindial sub-structures.16,22

To investigate the optoelectronic properties, UV/Vis absorption spectra of solutions of 1a and 1b in DCM were recorded and shown in Figure 3 a). The absorption of 1a,b is strongly red-shifted compared to the parent IF and broadband absorbances between 500 and 800 nm with local maxima at

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![Figure 2](https://example.com/figure2.png)

**Figure 2.** Molecular structure (a) and packing in solid state (b) of 1a; hydrogen atoms are omitted for clarity and the thermal ellipsoids are displayed at a 50% probability.
630 and 634 nm as well as global maxima at 676 and 682 nm, respectively are found. No fluorescence was detected when excited with UV light as expected for PHs with an antiaromatic character.

The corresponding, electrochemical derived, energy gaps (ΔEg) are 1.58 and 1.60 eV for 1a and 1b, respectively, which are in agreement with their calculated optical energy gaps (Table 1). Compared to the reported 6,12-dimesitylindeno[1,2-b]fluorene (ΔEg = 2.22 eV), the energy gap decreased by 0.6 eV as the HOMO energy raised from -5.78 eV up to -5.02 and -5.00 eV, for 1a and 1b, respectively. The LUMO energy increased from -3.56 eV for the parent IF to -3.44 and -3.40 eV for 1a and 1b, respectively.

The reversible oxidation found for 1a and 1b encouraged us to investigate the generation of the cation radical and dicaticonic species. First UV/Vis oxidation titration of both solutions in anhydrous dichloromethane (DCM) was performed with the one-electron-oxidant AgSbF6.

The redox properties of 1a and 1b were investigated by cyclic voltammetry (CV) measurements (Figure 3 b)). IDP 1a shows two reversible oxidation waves with half wave potentials E1/2,ox at 0.76 and 1.03 V and two reversible reduction waves with half-wave potentials E1/2,red at ΔEg = 1.24 V (vs Ag/AgCl). Two reversible oxidation waves with E1/2,ox at 0.72 and 0.97 V and two reversible reduction waves with E1/2,red at 0.88 and 1.28 V were observed for compound 1b. Thus, the HOMO/LUMO energy levels are estimated to be -5.02/-3.44 eV and -5.00/-3.40 eV for 1a and 1b, respectively, on the basis of the onset potentials of the first oxidation/reduction waves.

Table 1. Experimental and calculated values of optoelectronic data

<table>
<thead>
<tr>
<th>UV/Vis</th>
<th>Electrochemistry</th>
<th>DFT calculations</th>
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Addition of 1.0-2.0 equivalents (eq) AgSbF₆ to the solution of 1a induced a strong bathochromic shift of the maximum absorption to 1007 nm and minor absorptions arose between 1050 and 1700 nm with local maxima at 113, 1271 and 1452 nm as exemplified in Figure 4 a) for 1a (see Supporting Information, Figure S20 a) for 1b). These absorptions can be attributed to the formation of radical cations 1a•⁺, most likely paired with SbF₆⁻ as the counter ion. After addition of 4.5 eq AgSbF₆, the initial IDP 1a was completely converted according to the vanished absorptions between 600 and 800 nm. Upon further addition of an excess of 40 eq AgSbF₆ a hypsochromic shift to 858 nm (Figure 4 b, see Supporting Information Figure S20 b) for 1b) was observed what we interpret as the formation of a dication 1a•++. No further changes of the UV/Vis absorption spectra were detected after addition of more than 50 eq AgSbF₆ for both compounds.

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculation were performed using the Gaussian 09 package. The geometry of all the structures were optimized at the B3LYP level of theory with the 6-311G(d) basis set. TD-DFT calculation was performed on the neutral, radical cation and dication compounds in order to study the excited states. The graphical representation of the calculated UV/Vis spectra for 1a, 1a•⁺, 1a•++ and 1b, 1b•⁺, 1b•++ and the shapes of the frontier orbital as well as the values for neutral structures in vacuo calculated by Gaussian 09 package are summarized in the Supporting Information (Figure S30-S35).

The HOMO and LUMO orbitals are mainly distributed around the s-indacene core as well as at the margin areas of the pyrene scaffold for both compounds 1a and 1b as pictured in Figure 5 for 1a (see Supporting Information Figure S25-S27 for 1b). The DFT calculated energy gaps for 1a and 1b are 1.77 eV. These results are in agreement with the experimental data and are summarized together in Table 1. The calculated energy gaps are located in between the experimental UV/Vis and electrochemical results and closer to the optical derived values of 1.84 and 1.82 eV for 1a and 1b, respectively. The differences in energy gaps derived by calculation, absorption spectroscopy and CV may arise from polarization effects during the measurement in DCM.

To verify the antiaromatic feature at the internal s-indacene core, NICS(i) calculation using the GIAO B3LYP/6-311+G(2d,p) method have been performed.

### Table 1

<table>
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<th>compd</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (nm)</th>
<th>opt. ΔE&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (eV)</th>
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<th>E&lt;sub&gt;LUMO&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; (eV)</th>
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<th>ΔE&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;h&lt;/sup&gt; (eV)</th>
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<sup>a</sup>Absorption at maximum wavelength; <sup>b</sup>optical energy gap calculated from the UV/Vis absorption maxima using the Planck-Einstein relation; <sup>c</sup>HOMO estimated from the onset potential of the first oxidation wave; <sup>d</sup>LUMO estimated from the onset potential of the first reduction wave; <sup>e</sup>energy gap calculated according to ΔE<sub>g</sub> = E<sub>ΗΟΜΟ</sub>-E<sub>LUMΟ</sub>; <sup>f</sup>HOMO calculated by DFT Gaussian 09 package; <sup>g</sup>LUMO calculated by DFT Gaussian 09 package; <sup>h</sup>energy gap calculated according to ΔE<sub>g</sub> = E<sub>ΗΟΜΟ</sub>-E<sub>LUMΟ</sub>.
the proposed structure and electronic character of pyrene-fused s-indacene.\textsuperscript{32}

**CONCLUSION**

In summary, we present two novel antiaromatic s-indacenodipryenes (IDPs) with large bathochromic shift compared to the parent IF and its derivatives. Photophysical and electrochemical measurements demonstrated that IDPs 1a and 1b possess absorption maxima approaching the NIR region combined with excellent redox behavior. The simple and scalable synthetic protocols towards antiaromatic PHs by combining two pyrene scaffolds with a functionalized benzene core enables the extension towards stable and π-expanded ladder-type polymers representing a repeating IF motive.

**EXPERIMENTAL SECTION**

**General Methods.** Unless otherwise stated, commercially available starting materials, catalysts, reagents and dry solvents were used without further purification. Reactions were performed using standard vacuum-line and Schlenk techniques. Purification of 4a-b and 5a-b was carried out under ambient conditions using reagent-grade solvents. Purification of 1a-b was carried out under argon conditions using dry and bubbled toluene and methanol. Column chromatography was performed on silica (SiO₂, particle size 0.063-0.200 mm purchased from VWR) or aluminium oxide (Al₂O₃, Alox 90 active neutral, activity stage I, purchased from Merck KGaA). Silica coated aluminum sheets with fluorescence indicator (TLC Silica gel 60 F₅₂₄ purchased from Merck KGaA) were used for thin layer chromatography. The starting materials 4a-b\textsuperscript{40} and 2,5-dibromoterephtalaldehyde\textsuperscript{41} were synthesized according to literature procedures. HR-MALDI-TOF MS spectra were recorded on a Bruker Autoflex Speed MALDI-TOF MS (Bruker Daltonics, Bremen, Germany). All samples were prepared by mixing the analyte and the matrix, 1,8-dihydroxyanthracen-9(10H)-one (dithanol, purchased from Fluka Analytical, purity >98%), in the solid state. NMR Data were recorded on a Bruker AV-II 300 spectrometer operating at 300 MHz for H and 75 MHz for 13C and on a Bruker AV-III 600 spectrometer operating at 600 MHz for H and 151 MHz for 13C with standard Bruker pulse programs at room temperature (296 K). Chemical shifts were referenced to δ\textsubscript{MS} = 0.00 ppm (H, 13C). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. Dichloromethane-d₂ (δ (H) = 5.32 ppm, δ(13C) = 53.8 ppm), tetrachloroethane-d₂ (δ (H) = 5.91 ppm, δ (13C) = 74.2 ppm) or chloroform-d (δ (H) = 7.26 ppm, δ (13C) = 77.16 ppm) were used as solvents. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Dichloromethane-d₂ (99.9 Atom% D) was purchased from euriso-top, tetrachloroethane-d₂ (99.6 Atom% D) was purchased from Carl Roth GmbH and chloroform-d (99.8 Atom% D) was purchased from deuto GmbH. UV/Vis-NIR absorption spectroscopy was conducted on an Agilent Technologies Cary Series 5000 using a 10 mm optical-path quartz cell at room temperature. Unless otherwise stated, a solution of the target compounds at a concentration of 10⁻⁵ moll⁻¹ in dichloromethane was measured. Fluorescence spectra were recorded at room temperature on a Perkin Elmer Fluorescence Spectrometer LS 55 using a 10 mm fluorescence quartz cell and argon-purged solutions of the respective compounds (10⁻³ moll⁻¹ in anhydrous dichloromethane). Cyclic voltammetry measurements were carried out on a CHI 760 E potentiostat (CH Instruments, USA) in a three-electrode cell. Electrolyte solutions were prepared by solving [nBu₄N][PF₆] 0.1 M in dichloromethane and the experiments were performed with a scan rate of 50 mVs⁻¹ at room temperature. All measurements were recorded in argon-purged solutions of 1a-b in anhydrous dichloromethane. A Pt-electrode and a Pt-wire were used as working and counter electrode, respectively. Ag/AgCl (3 M KCl solution) was used as reference electrode. All electrochemical measurements were referenced by adding an adequate amount of Cp₂Fe. The oxidation potential for ferrocene E\textsubscript{o,c}(Cp₂Fe/CpFe⁺) in dichloromethane was observed at 0.44 eV. Melting Points were determined on a Büchi Melting Point M-560 in a range of 50-400 °C with a temperature rate of 10 °C/min. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculation were performed using the Gaussian 09 Rev. A02 package.\textsuperscript{31} The geometry of all the structures were optimized at the B3LYP level of theory with the 6-31G(d) basis set. TD-DFT calculation has been performed on the neutral, radical cation and dication compounds in order to study the excited states.

**Preparation of s-indacenodipryenes 1a,b, 2.5-di(pyren-2-yl)terephthalaldehyde (5a).**

2,5-Dibromoterephtalaldehyde (162 mg, 0.55 mmol, 1.0 eq), 4a (546 mg, 1.66 mmol, 3.0 eq) and K₂CO₃ (460 mg, 3.33 mmol, 6.0 eq) were added to a mixture of toluene (9 ml), ethanol (3 ml) and water (3 ml) in a 25 ml Schlenk flask and purged for 30 minutes with argon. After the addition of Pd(PPh₃)₄ (128 mg, 0.11 mmol, 0.2 eq) as catalyst, the reaction mixture was stirred under reflux at 90 °C for 20 hours in an oil bath. The reaction mixture was allowed to cool to room temperature and water (50 ml) as well as chloroform (100 ml) were added. The organic phase was collected and all volatiles removed under reduced pressure. The remaining solid was suspended in methanol and filtered to give crude precursor 5a as yellow powder (94%, 278 mg, 0.52 mmol), which was used without further purification. Due to the extreme low solubility of 5a in common NMR solvents such as deuterated dichloromethane-d₂, chloroform-d, tetrachloroethane-d₂, tetrahydrofuran-d₄, toluene-d₈ or chlorobenzene-d₅, a detailed spectroscopic NMR investigation was not possible. The precursor 5a was confirmed by high resolution mass spectrometry. HR-MS (MALDI-TOF): m/z = 534.1630, calculated for C₂₉H₂₂O₂: m/z = 534.1620, error = +0.87 ppm.

2,5-bis(7-(tert-butyl)pyren-2-yl)terephthalaldehyde (5b).

2,5-Dibromoterephtalaldehyde (50 mg, 0.17 mmol, 1.0 eq), 4b (197 mg, 0.51 mmol, 3.0 eq) and K₂CO₃ (142 mg, 1.03 mmol, 6.0 eq) were added to a mixture of toluene (3 ml), ethanol (1 ml) and water (1 ml) in a 10 ml Schlenk flask and purged for 30 minutes with argon. After the addition of the
catalyst Pd(PPh)$_4$ (39 mg, 0.03 mmol, 0.2 eq), the reaction mixture was heated under reflux at 90 °C for 20 hours in an oil bath. After cooling down to room temperature, the reaction was quenched by adding water (100 ml). The aqueous phase was extracted three times with chloroform (100 ml). The combined organic layers were dried over MgSO$_4$, filtered and all volatiles were evaporated under reduced pressure. The remaining solid was suspended in methanol and filtered to yield precursor 5b as pale green powder (96%, 105 mg, 0.16 mmol), which was used without further purification. $^1$H NMR (300 MHz, tetrachloroethane-d$_2$), $\delta$ = 10.12 (s, 2H), 8.37 (s, 2H), 8.25 (s, 4H), 8.21 (s, 4H), 8.14 (d, $J$ = 9.0 Hz, 4H), 8.08 (d, $J$ = 9.0 Hz, 4H), 1.54 (s, 18H) ppm; $^1$C NMR (75 MHz, tetrachloroethane-d$_2$), $\delta$ = 192.6, 150.3, 145.4, 137.0, 133.8, 131.4, 131.3, 129.3, 124.6, 124.5, 123.4, 122.6, 35.6, 32.2 ppm; HR-MS MALDI-TOF: m/z = 738.3287, error = 0.8 ppm. Full analytical data of target compound 1a: $^1$H NMR (600 MHz, tetrachloroethane-d$_2$, after addition of hydrazine), $\delta$ = 8.02 (s, 2H), 7.91 (d, $J$ = 7.4 Hz, 2H), 7.83 - 7.79 (m, 4H), 7.77 (d, $J$ = 8.9 Hz, 2H), 7.72 (t, $J$ = 7.5 Hz, 2H), 7.56 (d, $J$ = 9.4 Hz, 2H), 7.20 (d, $J$ = 9.3 Hz, 2H), 7.07 (s, 4H), 7.04 (s, 2H), 2.44 (s, 6H), 2.18 (s, 12H) ppm; $^1$C NMR (151 MHz, tetrachloroethane-d$_2$, after addition of hydrazine), $\delta$ = 147.1, 138.9, 138.0, 137.7, 137.3, 137.2, 137.0, 132.4, 134.1, 131.2, 128.8 (4 CH), 128.7 (2 CH), 128.6 (2 CH), 127.7 (2 CH), 127.6, 126.3 (2 CH), 125.9 (2 CH), 125.5 (2 CH), 123.8, 122.8 (2 CH), 119.2 (2 CH), 118.5 (2 CH), 117.1, 116.9, 116.7, 21.8 (2 CH), 20.8 (4 CH) ppm; HR-MS MALDI-TOF: m/z = 736.3130, calculated for C$_{58}$H$_{80}$: m/z = 736.3130, error = ± 2 ppm; mp: >400 °C.

2,12-di-tert-butyl-8,18-dimethyl-s-indaceno[2,1-a:6,5-a']dipyrene (ib). Precursor 5b (100 mg, 0.17 mmol, 1.0 eq) was dissolved in 50 ml THF in a dry Schlenk flask and a solution of 2-mesityl magnesiumbromide in THF (2.6 ml, 1.0 M, 2.55 mmol, 15.0 eq) was added slowly at room temperature. The mixture was stirred overnight and quenched afterwards by slow addition of water (50 ml). The aqueous phase was extracted three times with chloroform (50 ml). The combined organic layers were dried over MgSO$_4$, filtered and all volatiles removed under reduced pressure. The obtained residue was filtered over a short silica plug (chloroform:hexane: 1:4) to give an isomeric mixture of intermediate 6b (see Scheme 1 in manuscript) as light green solid. Intermediate 6a (20 mg, 0.027 mmol, 1.0 eq) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 6 mg, 0.027 mmol, 2.0 eq) were dissolved in toluene (2 ml) in a dry 10 ml Schlenk flask and the mixture was allowed to cool down to room temperature. The mixture was stirred for one hour and carefully quenched by addition of a saturated NaHCO$_3$ solution (5 ml) afterwards. The aqueous phase was extracted three times with chloroform (50 ml) and the resulting combined organic phases were dried over MgSO$_4$, filtered and all volatiles removed under reduced pressure. The obtained residue was filtered over a short silica plug (chloroform:iso-hexane: 1:4) to give an isomeric mixture of intermediate 6b (see Scheme 1 of manuscript) as light green solid. Intermediate 6a (20 mg, 0.027 mmol, 1.0 eq) was redissolved in toluene (2 ml) in a dry 50 ml Schlenk flask and the mixture was heated at 80 °C in an oil bath. After two hours the reaction mixture was allowed to cool down to room temperature. Due to its low stability, the solution was quickly filtered through an aluminum oxide (neutral) column with dry toluene as eluent under argon atmosphere. All volatiles were evaporated under reduced pressure, the remaining solid was suspended in dry and argon-purged methanol and filtered to yield the greenish target compound 1a in a good yield (60%, 7 mg, 0.082 mmol). The intermediate 6b was confirmed by HR-MALDI-TOF (measured: m/z = 850.4593, calculated for C$_{58}$H$_{80}$: m/z = 850.4539, error = 6.35 ppm). Due to the bad solubility (1.3 mg/ml) of 1b the $^1$C-NMR measurements only show a low resolution. Full analytical data of target compound 1a: $^1$H NMR (600 MHz, tetrachloroethane-d$_2$, after addition of hydrazine), $\delta$ = 8.02 (s, 2H), 7.91 (d, $J$ = 7.4 Hz, 2H), 7.83 - 7.79 (m, 4H), 7.77 (d, $J$ = 8.9 Hz, 2H), 7.72 (t, $J$ = 7.5 Hz, 2H), 7.56 (d, $J$ = 9.4 Hz, 2H), 7.20 (d, $J$ = 9.3 Hz, 2H), 7.07 (s, 4H), 7.04 (s, 2H), 2.44 (s, 6H), 2.18 (s, 12H) ppm; $^1$C NMR (151 MHz, tetrachloroethane-d$_2$, after addition of hydrazine), $\delta$ =
149.4 (2C), 147.0 (2C), 139.0 (2C), 138.0 (2C), 137.6 (2C), 137.2 (2C), 137.0 (2C), 132.8 (2C), 131.9 (2C), 131.2 (2C), 131.0 (2C), 128.9 (2CH), 128.7 (2CH), 128.5 (2CH), 127.9 (2CH), 127.4 (2CH), 125.9 (2C), 124.1 (2C), 123.8 (2CH), 123.1 (2CH), 122.9 (2CH), 122.7 (2CH), 119.0 (2CH), 118.3 (2CH), 116.9 (2C), 35.2 (2C), 32.0 (6CH), 21.8 (2CH), 20.8 (4CH2) ppm; HR-MS (MALDI-TOF): m/z = 848.4393, calculated for C56H36: m/z = 848.4382, error = +1.30 ppm; mp: >400 °C.

ASSOCIATED CONTENT
The Supporting Information is available free of charge on the ACS Publications website.

HR-MALDI-TOF spectra for 1a.b. Copies of the 1H- and 13C-NMR spectra for 5a.b and 1a.b. Single-crystal X-ray data (CIF) for 1a.b. UV/Vis absorption spectra for 1a, 1a", 1a"*, and 1b, 1b"*, 1b"*. Fluorescence emission spectra and cyclic voltammograms for 1a,b. Computational data for 1a, 1a", 1a"*, and 1b, 1b"*, 1b"*.

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Notes
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REFERENCES


25. Initially solutions of 1a and 1b only showed broad signals in the aromatic area (see Supporting Information) what we attribute to the presence of trace amounts of radical impurities arising from immediate oxidation processes.
