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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'*]dipyrene (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.¹ In contrast to polycyclic aromatic hydrocarbons (PAHs) their absorption maxima are significantly bathochromic shifted as the energy difference of their frontier orbitals is significantly reduced and comparable to those of the acene series.² The narrow optical energy gap renders antiaromatic PHs promising materials for application in optoelectronic devices.^{3, 4} 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.⁵ This strategy has been widely used to synthesize antiaromatic but also proaromatic PHs with partial diradical character.⁶ Several *ortho*-,⁷ *meta*-⁸ and *para*-QDM⁹ structures have been synthesized in the past years by Wu, Tobe 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 diphenalenes¹⁰ and octazethrenes¹¹ which feature a biradical character up to 0.68,¹² as well as indeno[1,2-*b*]fluorenes (IF, red sub-structures in the formula displayed in Figure 1)² which can be regarded as benzo-fused *s*-indacenes with an usually insignificant biradical character.¹³ 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.¹⁴

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.

The stability enables processibility for potential application in organic field-effect transistors (OFETs), photovoltaics (OPVs) and light-emitting diodes (OLEDs).¹⁵⁻¹⁷ 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**¹⁸ and also heteroatom containing analogs are fused in *ortho*-fashion to the parent IF.¹⁹⁻²¹ Recently, our group reported also lateral *ortho*-*peri* - along the “bay-position” -extended indeno[1,2-*b*]fluorenes **3a,b** resulting in twisted geometries.²² 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.⁹

Scheme 1. Synthesis of 1a,b.

RESULTS AND DISCUSSION

In this work, we report a scalable four-step synthetic route to *s*-indacenodipyrenes (IDPs), namely 8,18-dimesityl-*s*-indaceno[2,1-*a*:6,5-*a'*]dipyrene (**1a**) and 2,12-di-*tert*-butyl-8,18-dimesityl-*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 (**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-dibromoterephthalaldehyde²⁴ provided linear 2,5-di(pyren-2-yl)terephthalaldehyde (**5a**) and 2,5-bis(7-(*tert*-butyl)pyren-2-yl)terephthalaldehyde (**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-dimesityl-8,18-dihydro-*s*-indaceno[2,1-*a*:6,5-*a'*]dipyrene (**6a**) and 2,12-di-*tert*-butyl-8,18-dimesityl-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 mgml⁻¹) in toluene and tetrachloroethane. Two-dimensional NMR spectroscopy (¹H/¹H-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.²⁵

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.

Single crystals of **1a** and **1b** suitable for X-ray analysis were obtained by slow evaporation of their solutions in a CS₂/*n*-hexane mixture and their molecular arrangements were unambiguously confirmed. Both compounds **1a** (Figure 2) and **1b** (Supporting Information Figure S18) possess a planar π -conjugated carbon skeleton and a C₂ point symmetry. The central core possesses two short C(sp²)-C(sp²) bonds (1.356(2) and 1.357(2) Å for **1a** and **1b**) and four long C(sp²)-C(sp²) 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*-quinoidal sub-structures.^{18, 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 broad absorptions between 500 and 800 nm with local maxima at

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.²⁶

Figure 3. a) UV/Vis absorption spectra of **1a** (black line) and **1b** (red line) in DCM at 10^{-5} mol l $^{-1}$; b) cyclic voltammograms of **1a** (black line) and **1b** (red line) in potential range of -2 to 2 V in dry DCM with 0.1 M *n*-BuNPF $_6$ as supporting electrolyte, Ag/AgCl was used as reference electrode, platinum as a working electrode and a Pt-wire as counter electrode performed at a scan rate of 50 mVs $^{-1}$.

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 $E_{1/2,ox}$ at 0.76 and 1.03 V and two reversible reduction waves with half-wave potentials $E_{1/2,red}$ at -0.86 and -1.24 V (vs Ag/AgCl). Two reversible oxidation waves with $E_{1/2,ox}$ at 0.72 and 0.97 V and two reversible reduction waves with $E_{1/2,red}$ 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.

The corresponding, electrochemical derived, energy gaps (ΔE_g) 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 ($\Delta E_g = 2.22$ eV),¹⁴ 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.²² 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 dicationic species. First UV/Vis oxidation titration of both solutions in anhydrous dichloromethane (DCM) was performed with the one-electron-oxidant AgSbF $_6$.

Figure 4. UV/Vis absorption titration spectra using a solution of one-electron-oxidant AgSbF $_6$ in dry DCM at 10^{-5} mol l $^{-1}$; UV/Vis spectra were directly measured after addition of the oxidant; a) UV/Vis absorption during titration of **1a** into **1a** $^{+\bullet}$ by adding 0-4.5 eq oxidant in steps of 0.5 eq; b) UV/Vis absorption during titration of **1a** $^{+\bullet}$ to **1a** $^{++}$ by further adding up to 40 eq of AgSbF $_6$.

Table 1. Experimental and calculated values of optoelectronic data

UV/Vis	Electrochemistry	DFT calculations
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compd	$\lambda_{\max}^a$ (nm)	opt. ΔE_g^b (eV)	E_{HOMO}^c (eV)	E_{LUMO}^d (eV)	ΔE_g^e (eV)	E_{HOMO}^f (eV)	E_{LUMO}^g (eV)	ΔE_g^h (eV)
1a	676	1.84	-5.02	-3.44	1.58	-4.57	-2.79	1.77
1b	682	1.82	-5.00	-3.40	1.60	-4.51	-2.74	1.77

^aAbsorption at maximum wavelength; ^boptical energy gap calculated from the UV/Vis absorption maxima using the Planck-Einstein relation; ^cHOMO estimated from the onset potential of the first oxidation wave; ^dLUMO estimated from the onset potential of the first reduction wave; ^eenergy gap calculated according to $\Delta E_g = E_{\text{HOMO}} - E_{\text{LUMO}}$; ^fHOMO calculated by DFT Gaussian 09 package; ^gLUMO calculated by DFT Gaussian 09 package; ^henergy gap calculated according to $\Delta E_g = E_{\text{HOMO}} - E_{\text{LUMO}}$.

Addition of 1.0-2.0 equivalents (eq) AgSbF_6 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 1113, 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 SbF_6^- as the counter ion. After addition of 4.5 eq AgSbF_6 , 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 AgSbF_6 , 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**²⁺. No further changes of the UV/Vis absorption spectra were detected after addition of more than 50 eq AgSbF_6 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 6-31G(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**²⁺ and **1b**, **1b**^{•+}, **1b**²⁺ 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(1) calculation using the GIAO B3LYP/6-311+G(2d,p) method have been performed.

Figure 5. Visualization of the frontier orbitals and NICS calculation; a) HOMO **1a** (-4.57 eV); b) LUMO **1a** (-2.79 eV) c) NICS(1) values of **1a**; d) NICS(1) values of **1b**.

For **1a** and **1b**, NICS values are positive at the five-membered (5.5 and 4.8, respectively) and central six-membered (3.2 and 2.8, respectively) rings, confirming the preserved antiaromaticity of the s-indacene unit (Figure 5 c), d)). The negative values for the outer pyrene units are in accordance with calculations by Jenneskens and confirm

the proposed structure and electronic character of pyrene-fused *s*-indacene.²⁷

CONCLUSION

In summary, we present two novel antiaromatic *s*-indacenodipyrenes (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 F₂₅₄ purchased from Merck KGaA) were used for thin layer chromatography. The starting materials **4a-b**^[1] and 2,5-dibromoterephthalaldehyde^[2] 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(10*H*)-one (dithranol, 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 ¹H and 75 MHz for ¹³C and on a Bruker AV-III 600 spectrometer operating at 600 MHz for ¹H and 151 MHz for ¹³C with standard Bruker pulse programs at room temperature (296 K). Chemical shifts were referenced to $\delta_{TMS} = 0.00$ ppm (¹H, ¹³C). Chemical shifts (δ) are reported in ppm. Coupling constants (*J*) are reported in Hz. Dichloromethane-d₂ (δ (¹H) = 5.32 ppm, δ (¹³C) = 53.8 ppm), tetrachloroethane-d₂ (δ (¹H) = 5.91 ppm, δ (¹³C) = 74.2 ppm) or chloroform-d₁ (δ (¹H) = 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-d₁ (99,8 Atom% D) was purchased from deutero 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 mol l⁻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 (10⁻⁵ mol l⁻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 (3M KCl solution) was used as reference electrode. All electrochemical measurements were referenced by adding an adequate amount of Cp₂Fe. The oxidation potential for ferrocene $E_{1/2}(\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+)$ 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 °Cmin⁻¹. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculation were performed using the Gaussian 09 Rev. A02 package.^[3] 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*-indacenodipyrenes **1a,b.** 2,5-di(pyren-2-yl)terephthalaldehyde (**5a**). 2,5-Dibromoterephthalaldehyde (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-d₁, 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 C₄₀H₂₂O₂; *m/z* = 534.1620, error = +1.87 ppm.

2,5-bis(7-(*tert*-butyl)pyren-2-yl)terephthalaldehyde (**5b**). 2,5-Dibromoterephthalaldehyde (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(PPh₃)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 MgSO₄, 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. ¹H NMR (300 MHz, tetrachloroethane-d₂), δ = 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; ¹³C NMR (75 MHz, tetrachloroethane-d₂), δ = 192.6, 150.3, 145.4, 137.0, 133.8, 131.4, 131.3, 129.3, 127.4, 126.4, 124.5, 123.4, 122.6, 35.6, 32.2 ppm; HR-MS (MALDI-TOF): m/z = 646.2892, calculated for C₄₈H₃₈O₂: m/z = 646.2872, error = +3.09 ppm.

8,18-dimesityl-s-indaceno[2,1-a:6,5-a']dipyrene (**1a**). Precursor **5a** (250 mg, 0.47 mmol, 1.0 eq) was dissolved in 150 ml tetrahydrofuran (THF) in a dry Schlenk flask and a solution of 2-mesityl magnesiumbromide in THF (7.0 ml, 1.0 M, 7.00 mmol, 15.0 eq) was added slowly at room temperature. The mixture was stirred overnight, quenched by slow addition of water (100 ml) and the aqueous phase extracted three times with chloroform (100 ml) afterwards. The combined organic layers were dried over MgSO₄, filtered and all volatiles evaporated under reduced pressure. The crude material was then transferred to a dry 50 ml Schlenk flask and dissolved in 30 ml dichloromethane. The mixture was cooled down to 0 °C and a solution of boron trifluoride diethyl etherate (230 µl, 1.87 mmol, 4.0 eq) was added slowly in the course of 5 min. The mixture was stirred for one hour and was carefully quenched with a saturated NaHCO₃ solution (10 ml) afterwards. The aqueous phase was extracted three times with chloroform (50 ml). The combined organic phases were again dried over MgSO₄, filtered and all volatiles removed under reduced pressure. The obtained residue was filtered over a short silica plug (chloroform/*iso*-hexane: 1:4) to result in isomeric mixture of intermediated **6a** (see Scheme 1 of 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, 12 mg, 0.055 mmol, 2.0 eq) were redissolved in toluene (3 ml) in a dry 10 ml Schlenk flask and the mixture 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 blue-greenish target compound **1a** in a good yield (69%, 14 mg, 0.019 mmol). The intermediate **6a** was confirmed by HR-MALDI-TOF spectrometry (m/z = 738.3281, calculated for C₅₈H₄₂: m/z = 738.3287, error = 0.81 ppm). Due to the bad solubility (1.3 mgml⁻¹) of **1b** the ¹³C-NMR measurements only show a low resolution. Full analytical data of target compound **1a**: ¹H NMR (600 MHz, tetrachloroethane-d₂,

after addition of hydrazine), δ = 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; ¹³C NMR (151 MHz, tetrachloroethane-d₂, after addition of hydrazine), δ = 147.1, 138.9, 138.0, 137.7, 137.3, 137.2, 137.0, 132.8, 132.0, 131.4, 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 CH₃), 20.8 (4 CH₃) ppm; HR-MS-MALDI-TOF: m/z = 736.3130, calculated for C₅₈H₄₀: m/z = 736.3130, error = ± 0 ppm; mp: >400 °C.

2,12-di-tert-butyl-8,18-dimesityl-s-indaceno[2,1-a:6,5-a']dipyrene (**1b**). 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 MgSO₄, filtered and all volatiles evaporated under reduced pressure. The crude material was transferred to a dry 50 ml Schlenk flask and dissolved in 20 ml dichloromethane. The mixture was cooled down to 0 °C and a solution of boron trifluoride diethyl etherate (85 µl, 0.68 mmol, 4.0 eq) was added slowly in the course of 5 min. The mixture was stirred for one hour and was carefully quenched by addition of a saturated NaHCO₃ solution (5 ml) afterwards. The aqueous phase was extracted three times with chloroform (50 ml) and the resulting combined organic phases were dried over MgSO₄, filtered and all volatiles removed under reduced pressure. The obtained residue was filtered over a short silica plug (chloroform/*i*-hexane: 1:4) to give an isomeric mixture of intermediate **6b** (see Scheme 1 in manuscript) as light green solid. **6b** (12 mg, 0.014 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 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 give the blue-greenish target compound **1b** 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 C₆₆H₅₈: m/z = 850.4539, error = 6.35 ppm). Due to the bad solubility (1.3 mgml⁻¹) of **1b** the ¹³C-NMR measurements only show a low resolution. Full analytical data of target compound **1b**: ¹H NMR (600 MHz, tetrachloroethane-d₂, after addition of hydrazine), δ = 7.97 (s, 2H), 7.92 (d, J = 1.6 Hz, 2H), 7.82 (d, J = 1.6 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 9.5 Hz, 2H), 7.15 (d, J = 9.2 Hz, 2H), 7.07 (s, 4H), 7.01 (s, 2H), 2.44 (s, 6H), 2.17 (s, 12H), 1.41 (s, 18H) ppm; ¹³C NMR (151 MHz, tetrachloroethane-d₂, after addition of hydrazine), δ =

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 (2C), 125.9 (2C), 124.1 (2C), 123.8 (2C), 123.1 (2CH), 122.9 (2CH), 122.7 (2CH), 119.0 (2CH), 118.3 (2CH), 116.9 (2C), 35.2 (2C), 32.0 (6CH₃), 21.8 (2CH₃), 20.8 (4CH₃) ppm; HR-MS (MALDI-TOF): m/z = 848.4393, calculated for C₆₆H₅₆: 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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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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