Naphthazarin-Polycyclic Conjugated Hydrocarbons and Iptycenes

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ABSTRACT. The synthesis of a set of naphthazarin-containing polycyclic conjugated hydrocarbons is described herein. Sequential Diels–Alder reactions on a tautomerized naphthazarin core were employed to access the final conjugated systems. Complete conjugation across the backbone can be achieved through complexation with BF$_2$, as observed by $^1$H NMR analysis and UV/vis spectroscopy. Precise synthetic control over the degree of oxidation of naphthazarin quinone Diels–Alder adduct 10 is additionally demonstrated, and enables us to direct its subsequent reactivity. Finally, this work serves to demonstrate the potential for naphthazarin as a building block in the synthesis of novel organic electronic materials.

Keywords: naphthazarin / Diels–Alder reactions / phenylene-containing oligoacenes / BF$_2$-complex / polycyclic conjugated hydrocarbons / iptycenes
INTRODUCTION

Polycyclic conjugated hydrocarbons are organic small molecules of interest as active materials in electronic and optoelectronic devices. Acenes, such as pentacene and trisopropylsilyl-pentacene (TIPS-pentacene), are among the top performers in organic field effect transistors (OFETs),\cite{1,2} and while they have achieved significant milestones,\cite{3} considerable efforts remain focused on the design and synthesis of new classes of compounds to achieve a desired boost in performance and material stability.

To this end, synthetic chemists have explored structural modifications to the acene core to achieve improved stability, processibility, and electronic properties. Strategies include appending bulky or electron-withdrawing substituents,\cite{1,4} or including heteroatoms into the core acene unit, such as in the synthesis of anthradithiophenes or azaacenes.\cite{1,5-13} Other efforts explore a redesign of the bonding architecture of the core molecule, such as through the incorporation of formally antiaromatic cyclobutadiene units, present in [N]phenylenes and phenylene-containing oligoacenes (POAs).\cite{14-19} Alternation of cyclobutadiene units with either benzene ([N]phenylenes) or acene units (POAs) results in localized conjugation along the molecular backbone, which can improve chromophore stability.\cite{15,16}

Key synthetic approaches to building acene or acene-like small molecules include sequential Diels–Alder reactions,\cite{16,20,21} cross-coupling methods,\cite{6,22} or the [2+2+2] methodology used by Vollhardt and coworkers to synthesize extended [N]phenylenes.\cite{15}

In this study, we capitalize on the ability of naphthazarin (1,4-dihydroxy-5,8-naphthaquinone)\cite{23-25} to act as a bifunctional Diels–Alder reagent to access new iptycene and POA molecules in a convergent manner. Examples of target structures are presented in Figure 1. Naphthazarin has the ability to react twice as a dienophile,\cite{26}
which can be achieved via oxidation and tautomerization of the initial Diels–Alder adduct to unmask a second dienophile equivalent on the opposite side of the naphthazarin core. This makes it an appealing building block to convergently synthesize multi-ring systems. Historically, naphthazarins have been utilized predominantly in the construction of anthracyclines,\textsuperscript{23–27} and in this study we intend to demonstrate its further potential as a useful building block in the synthesis of organic electronic materials.

We also demonstrate that the naphthazarin-derived Diels–Alder adducts presented herein can coordinate to two BF\textsubscript{2} groups to form conjugated electron-deficient complexes.\textsuperscript{28,29} These types of materials may prove useful as electron-transporting materials and n-type semiconductors.\textsuperscript{28,29} To this end, we report the synthesis and spectroscopic properties of a set of triptycene, pentiptycene, and POA naphthazarin-based structures (Figure 1), as well as a proof-of-concept demonstration of their complexation with BF\textsubscript{3}-OEt\textsubscript{2}.

\textbf{Figure 1.} Three of the naphthazarin-containing target molecules synthesized in this study.

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\textbf{RESULTS AND DISCUSSION}

\textbf{Synthesis of naphthazarin triptycene derivatives 7a–d.} Triptycene compounds 7a–d were accessed through an initial [4+2] Diels–Alder cycloaddition reaction of
naphthazarin (5) with a corresponding anthracene (4a–d) to furnish monocycloadducts 6a–d, followed by oxidation to the target triptycene intermediates 7a–d (Scheme 1).

**Scheme 1.** Synthesis of naphthazarin triptycenes 7a–d and pentiptycenes 1a–d.

Formation of cycloadducts 6a–d occurred in moderate to good yields (20–80%). Oxidation of 6a–d in the presence of air and excess of KO\textsubscript{t}Bu produced naphthazarin triptycenes 7a–d in nearly quantitative yields. Reactivity of the anthracene precursors with naphthazarin varies, and we observe anthracene 4d reacting in the highest yield, likely due to its more electron-rich character relative to the other selected anthracenes.

Single crystals of 6b, 7a, and 8a suitable for X-ray crystallography were obtained by slow evaporation from CH\textsubscript{2}Cl\textsubscript{2}/n-hexane at 25 °C (Figures 2 and S1–3, Supporting Information). Although DFT calculations support the tetrasubstituted quinone tautomer 7a as the more thermodynamically stable isomer,\textsuperscript{23} the crystal structure of 7a was elucidated as tautomer 7a-T. Calculations at the B3LYP/6-31G(d) level showed that the energy difference between structures 7a and 7a-T is 1.05
kcal/mol. (For further details on the computational investigations, see the Supporting Information.)

Figure 2. Three X-ray crystal structures of iptycenes 6b, 7a, and 8a.

Synthesis of naphthazarin pentiptycene compounds 1a–d. Naphthazarin-based cycloadducts are known to tautomerize to expose the quinone-based dienophile (7-T), which can undergo a second cycloaddition reaction with a diene. Upon heating, we observed a second equivalent of 4a–d to undergo a [4+2] cycloaddition with 7a–d to yield double-cycloadducts 8a–d in 31–61% yields (Scheme 1).

Similar to the conversion observed from 6a–d to 7a–d, we found that KO'Bu enolized cycloadducts 8a–c and, in the presence of air, cleanly transformed them into 1a–c in excellent yield. This method of oxidation is very mild, and enables us to access a portfolio of functionalized naphthazarin pentiptycenes with varying degrees of internal free volume. Isolation of pentiptycene 1d, however, was not possible. Although we observed characteristic changes in color that signified conversion of 8d to 1d (from yellow to dark blue upon addition of KO'Bu, then to dark red after work-up), our attempts to isolate 1d were unsuccessfull as a result of the limited solubility and unexpected decomposition of the product. (See Figure S46 for the UV/vis spectrum of the final reaction mixture.)

Synthesis of naphthazarin phenylene-containing-oligoacene compounds 2a–b and 3. We next hypothesized that the Diels–Alder reactivity of the naphthazarin core
could be extended to a synthetic approach to access novel POAs.\textsuperscript{16,19} Naphthazarin presents an opportunity to incorporate an electron-deficient acene unit into the POA backbone, in particular when complexed with BF\textsubscript{2}. The naphthazarin motif also provides functional handles for further synthetic manipulation or complexation to metals\textsuperscript{32,33} and boron moieties.\textsuperscript{28,29}

To synthesize naphthazarin-derived POAs, we utilized diene 9, which can be accessed in two steps according to literature procedures.\textsuperscript{16,19,34–39} Diene 9 was reacted with naphthazarin (5) to furnish mono-adduct 10 in 49\% yield (Scheme 2). Interestingly, X-ray crystallographic analysis of compound 10 shows a \textit{trans} arrangement of the hydrogen atoms located at the adduct site (Figure S4 in the SI). This is in stark contrast to the expected stereochemistry of Diels–Alder cycloaddition products, as the \textit{exo} and/or \textit{endo} product is often observed, and the resultant placement of hydrogen atoms in space depends on this product ratio.\textsuperscript{40} The \textit{trans} relationship in the crystal structure of 10 could signify that the operative mechanism of reaction is, in fact, step-wise instead of a true concerted cycloaddition. Alternatively, the \textit{trans} relationship may be due to epimerization resulting from enolization at the $\alpha$-carbon that occurs following a conventional \textit{cis} [4+2] cycloaddition. An explanation is that the hydrogen-bonding between the hydroxyl groups and the ketones of the naphthazarin core increases the likelihood of enolization at the $\alpha$-carbons, and, for sterically-induced reasons, the hydrogen atoms end up \textit{trans} to one another. While we observe a \textit{trans} relationship for compound 10 by X-ray analysis, we detect the presence of three isomers by NMR (Figure S84 in the SI), leading us to conclude that the \textit{trans} product is likely present alongside the \textit{endo} and \textit{exo} adducts.

\textbf{Scheme 2.} Targeted synthesis of naphthazarin POA mono-adducts 2a–b.
With 10 in hand, we next unmasked dienophile 11-T to enable further Diels–Alder reactivity (Scheme 3), and found an interesting dependence on the equivalents of KOtBu used. By adjusting the amount of KOtBu and reaction time, we were able to effectively tune the level of oxidation to produce either partially-oxidized product 11 or fully-oxidized product 12 (Scheme 2). This capability is significant, as we found that only partially-oxidized 11 is able to further tautomerize in situ to produce 11-T, which brandishes an external-facing dienophile. Fully-oxidized 12 contains an additional aromatic ring that stabilizes and “locks” the internal 9,10-quinone in place. Here, we found that when mono-adduct 10 was reacted with only three equivalents of KOtBu for a short period of time (five minutes), we were able to achieve the partially oxidized product 11 in 52% yield. When reacted in significant excess and for extended periods of time, the fully oxidized product 12 became the major or sole product (18 equiv., 78% yield). X-ray crystal structures of 10–12 are shown in Figures S4–S6 in the SI.

Fully-oxidized 12 can be converted to target compound 2a in 84% yield through hydrolysis of the bridging oxygen when exposed to an acidic solution of hydrochloric acid in chloroform and isopropyl alcohol. Poor solubility of 2a
prevented acquisition of a $^{13}$C NMR spectrum. An alternative target was found in 2b, which proved more soluble than 2a, and can be obtained through conversion from 12 (58% yield) or from 2a (49% yield) using $p$-TsOH/Ac$_2$O.

**Scheme 3.** Targeted synthesis of POA double-adduct 14.

We next induced tautomerization of partially-oxidized 11, and reacted the *in situ*-generated 11-T dienophile with diene 9 for a second cycloaddition reaction. Overall, Diels–Alder reaction of 11-T with diene 9 and subsequent oxidation with KO‘Bu in the presence of air yielded 13 in 13% yield. Unfortunately, multiple attempts to convert 13 to the final symmetrical POA double-adduct 14 failed. The challenges we faced in isolating 14 were likely due to poor solubility, as was similarly encountered with pentiptycene 1d and POA mono-adduct 2a. We did observe consumption of 13 upon exposure to acid and were able to detect 14 by MALDI-TOF mass spectrometry (see Figure S112). However, the reaction largely produced a substantial amount of insoluble material that we were unable to isolate for full characterization.
To circumvent these problems, we redesigned our synthetic plan and instead targeted compound 3 (Scheme 4). We hypothesized that the non-planar triptycene end-group of 3 would eliminate the aforementioned solubility and aggregation issues.\(^{31}\) We attempted to react the *in situ* generated 11-T dienophile with one equivalent of anthracene 4a, but were only able to observe trace amounts of product by TLC.

**Scheme 4.** Targeted synthesis of iptycene-POA 3.

Due to the insufficient reactivity of 11-T, we sought to access target compound 3 by reversing our synthetic strategy. To this end, we were able to successfully react 7a with diene 9 to yield double-adduct POA-iptycene 15 in 30% yield over two steps. The final product 3 could be accessed under acidic conditions and collected in 75% yield as a dark-orange product. This compound proved reasonably soluble in 1,1,2,2-tetrachloroethane and could be characterized, but was exemplary of the solubility challenges faced in trying to access the symmetrical double POA adduct.
**Spectroscopic Properties of mono- and double-adducts**

The UV/vis spectra of four selected naphthazarin derivatives 1a, 2a, 3, and 7a are shown in Figure 3a (See Figures S12–22 in the SI for the UV/vis spectra of all compounds). The UV/vis spectra of 1a, 2a, 3, and 7a are characteristic of naphthazarins, showing vibronically coupled bands with significant fine structures at lower energy. The deep red-colored compound 7a exhibits a fine-structure absorption band at $\lambda_{\text{max}} = 568$ nm (2.18 eV, $\varepsilon = 4800$ M$^{-1}$ cm$^{-1}$). The additional triptycene unit in 1a caused a bathochromic shift of 8 nm [$\lambda_{\text{max}} = 576$ nm (2.15 eV, $\varepsilon = 6900$ M$^{-1}$ cm$^{-1}$)].

Vertical optical transitions were calculated on the optimized structures of 7a and 1a by time-dependent density functional theory (TD-DFT), using the software package Gaussian 03 (See Supporting Information for further details). The computed transition energies in both cases are slightly lower than the experimental values (Table S1 and S2). The spectra of mono and double POA-naphthazarin compounds 2a and 3 display low energy bands at $\lambda_{\text{max}} = 551$ nm (2.25 eV, $\varepsilon = 3180$ M$^{-1}$ cm$^{-1}$) and $\lambda_{\text{max}} = 557$ nm (2.23 eV, $\varepsilon = 3745$ M$^{-1}$ cm$^{-1}$), respectively. Electrochemical analysis of these compounds reveals two quasireversible waves, consistent with literature studies (see Figure S114 and Table S5).

**Figure 3.** (a) UV/vis spectra of selected compounds 1a (red line), 2a (black line), 3 (green line), and 7a (blue line) in CH$_2$Cl$_2$ at 298 K. (b) Normalized absorbance (solid lines) and fluorescence (dashed lines) spectra of selected compounds 6a (red lines, $\lambda_{\text{ex}} = 355$ nm), 8a (blue lines, $\lambda_{\text{ex}} = 355$ nm), and 10 (green lines, $\lambda_{\text{ex}} = 375$ nm) in CH$_2$Cl$_2$ at 298 K.
Upon analysis, some of the compounds synthesized in this study showed interesting fluorescent properties (Table 1 and Figure 3b). The unoxidized cycloaddition adducts (compounds 6a–d, 8a–d, and 10) showed strong blue fluorescence with high quantum yields ($\Phi_F = 0.58–0.91$). Though fluorescent Diels–Alder adducts of naphthazarin have been reported, the strong fluorescence of 6a–d, 8a–d, and 10 was unexpected due to the lack of $\pi$-conjugation across the backbone. This strong blue emission was observed across the series, suggesting it may be due to the enolizable nature or the hydrogen-bonding capabilities of the unoxidized naphthazarin adduct.

**Table 1.** Photophysical characterization of emissive compounds synthesized. All measurements were performed in CH$_2$Cl$_2$ ($\lambda_{ex} = 375$ nm).

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Investigation of BF$_2$-complexation with the naphthazarin-cores Complexation of BF$_3$-OEt$_2$ with the naphthazarin core of various synthesized compounds renders the molecules fully conjugated, and was explored for potential n-type semiconducting applications.

Representative complexation studies were conducted with $^1$H NMR, UV/vis and mass spectroscopy. For example, we were able to observe the conversion of compound 1a to BF$_2$-1a following the addition of BF$_3$-OEt$_2$ to 1a in CH$_2$Cl$_2$. The product could be isolated through precipitation and was analyzed by $^1$H NMR as shown in Figure 4. Here, we observe the disappearance of the hydroxyl peak around 12 ppm, and see a distinct shift in the aromatic and bridgehead peaks upon complexation. Finally, a mixture of the two products clearly demonstrates the appearance of two discrete molecules in solution. The structure of BF$_2$-1a was also confirmed by HR-ESI-MS ($m/z$ calc'd for C$_{38}$H$_{20}$B$_2$F$_4$O$_4^{-}$: 638.1518; found: 638.1503 [M$^{-}$]) Susceptibility to hydrolysis was consistent with previous reports in the literature.$^{28,29}$ Presumably due to moisture present in the air, hydrolysis was observed for BF$_2$-1a to occur in CDCl$_3$ over 1-2 hours, precluding $^{13}$C NMR analysis.

Figure 4. $^1$H NMR spectra (400 MHz) of compounds 1a to BF$_2$-1a in CDCl$_3$ at 298 K demonstrating BF$_2$-complexation.
During the reaction of compound 1a with BF$_3$-OEt$_2$, the solution changed from dark red to dark purple, and was observed by UV/vis spectroscopy as a shift in absorbance bands from ~533 nm to ~561 nm (Figure 5). This red-shifted absorption maximum of BF$_2$-1a reveals the generation of a fully conjugated structure through BF$_2$ chelation. Similar spectral changes were observed with BF$_2$-1b and BF$_2$-1c (see Figures S39–42 in the SI for the UV/vis spectra of BF$_2$-1b and BF$_2$-1c). In studying this complexation spectroscopically for BF$_2$-2a and BF$_2$-3, our characterization attempts were hampered by the limited solubility of substrates 2a and 3, similar to that observed in literature.$^{28,29}$ Despite this challenge, we were still able to observe a color change from orange to dark blue upon addition of BF$_3$-OEt$_2$, which was similar to that observed for the BF$_2$-1 series (See Figures S43–45 in the SI for the UV/vis spectra of BF$_2$-2a and BF$_2$-3).

**Figure 5.** UV/vis spectra of compound 1a (black line) and BF$_2$-1a (blue line) in CH$_2$Cl$_2$ at 298 K.
CONCLUSION

In conclusion, a selection of naphthazarin-containing polycyclic conjugated hydrocarbon molecules were synthesized and characterized, and may find utility in optoelectronic and other electronic applications. The molecular design includes 1) iptycene wings to add free space around the chromophores for better solubility, and 2) structural motifs of POAs to achieve improved stability. Successful coordination with BF$_2$ as a proof-of-concept reveals the potential for new conjugated n-type electronic materials or expanded coordination complex structures, such as conducting metallopolymers.

Experimental Section

**General.** Reagents were purchased as reagent grade and used without further purification. All solvents were of ACS reagent grade or better. Toluene was passed through a solvent purification system *via* columns of activated alumina, and stored over 3 Å sieves. Reactions in the absence of air and moisture were performed in oven-dried glassware under Ar or N$_2$ atmosphere. Flash column chromatography (FC) was performed using SiO$_2$ (60 Å, 230–400 mesh, particle size 0.040–0.063 mm) at 25 °C with a head pressure of 0.0–0.5 bar. The used solvent compositions are reported individually in parentheses. Analytical thin layer chromatography (TLC) was performed on sheets coated with silica gel (200 µm, IB-F). Visualization was achieved using UV light (254 or 366 nm). Evaporation *in vacuo* was performed at 25–60 °C and 900–10 mbar. Reported yields refer to spectroscopically and chromatographically pure compounds that were dried under high vacuum (0.1–0.05 mbar) before analytical characterization. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded at 500 or 400 MHz ($^1$H) and 125 or 100 MHz ($^{13}$C),
respectively. Chemical shifts $\delta$ are reported in ppm downfield from tetramethylsilane using the residual solvent signals as an internal reference (CDCl$_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm / Cl$_2$CDCl$_2$: $\delta_H = 6.0$ ppm, $\delta_C = 73.78$ ppm). For $^1$H NMR, coupling constants $J$ are given in Hz and the resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), m (multiplet), and br. (broad). All spectra were recorded at 298 K. High-resolution mass spectrometry (HRMS) was performed by the MS-service of the MIT Department of Chemistry Instrumentation Facility using an Ion Cyclotron Resonance Mass Spectrometer with either electrospray (ESI) or Direct Analysis in Real Time (DART) as the ionization technique. Where noted, additional mass spectra were obtaining using Matrix-Assisted Laser Desorption/Ionization-Time-of-Flight (MALDI-TOF)), by depositing samples directly onto the target without a matrix. UV/vis spectroscopy was recorded on a UV/vis spectrophotometer and corrected for background signal with a solvent-filled cuvette. Fluorescence spectra were measured using right-angle detection. Absolute quantum yield measurements were carried out using an integrating sphere, which was coupled to the fluorometer via a optical fiber bundle. Samples were excited with a 450W Xenon short arc lamp and fluorescence was detected with a detector. All photophysical measurements were performed with spectral grade dichloromethane.

Naphthazarin (5) was used without further purification. Anthracene (4a) was recrystallized from ethanol/toluene prior to use. Compounds 4b (2,3,6,7-tetramethylanthracene), 4c (2,6-di-tert-butylanthracene), 4d (1,1,4,4,8,8,11,11-Octamethyl-1,2,3,4,8,9,10,11-octahydro-pentacene), and diene 911 were synthesized according to literature procedures.

**Monoadduct triptycene synthesis: Compounds 6a–d**
Naphthazarin (5) (1 equiv.) and the appropriate anthracene 4a–d (1 equiv.) were added to a flame-dried Schlenk flask with stirrer bar, and were dissolved in the minimal amount of anhydrous toluene (1-2 mL). The headspace was purged with argon for 30 minutes, then heated to reflux overnight (111 °C). The solvent was concentrated in vacuo. FC (SiO₂; CH₂Cl₂, or hexanes then CH₂Cl₂ in scenarios where separation was poor) gave target adducts 6a–d.

**Compound 6a**

Naphthazarin (5) (200 mg, 1.05 mmol), anthracene 4a (188 mg, 1.05 mmol), FC (CH₂Cl₂): 6a, yellow solid (241 mg, 62% yield). Mp: 228–230 °C. Rᵣ = 0.66 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 12.43 (s, 2H), 7.45 (br. dd, 2H, J = 5.4, 3.4 Hz), 7.21 (br. dd, 2H, J = 5.4, 3.4 Hz), 7.15 (br. t, 2H, J = 4.4 Hz), 7.10 (s, 2H), 6.95 (br. t, 2H, J = 4.4 Hz), 5.04 (s, 2H), 3.35 ppm (br. s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 202.2, 155.8, 141.9, 139.8, 128.7, 126.9, 124.6, 124.1, 114.2, 49.63, 49.55 ppm. UV/vis (CH₂Cl₂): λmax (ε) = 258 (9371), 402 (7438), 424 (5973), 432 nm (3860 M⁻¹ cm⁻¹).


**Compound 6b**

Naphthazarin (5) (200 mg, 1.05 mmol), anthracene 4b (247 mg, 1.05 mmol), FC (CH₂Cl₂): 6b, yellow solid (205 mg, 53% yield). Mp: 206–208 °C. Rᵣ = 0.74 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 12.48 (s, 2H), 7.19 (s, 2H), 7.10 (s, 2H), 6.88 (s, 2H), 4.89 (s, 2H), 3.31 (s, 2H), 2.23 (s, 6H), 2.02 ppm (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 202.6, 155.8, 140.0, 137.7, 134.7, 128.5, 125.7, 125.2, 114.4, 50.0, 48.6, 19.7, 19.6 ppm (13 of 14 signals expected). UV/vis (CH₂Cl₂): λmax (ε) = 263 (9368), 402 (6465), 425 (4931), 434 nm (2926 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C₂₈H₂₃O₄⁻: 423.1602; found: 423.1617 [M – H]⁻.
Naphthazarin (5) (100 mg, 0.53 mmol), anthracene 4c (153 mg, 0.53 mmol), FC (100% n-hexanes to 100% CH₂Cl₂): 6c, yellow solid (51 mg, 20% yield). Mp: 81–83 °C. Rᵣ = 0.48 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 12.30 (s, 1H), 12.26 (s, 1H), 7.47 (s, 1H), 7.37 (d, 1H, J = 7.8 Hz), 7.23 (d, 1H, J = 7.7 Hz), 7.14 (s, 1H), 7.05 – 6.99 (m, 3H), 6.91 (d, 1H, J = 7.8 Hz), 4.94 (s, 1H), 4.91 (s, 1H), 3.32 (s, 2H), 1.32 (s, 9H), 1.10 ppm (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 202.88, 202.86, 155.4, 155.3, 150.1, 150.0, 141.6, 139.5, 138.5, 136.6, 128.24, 128.19, 124.0, 123.7, 123.5, 123.3, 121.7, 121.2, 114.40, 114.36, 50.5, 50.3, 50.2, 50.0, 34.9, 34.6, 31.7, 31.4 ppm.

UV/vis (CH₂Cl₂): λ_max (ε) = 260 (12872), 403 (7475), 432 nm (3898 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C₃₂H₃₁O₄⁻: 479.2228; found: 479.2223 [M – H]⁻.

**Compound 6d**

Naphthazarin (5) (100 mg, 0.53 mmol), anthracene 4d (210 mg, 0.56 mmol): 6d, yellow solid (247 mg, 80%). Mp: 260–262 °C (decomp.). Rᵣ = 0.83 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 12.14 (s, 2H), 7.34 (s, 2H), 7.02 (s, 2H), 6.98 (s, 2H), 4.77 (s, 2H), 3.28 (quasi t, 2H), 1.70 – 1.62 (m, 4H), 1.49 – 1.38 (m, 4H), 1.33 (s, 6H), 1.22 (s, 6H), 1.11 (s, 6H), 0.96 ppm (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 203.5, 154.9, 143.33, 143.26, 138.3, 136.4, 127.9, 122.5, 122.0, 114.6, 50.9, 50.4, 35.3, 35.0, 34.5, 34.1, 32.19, 32.15, 31.8, 31.6 ppm. UV/vis (CH₂Cl₂): λ_max (ε) = 263 (11458), 403 (7872), 427 (5724), 435 nm (3495 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C₄₀H₄₃O₄⁻: 587.3167; found: 587.3142 [M – H]⁻.

**Oxidation to conjugated triptycene monoadducts: Compounds 7a–d.**

To a 25 mL round-bottom flask was added 6a–d (1 equiv.), KO’Bu (6 equiv.), and 20 mL THF. After stirring under ambient conditions for 1–3 h, the blue reaction mixture was poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. FC (SiO₂; CH₂Cl₂) gave 7a–d as a red solid.
**Compound 7a**

6a (110 mg, 0.299 mmol), KO\textsuperscript{t}Bu (201 mg, 1.79 mmol): 7a, red solid (107 mg, 98% yield). Mp: 317–319 °C. R\textsubscript{f} = 0.75 (CH\textsubscript{2}Cl\textsubscript{2}). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 12.61 (s, 2H), 7.48 (br. dd, 4H, J = 5.3, 3.3 Hz), 7.09 (s, 2H), 7.06 (br. dd, 4H, J = 5.3, 3.3 Hz), 6.04 ppm (s, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 175.2, 167.0, 152.9, 143.6, 132.7, 125.9, 124.6, 111.4, 47.6 ppm. UV/vis (CH\textsubscript{2}Cl\textsubscript{2}): λ\textsubscript{max} (ε) = 235 (22860), 262 (8250), 274 (8070), 496 (6520), 526 (7610), 568 nm (4800 M\textsuperscript{-1} cm\textsuperscript{-1}). HR-DART-MS: m/z calcd for C\textsubscript{24}H\textsubscript{15}O\textsubscript{4}: 367.0965; found: 367.0954 [M + H]\textsuperscript{+}.

**Compound 7b**

6b (210 mg, 0.495 mmol), KO\textsuperscript{t}Bu (333 mg, 2.97 mmol): 7b, red solid (159 mg, 76% yield). Mp: 315–317 °C. R\textsubscript{f} = 0.83 (CH\textsubscript{2}Cl\textsubscript{2}). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 12.64 (s, 2H), 7.28 (s, 4H), 7.09 (s, 2H), 5.92 (s, 2H), 2.20 ppm (s, 12H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 175.7, 166.4, 153.7, 141.5, 133.7, 132.4, 125.8, 111.4, 46.7, 19.6 ppm. UV/vis (CH\textsubscript{2}Cl\textsubscript{2}): λ\textsubscript{max} (ε) = 245 (14350), 263 (15200), 283 (10700), 489 (4810), 526 (5610), 567 nm (3570 M\textsuperscript{-1} cm\textsuperscript{-1}) HR-DART-MS: m/z calcd for C\textsubscript{28}H\textsubscript{23}O\textsubscript{4}: 423.1591; found: 423.1573 [M + H]\textsuperscript{+}.

**Compound 7c**

6c (40 mg, 0.083 mmol), KO\textsuperscript{t}Bu (56 mg, 0.499 mmol): 7c, red solid (39 mg, 99% yield). Mp: 115–117 °C. R\textsubscript{f} = 0.58 (DCM). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 12.62 (s, 2H), 7.50 (s, 2H), 7.39 (d, 2H, J = 7.9 Hz), 7.09 (s, 2H), 7.06 (d, 2H, J = 7.9 Hz), 5.97 ppm (s, 2H), 1.26 ppm (s, 18H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 176.4, 165.9, 153.7, 149.1, 143.7, 140.8, 132.3, 124.0, 122.4, 121.9, 111.5, 47.5, 34.8, 31.6 ppm. UV/vis (CH\textsubscript{2}Cl\textsubscript{2}): λ\textsubscript{max} (ε) = 237 (13700), 260 (7590), 278 (6480), 496 (3940), 526 (4590), 568 nm (2960 M\textsuperscript{-1} cm\textsuperscript{-1}) HR-DART-MS: m/z calcd for C\textsubscript{32}H\textsubscript{31}O\textsubscript{4}: 479.2217; found: 479.2215 [M + H]\textsuperscript{+}.
**Compound 7d**

6d (100 mg, 0.170 mmol), KO\textsuperscript{t}Bu (114 mg, 1.02 mmol): 7d, red solid (85 mg, 85% yield). Mp: >350 °C \( R_f = 0.84 \) (CH\textsubscript{2}Cl\textsubscript{2}). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 12.62 (s, 2H), 7.39 (br. s, 4H), 7.05 (br. s, 2H), 5.88, (s, 2H), 1.62 (s, 8H), 1.24 ppm (s, 24H).

13C NMR (101 MHz, CDCl\textsubscript{3}): \( \delta \) 177.8, 164.6, 154.0, 142.2, 140.6, 131.7, 122.6, 111.6, 47.1, 35.2, 34.5, 32.1, 32.0 ppm. UV/vis (CH\textsubscript{2}Cl\textsubscript{2}): \( \lambda_{\text{max}} (\epsilon) = 240 \) (16870), 273 (12120), 284 (12600), 489 (6370), 526 (7630), 568 nm (4830 M\textsuperscript{–1} cm\textsuperscript{–1}). HR-DART-MS: \( m/z \) calcd for C\textsubscript{40}H\textsubscript{42}O\textsubscript{4}: 587.3078; found: 587.3083 [M + H]\textsuperscript{+}.

**Double-adduct pentiptycene synthesis: Compounds 8a–d**

Compound 7a–d (1 equiv.) and the appropriate anthracene 4a–d (1 equiv.) were added to a flame-dried Schlenk flask with stir bar, and were dissolved in the minimal amount of anhydrous toluene (<1 mL). The headspace was purged with argon for 30 minutes, then heated to reflux overnight (111 °C). The solvent that remained was concentrated \textit{in vacuo}. FC (SiO\textsubscript{2}; 100% n-hexanes to 100% CH\textsubscript{2}Cl\textsubscript{2}).

**Compound 8a**

7a (36 mg, 0.098 mmol), 4a (17.5 mg, 0.098 mmol): 8a, yellow solid (22 mg, 41% yield). Mp: 190–192 °C (decomp). \( R_f = 0.89 \) (CH\textsubscript{2}Cl\textsubscript{2}). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 12.75 (s, 2H), 7.50 – 7.35 (m, 6H), 7.17 (quasi t, 2H, \( J = 4.3 \) Hz), 7.12 (quasi t, 2H, \( J = 4.3 \) Hz), 7.06 – 7.01 (m, 2H), 7.01 – 6.97 (m, 2H), 6.91 – 6.86 (m, 2H), 5.99 (s, 2H), 5.05 (s, 2H), 3.27 ppm (s, 2H). 13C NMR (101 MHz, CDCl\textsubscript{3}): \( \delta \) 201.9, 151.2, 145.5, 144.1, 143.8, 142.1, 140.0, 126.9, 126.7, 125.74, 125.72, 124.6, 124.4, 124.3, 124.0, 113.1, 49.5, 48.8, 47.6 ppm. UV/vis (CH\textsubscript{2}Cl\textsubscript{2}): \( \lambda_{\text{max}} (\epsilon) = 269 \) (13378), 408 (5423), 429 nm (4503 M\textsuperscript{–1} cm\textsuperscript{–1}). HR-DART-MS: \( m/z \) calcd for C\textsubscript{38}H\textsubscript{23}O\textsubscript{4}: 543.1602; found: 543.1620 [M – H].

**Compound 8b**
7b (127 mg, 0.301 mmol), 4b (70 mg, 0.301 mmol): 8b, yellow solid (94 mg, 48% yield). Mp: 249–251 °C. Rf = 0.88 (CH2Cl2). 1H NMR (400 MHz, CDCl3): δ 12.72 (s, 2H), 7.22 (s, 2H), 7.17 (s, 2H), 7.14 (s, 2H), 6.82 (s, 2H), 5.85 (s, 2H), 4.87 (s, 2H), 3.21 (s, 2H), 2.20 (s, 6H), 2.16 (s, 6H), 2.12 (s, 6H), 1.91 ppm (s, 6H).

13C NMR (101 MHz, CDCl3): δ 202.3, 150.9, 146.0, 142.0, 141.8, 140.2, 137.7, 134.8, 134.5, 133.7, 133.6, 125.7, 125.6, 125.1, 113.3, 50.0, 48.0, 46.6, 19.7, 19.6, 19.5 ppm (21 out of 23 signals expected). UV/vis (CH2Cl2): λmax (ε) = 279 (27051), 409 (11980), 433 nm (8708 M⁻¹ cm⁻¹). HR-QDART-MS: m/z calcd for C46H40O4Na⁺: 679.2819; found: 679.2826 [M + Na]⁺.

Compound 8c

7c (40 mg, 0.084 mmol), 4c (24 mg, 0.084 mmol): 8c, yellow solid (21 mg, 31% yield). Mp: 220–222 °C (decomp.). Rf = 0.71 (CH2Cl2). Note that by NMR we observe 4 isomers in a 1:1:1:1 ratio, based on the hydroxyl peak integration in the 1H NMR spectrum.

1H NMR (400 MHz, CDCl3): δ 12.59 (s, 2H), 12.57 (s, 2H), 12.55 (s, 2H), 12.54 (s, 2H), 7.43 (m, 12H), 7.36 (br. s, 2H), 7.31 (m, 12H), 7.20 (br. d, J = 1.86 Hz, 2H), 7.18 (br. d, J = 1.86 Hz, 2H), 7.05 (m, 4H), 7.02 (m, 2H), 6.98 (m, 8H), 6.74 (dd, J = 7.82, 2.01 Hz, 2H), 6.69 (dd, J = 7.82, 2.01 Hz, 2H), 5.88 (m, 8H), 4.90 (m, 8H), 3.23 (m, 8H), 1.29 (m, 36H), 1.26 (m, 36H), 1.22 (m, 36H), 0.87 (s, 18H), 0.84 (s, 18H).

13C NMR (101 MHz, CDCl3): δ 202.73, 202.68, 150.6, 150.55, 150.53, 150.4, 149.83, 149.78, 148.8, 148.7, 145.7, 145.6, 144.23, 144.17, 143.8, 143.7, 141.7, 141.6, 141.4, 141.3, 140.9, 139.5, 139.4, 138.84, 138.77, 136.7, 123.9, 123.7, 123.6, 123.5, 123.4, 123.1, 123.0, 122.4, 122.19, 122.17, 121.8, 121.6, 121.4, 121.2, 121.1, 113.2, 113.12, 113.07, 50.1, 50.0, 49.9, 49.8, 47.4, 36.8, 34.84, 34.75, 34.4, 34.3, 31.69, 31.65, 31.59, 31.2. UV/vis (CH2Cl2): λmax (ε) = 275 (21100), 410 (8330), 431
nm (6640 M⁻¹ cm⁻¹). HR-ESI-MS: m/z calcd for C_{54}H_{56}O_{4}Na⁺: 791.4071; found: 791.4055 [M + Na]⁺.

**Compound 8d**

7d (61 mg, 0.104 mmol), 4d (41 mg, 0.104 mmol): 8d, yellow solid (62 mg, 61%).

Mp: > 350 °C. R_{f} = 0.97 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 12.42 (s, 2H), 7.31 (s, 4H), 7.27 (s, 2H), 6.89 (s, 2H), 5.77 (s, 2H), 4.72 (s, 2H), 3.18 (s, 2H), 1.70 – 1.60 (m, 8H), 1.57 (s, 4H), 1.40 – 1.10 (m, 38H), 1.00 (s, 6H), 0.74 (m, 2H), 0.62 ppm (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 203.6, 150.1, 145.5, 143.2, 143.0, 141.7, 141.5, 140.6, 138.1, 136.2, 128.4, 122.5, 122.4, 122.1, 122.0, 113.0, 51.1, 50.4, 47.0, 35.4, 35.3, 34.6, 34.46, 34.45, 34.4, 33.9, 32.5, 32.2, 32.1, 32.0, 31.9, 31.8, 31.50 ppm.

UV/vis (CH₂Cl₂): λ_{max} (ε) = 279 (25616), 411 (10015), 434 nm (7830 M⁻¹ cm⁻¹). HR-ESI-MS: m/z calcd for C_{70}H_{80}O_{4}Na⁺: 1007.5949; found: 1007.5963 [M + Na]⁺.

**Oxidation to conjugated pentiptycene double-adducts 1a–c.**

To a 25 mL round-bottom flask was added 8a–c (1 equiv.), KOtBu (6 equiv.), and 20 mL THF. After stirring under ambient conditions for 1–3 h, the blue reaction mixture was poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. FC (SiO₂; CH₂Cl₂) gave 1a–d as a red solid.

**Compound 1a**

8a (55 mg, 0.101 mmol), KOtBu (68 mg, 0.606 mmol): 1a, red solid (38 mg, 69% yield). Mp: >350 °C. R_{f} = 0.91 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 12.88 (s, 2H), 7.42 (br. dd, 8H, J = 5.3, 3.2 Hz), 7.01 (br. dd, 8H, J = 5.3, 3.2 Hz), 5.98 ppm (s, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 169.1, 151.1, 143.7, 125.8, 124.5, 110.2, 47.6 ppm. UV/vis (CH₂Cl₂): λ_{max} (ε) = 242 (47370), 262 (15520), 291 (4270), 502 (8140), 533 (10070), 576 nm (6900 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C_{38}H_{23}O_{4}⁺: 543.1591; found: 543.1583 [M + H]⁺.
**Compound 1b**

8b (94 mg, 0.143 mmol), KOtBu (96 mg, 0.859 mmol): 1b, red solid (51 mg, 54% yield). Mp: >350 °C. Rf = 0.80 (CH2Cl2). 1H NMR (400 MHz, CDCl3): δ 12.87 (s, 2H), 7.18 (s, 8H), 5.82 (s, 4H), 2.13 ppm (s, 24H). 13C NMR (101 MHz, CDCl3): δ 169.0, 151.6, 141.7, 133.5, 125.7, 110.1, 46.7, 19.6 ppm. UV/vis (CH2Cl2): λmax (ε) = 248 (30200), 273 (20415), 283 (17150), 502 (7500), 534 (9160), 577 nm (6420 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C46H39O4+: 655.2843; found: 655.2856 [M + H]+.

**Compound 1c**

8c (111 mg, 0.144 mmol), KOtBu (97 mg, 0.866 mmol): 1c, red solid (50 mg, 45% yield). Mp: 264–266 °C. Rf = 0.97 (CH2Cl2). 1H NMR (400 MHz, CDCl3): δ 12.95 (s, 2H), 7.46 (s, 4H), 7.36 (br. d, 4H, J = 7.7 Hz), 7.03 (br. d, 4H, J = 7.7 Hz), 5.94 (s, 4H), 1.25 ppm (s, 36H). 13C NMR (101 MHz, CDCl3): δ 169.2, 151.6, 148.9, 143.8, 140.9, 123.8, 122.3, 121.7, 110.1, 47.3, 54.8, 31.6 ppm. UV/vis (CH2Cl2): λmax (ε) = 245 (41075), 267 (19620), 278 (15230), 504 (8130), 533 (10010), 577 nm (6910 M⁻¹ cm⁻¹). HR-ESI-MS: m/z calcd for C54H55O4+: 767.4095; found: 767.4088 [M + H]+.

**Synthesis of the POA series**

**Compound 10**

Naphthazarin (5) (100 mg, 0.526 mmol) and diene 9 (238 mg, 0.684 mmol) were added to either an oven-dried pressure tube or flame-dried Schlenk flask with stirrer bar, and were dissolved in the minimal amount of anhydrous toluene (1–2 mL). The headspace was purged with argon for 30 minutes, then heated to reflux overnight (111 °C). The solvent was concentrated in vacuo. Gravity column chromatography (SiO2: CH2Cl2) or FC (SiO2; 100% n-hexanes to 100% CH2Cl2) yielded 138 mg (49% yield) of a yellow solid. Note that while the highest yields were obtained when carried out in.
a pressure tube, similar yields are obtained when carried out under refluxing conditions. Note also that by NMR we observe 1:0.20:0.20 ratio of isomers, based on the hydroxyl peaks. The $^1$H NMR integrations are calculated such that hydroxyl peaks in 11.94–11.79 integrate to a total of 2H. Mp: 301–303 °C. $R_f$ = 0.32 (DCM).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.94 (s, 0.28 H), 11.90 (s, 0.28 H), 11.78 (s, 1.43 H), 7.66 (m, 4 H), 7.44 (m, 6 H), 7.20 (s, 2 H), 7.12 (m, 2 H), 6.95 (m, 2 H), 3.47 (m, 2 H), 3.13 (m, 2 H), 2.20 (m, 4 H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 203.5, 202.7, 155.3, 155.2, 155.1, 148.1, 140.7, 140.5, 137.2, 137.1, 128.7, 128.62, 128.57, 128.51, 128.4, 128.3, 128.2, 128.16, 128.1, 127.0, 126.9, 126.8, 119.4, 119.3, 113.4, 86.43, 86.39, 86.3, 54.0, 53.6, 53.3, 46.3, 46.0, 45.8, 25.4, 24.8, 23.7. UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) = 259 (8606), 398 (6903), 421 nm (4804 M$^{-1}$ cm$^{-1}$). HR-DART-MS: $m/z$ calcld for C$_{36}$H$_{27}$O$_5$$^+$: 539.1853, found 539.1852 [M+H]$^+$.

**Compound 11**

To a 25 mL round-bottom flask was added 10 (330 mg, 0.613 mmol) and KO'Bu (206 mg, 1.84 mmol) in 20 mL THF. The reaction was stirred under ambient conditions for 1–5 min, and was monitored by TLC for the appearance of the red partially oxidized product 11 and stopped immediately following the appearance of the orange fully oxidized 12. The dark blue reaction mixture was poured over NH$_4$Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO$_4$, filtered and evaporated. FC (SiO$_2$; CH$_2$Cl$_2$) gave 11 as a red solid (171 mg, 52% yield). Mp: 293–295 °C. $R_f$ = 0.40 (CH$_2$Cl$_2$). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.41 (s, 2H), 7.70 (d, 4H, $J = 6.9$ Hz), 7.50 (t, 4H, $J = 7.4$ Hz), 7.45–7.39 (m, 2H), 7.19–7.07 (m, 4H), 6.98 (dd, 2H, $J = 5.3$, 3.0 Hz), 3.62 (s, 2H), 3.18–3.05 (m, 2H), 2.87–2.74 ppm (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 186.3, 158.6, 148.1, 143.9, 138.5, 137.0, 129.6, 128.7, 128.3, 127.0, 126.8, 119.4, 111.4, 86.4, 54.0, 24.2 ppm. UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$
(ε) = 279 (7718), 482 (6380), 511 (7071), 550 nm (4181 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C₃₆H₂₅O₅⁺: 537.1697; found: 537.1684 [M + H]⁺.

**Compound 12**

To a 25 mL round-bottom flask was added **10** (105 mg, 0.195 mmol) and KOtBu (394 mg, 3.51 mmol) in 20 mL THF. After stirring under ambient conditions for 1–3 h, the blue reaction mixture was poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. FC (SiO₂; CH₂Cl₂) gave **12** as an orange solid (81 mg, 78% yield). Mp: 304–305 °C. Rf = 0.47 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 12.80 (s, 2H), 7.75 – 7.70 (m, 6H), 7.56 – 7.52 (m, 4H), 7.49 – 7.44 (m, 2H), 7.22 (dd, 2H, J = 5.4, 3.0 Hz), 7.19 (s, 2H), 7.11 (dd, 2H, J = 5.4, 3.0 Hz), 4.34 ppm (s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 187.1, 157.7, 151.0, 147.5, 135.7, 134.5, 129.2, 128.9, 128.6, 127.5, 126.8, 121.2, 119.7, 112.5, 89.0, 55.7 ppm. UV/vis (CH₂Cl₂): λmax (ε) = 275 (38000), 486 nm (8080 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C₃₆H₂₃O₅⁺: 535.1540; found: 535.1541 [M + H]⁺.

**Compound 2a**

In a flame-dried 25 mL Schlenk flask, compound **12** (21 mg, 0.039 mmol) was dissolved in 1:1 isopropyl alcohol-CHCl₃ (0.5 mL each). Concentrated HCl (0.2 mL) was added slowly to the solution under argon. The solution was heated to 80 °C for 4 hours. The product was washed with deionized water and extracted with CH₂Cl₂, then concentrated in vacuo. The product was washed with hexanes, then filtered and dried overnight under vacuum, affording **2a** as a red solid (17 mg, 84% yield). Mp: > 350 °C. Rf = 0.53 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 12.88 (s, 2H), 7.87 (dd, 2H, J = 6.3, 3.4 Hz), 7.65 – 7.60 (m, 8H), 7.56 (s, 2H), 7.55 – 7.50 (m, 2H), 7.37 (dd, 2H, J = 6.3, 3.4 Hz), 7.27 ppm (s, 2H). UV/vis (CH₂Cl₂): λabs (ε) = 298 (31300), 370
(23900), 511 (7270), 551 nm (3180 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C₃₆H₂₁O₄⁺: 517.1434; found: 517.1422 [M + H]⁺.

**Compound 2b**

In a flame-dried 25 mL Schlenk flask, compound 12 (154 mg, 0.288 mmol) was dissolved in 10 mL acetic anhydride with p-TsOH crystals (694 mg, 4.0 mmol). The solution was heated to 120 °C for 12 hours. The product was precipitated by pouring solution over ice, and adding water until a solid precipitate formed. The product was filtered and dried overnight under vacuum, affording 2b as an orange solid (100 mg, 58% yield). Mp: 285–287 °C. Rₛ = 0.33 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 7.84 (dd, 2H, J = 6.2, 3.4 Hz), 7.62 – 7.57 (m, 8H), 7.55 – 7.48 (m, 2H), 7.40 – 7.32 (m, 6H), 2.45 ppm (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 183.3, 169.6, 155.7, 148.1, 142.2, 136.1, 135.7, 135.2, 131.5, 130.9, 129.6, 129.1, 128.5, 127.6, 127.4, 125.8, 115.3, 21.3 ppm. UV/vis (CH₂Cl₂): λₘₐₓ (ε) = 299 (41950), 368 (39395), 463 nm (2878 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C₄₀H₂₅O₆⁺: 601.1646; found: 601.1643 [M + H]⁺.

**Compound 13**

11 (32 mg, 0.060 mmol) and diene 9 (21 mg, 0.060 mmol) were added to a flame-dried Schlenk flask with stir bar, and were dissolved in the minimal amount of anhydrous toluene (1–2 mL). The headspace was purged with argon for 30 minutes, then heated to reflux overnight (111 °C). The solvent was concentrated in vacuo. KO'Bu (121 mg, 1.07 mmol) and 20 mL THF were added to the flask, and the reaction was allowed to stir 1–3 h under ambient conditions. The blue reaction mixture was then poured over NH₄Cl (aq) and extracted with EtOAc. The organic layer was dried with MgSO₄, filtered and evaporated. Gravity column chromatography (SiO₂: CH₂Cl₂) gave 13 (7 mg, 13% yield) as an orange solid. Mp:
315–317 °C. Rf = 0.75 (CH2Cl2). 1H NMR (400 MHz, CDCl3): δ 15.03 (s, 2H), 7.80 (s, 4H), 7.75 – 7.71 (m, 8H), 7.52 (t, 8H, J = 7.4 Hz), 7.47 – 7.42 (m, 4H), 7.20 (dd, 4H, J = 5.4, 3.0 Hz), 7.09 (dd, 4H, J = 5.4, 3.0 Hz), 4.34 ppm (s, 4H). 13C NMR (100 MHz, CDCl3): δ 179.6, 172.7, 148.8, 147.8, 135.9, 133.3, 128.8, 128.5, 127.4, 126.9, 120.1, 119.7, 113.6, 105.8, 89.2, 55.5 ppm. UV/vis (CH2Cl2): λmax (ε) = 285 (76508), 491 (24618), 462 (15226), 315 (24907), 526 nm (22821 M–1 cm–1). HR-DART-MS: m/z calcd for C62H38O6Na+: 901.2561; found: 901.2549 [M + Na]+.

**Compound 14**

In a flame-dried 25 mL Schlenk flask, compound 13 (21 mg, 0.039 mmol) was dissolved in 1:1 isopropyl alcohol-CHCl3 (0.5 mL each). Concentrated HCl (0.2 mL) was added slowly to the solution under argon. The solution was heated to 80 °C for four hours. The product was washed with deionized water and extracted with CH2Cl2, then concentrated in vacuo, affording insoluble dark colored solid. Poor solubility and decomposition precluded further characterization beyond mass detection by MALDI-TOF. MALDI-TOF-MS: m/z calcd for C62H34O4+: 842.24, found 842.08 [M]+ (See S112–113. for mass spectrum).

**Iptycene-POAs**

**Compound 15**

7a (90 mg, 0.246 mmol) and diene 9 (86 mg, 0.246 mmol) were added to a flame-dried Schlenk flask with stir bar, and were dissolved in the minimal amount of anhydrous toluene (1–2 mL). The headspace was purged with argon for 30 minutes, then heated to reflux overnight (111 °C). The solvent was concentrated in vacuo. KOtBu (496 mg, 4.42 mmol) and 20 mL THF were added to the flask, and the reaction was allowed to stir 1–3 h under ambient conditions. The blue reaction mixture was then poured over NH4Cl (aq) and extracted with EtOAc. The organic
layer was dried with MgSO₄, filtered and evaporated. Gravity column (SiO₂: CH₂Cl₂) or FC (SiO₂; hexanes then CH₂Cl₂) yielded an orange solid 15 (53 mg, 30% yield). Mp: 251–253 °C. Rf = 0.88 (CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ 13.13 (s, 2H), 7.72 (d, 4H, J = 6.9 Hz), 7.69 (s, 2H), 7.52 (t, 4H, J = 7.4 Hz), 7.49 – 7.41 (m, 6H), 7.20 (dd, 2H, J = 5.4, 3.0 Hz), 7.08 (dd, 2H, J = 5.4, 3.0 Hz), 7.05 – 6.99 (m, 4H), 6.07 (s, 2H), 4.31 ppm (s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 180.2, 153.3, 150.6, 147.6, 146.2, 144.2, 144.0, 135.7, 134.6, 128.9, 128.6, 127.5, 126.8, 125.8, 125.7, 124.5, 124.4, 121.2, 119.7, 111.2, 89.0, 55.6, ppm. UV/vis (CH₂Cl₂): λ max (ε) = 280 (68245), 494 (13190), 529 nm (7575 M⁻¹ cm⁻¹). HR-DART-MS: m/z calcd for C₅₀H₂₉O₅⁺: 709.2020; found: 709.2000 [M – H]⁺.

**Compound 3**

In a flame-dried 25 mL Schlenk flask, compound 15 (22 mg, 0.031 mmol), was dissolved in 1:1 isopropyl alcohol-CHCl₃ (0.5 mL each). Concentrated HCl (0.2 mL) was added slowly to the solution under argon. The solution was heated to 80 °C for 4 hours. The product was washed with deionized water and extracted with CH₂Cl₂, then concentrated in vacuo. The product was washed with hexanes, then filtered and dried overnight under vacuum, affording 3 as an orange solid (16 mg, 75% yield). Mp: >350 °C. Rf = 0.95 (CH₂Cl₂). ¹H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d₂): δ 13.10 (s, 2H), 7.84 (dd, 2H, J = 6.3, 3.4 Hz), 7.64 – 7.59 (m, 8H), 7.58 – 7.50 (m, 6H), 7.49 (s, 2H), 7.32 (dd, 2H, J = 6.3, 3.4 Hz), 7.09 (dd, 4H, J = 5.5, 3.1 Hz), 6.11 ppm (s, 2H). ¹³C NMR (125 MHz, 1,1,2,2-tetrachloroethane-d₂): δ 186.0, 155.8, 153.1, 146.0, 143.7, 141.7, 135.8, 135.1, 134.7, 131.3, 129.3, 128.9, 128.4, 127.34, 127.30, 125.6, 124.4, 114.9, 110.7, 47.2 ppm. UV/vis (CH₂Cl₂): λ max (ε) = 301 (26248), 373, (20280), 517 (6910), 604 nm (3745 M⁻¹ cm⁻¹). MALDI-TOF-MS: m/z
calcd for C_{50}H_{29}O_5\textsuperscript{−}: 692.20; found: 692.538 [M]\textsuperscript{−}. HR-DART-MS: m/z calcd for C_{50}H_{29}O_4\textsuperscript{+}: 693.2060; found: 693.2050 [M + H]\textsuperscript{+}.

**Synthesis of BF\textsubscript{2} complexes**

Naphthazarin derivative (20 mg) was added to a flame-dried Schlenk flask with stirrer bar, and were dissolved in dry CH_2Cl_2 (5 mL) and BF_3-OEt_2 (0.5 mL). The headspace was purged with argon, then stirred at room temperature for 1 h. The solvent was concentrated in vacuo. The product was washed with hexanes and dried overnight under vacuum, affording BF\textsubscript{2} complexes.

**Compound 1a-BF\textsubscript{2}**

1a (20 mg, 0.037 mmol): 1a-BF\textsubscript{2}, dark purple solid (18 mg, 77% yield). R\textsubscript{f} = 0.89 (CH_2Cl_2). \textsuperscript{1}H NMR (300 MHz, CDCl_3): δ 7.49 (br. dd, 8H, J = 5.4, 3.2 Hz), 7.09 (br. dd, 8H, J = 5.4, 3.2 Hz), 6.10 ppm (s, 4H). HR-ESI-MS: m/z calcd for C_{38}H_{20}B_2F_4O_4\textsuperscript{−}: 638.1518; found: 638.1503 [M]\textsuperscript{−}.

**ASSOCIATED CONTENT**

Supporting Information.

\textsuperscript{1}H and \textsuperscript{13}C NMR spectra of all new compounds, crystal structure data for compounds 6b, 7a, 8a, 10, 11, and 12, UV/vis and fluorescence characterization, and TD-DFT calculations can be found in the Supporting Information for this manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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