



Synthesis of aza-polycyclic aromatic hydrocarbons as organic optoelectronic materials via the Povarov reaction

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ABSTRACT

The Povarov reaction, a classical [4+2] cycloaddition of imines and unsaturated compounds, provides a versatile synthetic platform for the synthesis of nitrogen-doped π -conjugated molecules. This review highlights the recent advances in the application of the Povarov reaction in the synthesis of aza-polycyclic aromatic hydrocarbons (aza-PAHs), which are important components of emerging organic optical and electronic materials. The modularity, one-pot multicomponent compatibility, and broad catalyst scope of the Povarov reaction afford structurally diverse aza-PAHs. Representative examples spanning small molecules, conjugated polymers, covalent organic frameworks (COFs), and molecular cages are discussed, with particular emphasis on their functional properties, including photoluminescence, sensing, circularly polarized luminescence, hole-blocking, and electron transport properties in organic light-emitting diodes. Mechanistic insights into regioselectivity and π -extension are also reviewed to facilitate the future design of aza-PAHs. The Povarov reaction is a powerful synthetic tool for the development of advanced aza-PAH-based materials for optical and electronic applications.

Introduction

In 1963, Povarov pioneered a methodology for the synthesis of quinoline derivatives via the reaction of imines and alkenes in the presence of an acid catalyst (Scheme 1) [1]. This reaction fundamentally represents a Diels-Alder (D-A) reaction involving the participation of a nitrogen atom. Analogous to the classical D-A reaction, this protocol demonstrates remarkable substrate scope, accommodating electron-rich and electron-poor aromatic amines and aldehydes.

The Povarov reaction proceeds through Schiff base (imine) intermediates, which are typically formed by the condensation of aniline derivatives and aldehydes. The initial imine formation and the subsequent cycloaddition steps were acid-catalyzed. Contemporary applications of the Povarov reaction often employ a one-pot, three-component approach (Scheme 2) owing to the quantitative formation of Schiff base intermediates from amines and aldehydes [2–11]. This strategy streamlines the synthetic process and enhances overall efficiency. The final aromatization step of the Povarov reaction requires an oxidant. In the absence of oxidants, Schiff base intermediates are consumed in undesired ways [12]. Representative oxidants include O₂, chloranil, and

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [2–8].

Extensive research has significantly advanced our understanding of the mechanism of the Povarov reaction and expanded its catalytic scope. The Povarov reaction tolerates a broad spectrum of catalysts, including Lewis acids such as BF₃·OEt₂ [6], FeCl₃ [13], CuCl [14], AuCl₃ [15], and Yb(OTf)₃ [16], which efficiently activate imines. Similarly, Brønsted acids, including hydrochloric acid [17], triflic acid [18], and acetic acid [19] (Fig. 1), have been successfully employed. Recent developments have produced more sustainable heterogeneous catalysts, including acidic ionic liquids and metal-organic frameworks (MOFs), which catalyze the Povarov reaction under mild and solvent-free conditions [20–26]. These catalytic innovations have expanded the scope of the Povarov reaction to less reactive alkenes and alkynes and enabled versatile one-pot, three-component reactions.

The Povarov reaction affords aza-polycyclic aromatic hydrocarbons (aza-PAHs) with electron-deficient π -conjugated structures, which have important applications in organic electronics, such as materials in organic light-emitting diodes (OLEDs) [27–34] and carrier transport materials in organic field-effect transistors (OFETs) [35–38]. The high performance of these materials stems from their tunable energy levels

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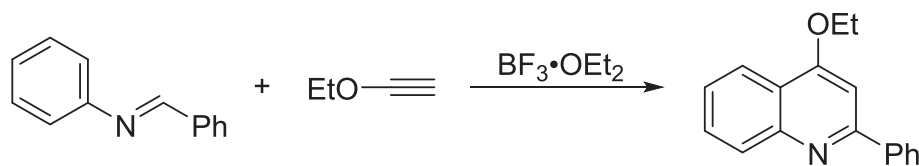
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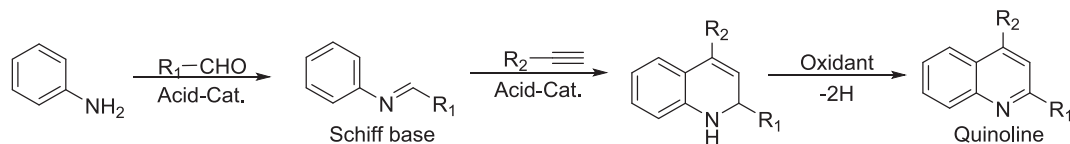
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Scheme 1. The original Povarov reaction.



Scheme 2. One-pot and three-component approach of the Povarov reaction.

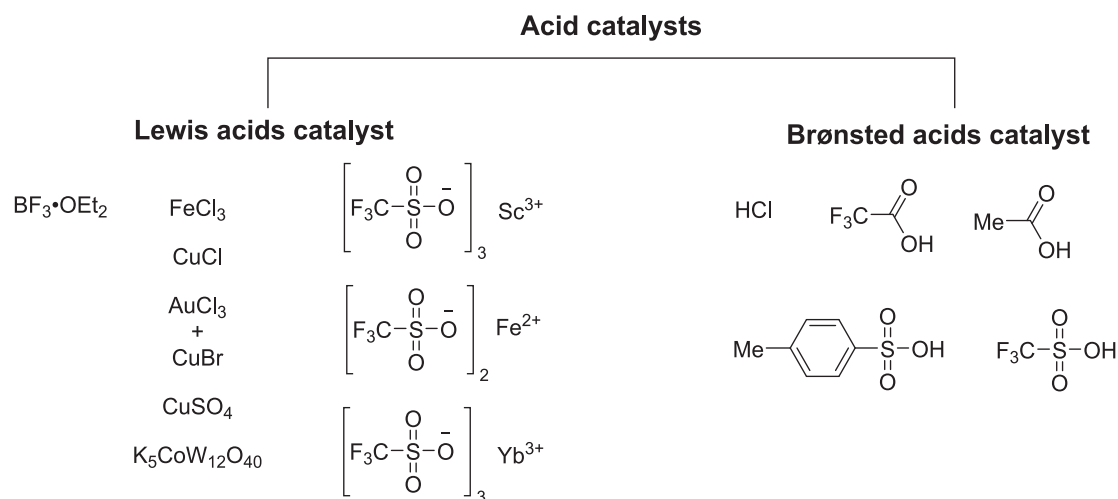
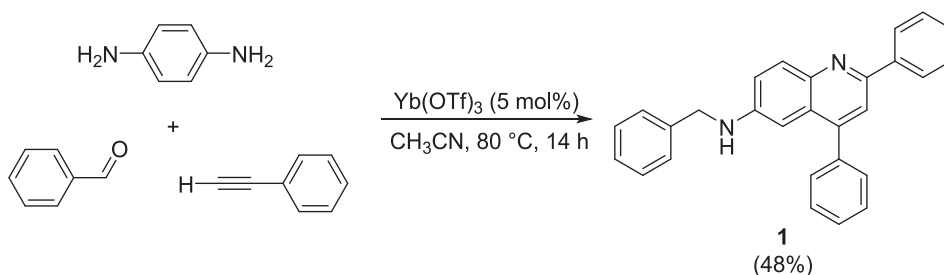


Fig. 1. Catalyst scope of the Povarov reaction.

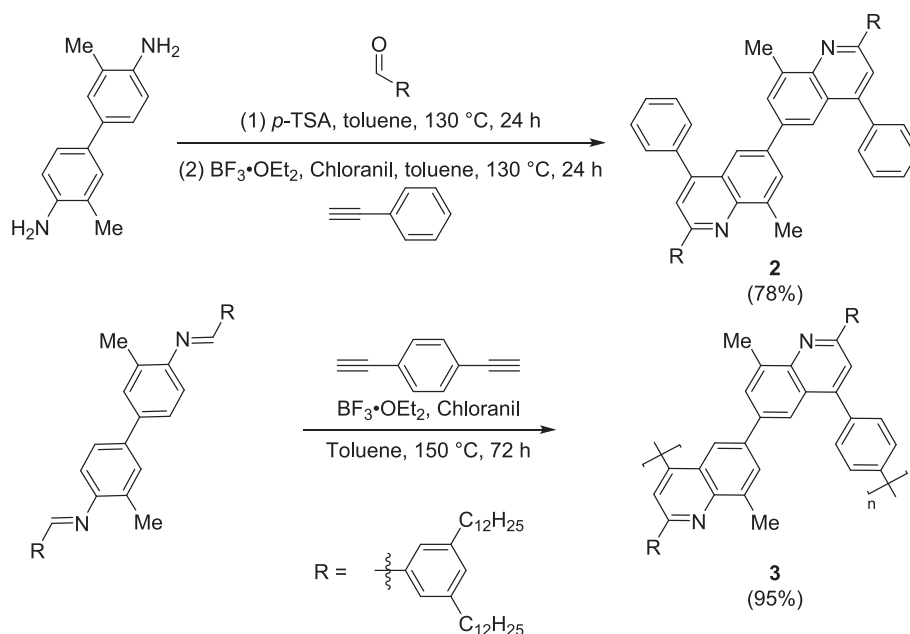


Scheme 3. Reaction of diamine with benzaldehyde and acetylene using an Yb catalyst.

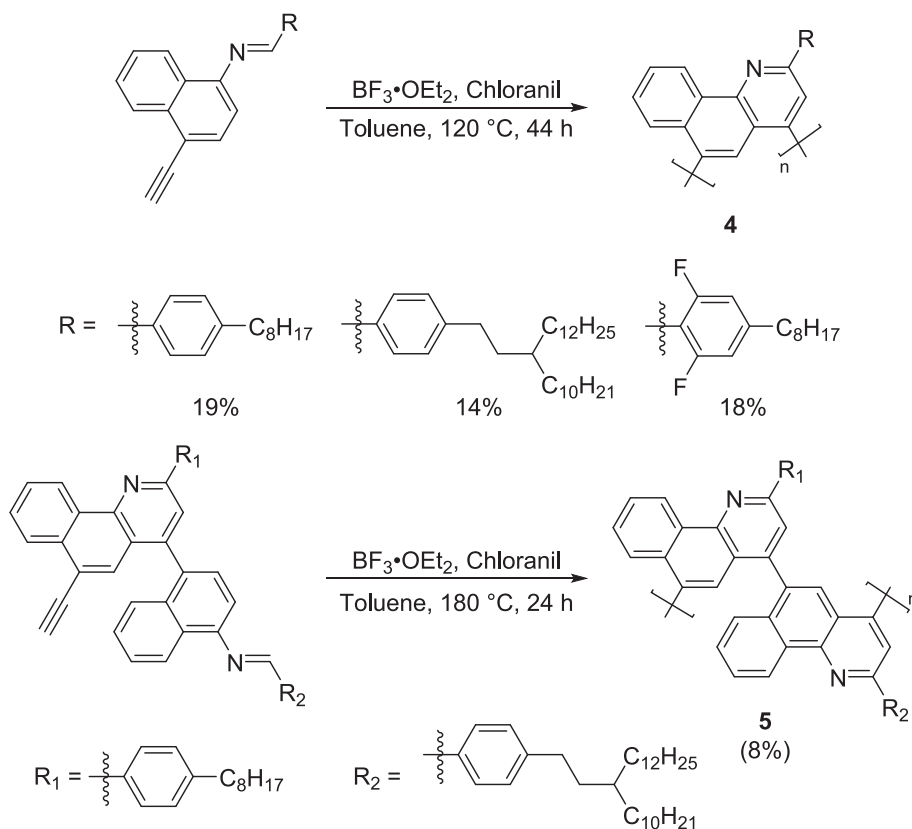
and intermolecular interactions. The Povarov reaction provides a straightforward pathway for constructing aza-PAHs via one-pot, multi-component approaches. Despite significant progress in the development and application of the Povarov reaction, a comprehensive and systematic overview of its role in the synthesis of aza-PAHs for organic electronic materials remains limited. This review aims to bridge the gap between the conventional Povarov reaction and multiple Povarov strategies for the synthesis of large π -conjugated frameworks for optoelectronic applications. This review examines representative examples that highlight the versatility of the Povarov reaction across small molecules, polymers, and porous frameworks, demonstrating its utility in the synthesis of nitrogen-containing materials.

The Povarov reaction of aromatic diamine

Povarov reactions of aromatic diamines are expected to afford aza-PAHs via double cyclization reactions. In 2013, Pericherla et al. introduced the Povarov reaction of a 1:2:1.5 mixture of 1,4-phenylenediamine, benzaldehyde, and phenylacetylene catalyzed by ytterbium triflate ($\text{Yb}(\text{OTf})_3$) (Scheme 3) [16]. This reaction yielded *N*-benzyl-6-amino-2,4-diphenylquinoline (compound 1) in a 48 % yield rather than the expected aza-PAHs owing to imine reduction following the Povarov reaction. During the aromatization step of the Povarov reaction, the imine group serves as an oxidant. This report demonstrates the high efficiency of $\text{Yb}(\text{OTf})_3$ as a catalyst for the Povarov reaction and the importance of an oxidant to prevent imine reduction in syntheses of aza-PAHs via the Povarov reaction.



Scheme 4. Synthesis of a zigzag polyquinoline via the Povarov reaction.

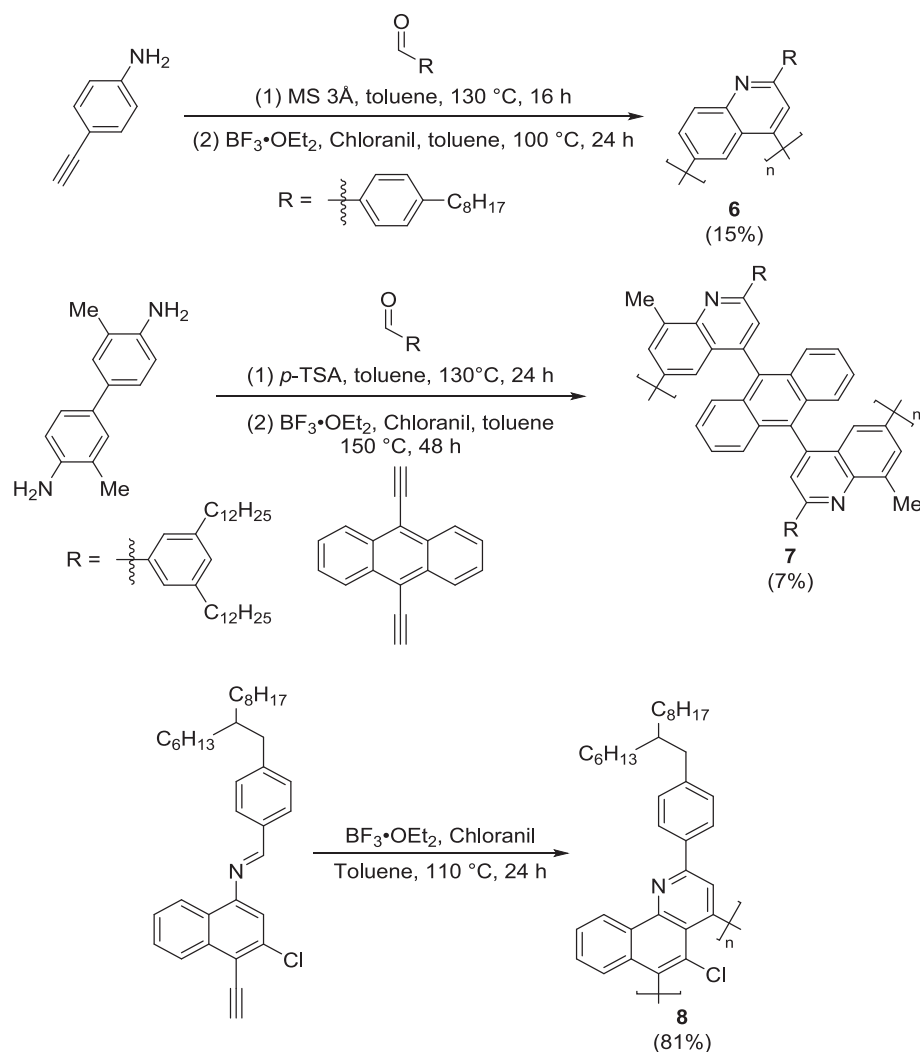


Scheme 5. Synthesis of polybenzoquinolines **4** and **5**.

The double Povarov reaction and polymer synthesis

Multiple Povarov reactions have emerged as a powerful tool for the step-economical construction of nitrogen-rich conjugated polymers. Gorodetsky et al. developed a double Povarov reaction of diamines, aldehydes, and phenylacetylene in the presence of a $\text{BF}_3 \cdot \text{OEt}_2$ catalyst and chloranil as an oxidant (Scheme 4) [39]. This protocol afforded

bisquinoline derivatives in high yields. Extension of this protocol to AA/BB-type polymerization produced polyquinolines with moderate molecular weights ($M_n = 14,500$) and polydispersities ($\text{PDI} = 2.28$). This method provides a modular approach to the synthesis of nitrogen-rich polymers from simple monomers in a one-step procedure, and establishes the reaction conditions for constructing complex nitrogen-doped materials via multiple Povarov reactions.

Scheme 6. Synthesis of polybenzoquinolines **6**, **7**, and **8**.

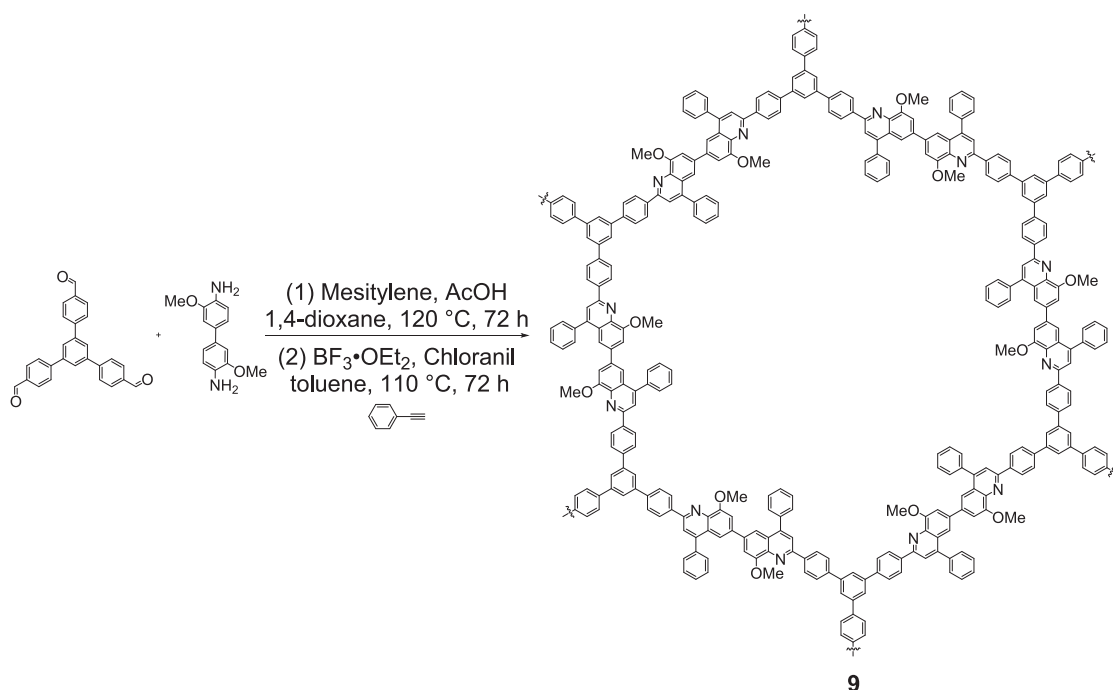
This methodology was extended to the synthesis of various polybenzoquinolines, which are precursors of nitrogen-doped graphene nanoribbons (NGNRs). Polymerization of A-B-type bifunctional monomers afforded polymers **4** and **5**, which contain peripheral substituents that improve the solubility of the polymer while limiting steric hindrance (Scheme 5) [40]. Polymers **4** and **5** feature large conjugated repeating units with alkyl chains that provide high solubility in organic solvents. Structural elucidation using NMR spectroscopy confirmed the high regioselectivity of the reaction, and size exclusion chromatography confirmed the high molecular weight of the polymer ($M_n = 29,600$). This strategy highlights the modularity and versatility of the Povarov reaction in the synthesis of the NGNR precursor.

The synthesis of quinoline-based conjugated polymers was initially achieved via an acid-catalyzed Friedlander reaction [41] and dehalogenative polycondensation [42]. The Povarov reaction improves upon these earlier approaches by enabling the modular construction of similar frameworks through multicomponent reactions (Scheme 6). Gorodetsky et al. synthesized well-defined 4,6-polyquinolines (polymer **6**, $M_n = 10,100$) via AB-type polymerization without the need for bulky solubilizing groups [43]. This method was extended to synthesize polydiquinoline from diamine and diethynylantracene monomers, resulting

in a main chain in which two quinoline moieties are separated by an anthracene unit (polymer **7**) [44]. The polymers were characterized by density functional theory (DFT) calculations, UV–Vis absorption spectroscopy, and cyclic voltammetry [44]. Introduction of chlorine substituents into polybenzoquinolines (compound **8**) enabled precise electronic tuning and post-synthetic modifications for potential applications in organic electronics and the preparation of NGNRs [45].

Synthesis of covalent organic frameworks

In 2023, Mao et al. synthesized covalent organic frameworks (COFs) via the Povarov reaction, converting imine bonds into quinoline linkages (compound **9**, Scheme 7) [46]. The electrochemiluminescence (ECL) properties of two structurally isomeric COFs differing solely in linkage orientation differed significantly. The superior ECL of one isomer is attributed to its enhanced polarity-driven charge transport. This material can be used for the highly sensitive and selective detection of extremely low concentrations of As(V) species. This study demonstrates the efficacy of Povarov-based modifications for precisely tuning the photophysical and electronic properties of COFs.



Scheme 7. Synthesis of COF using the Povarov Reaction.

Synthesis of a cage molecule

Alexandre et al. demonstrated synthesis of a robust porous quinoline cage obtained via a 12-fold Povarov reaction of a [4+6] salicylimine cage precursor (Scheme 8) [47]. The resulting cage (compound 10) exhibited high chemical and thermal stability across a broad pH range and displayed notable acidochromism in solution and thin-film forms, enabling the visual detection of acidic vapors. This study demonstrates the versatility and practical utility of the Povarov reactions for generating stable, shape-persistent organic cages suitable for sensing applications.

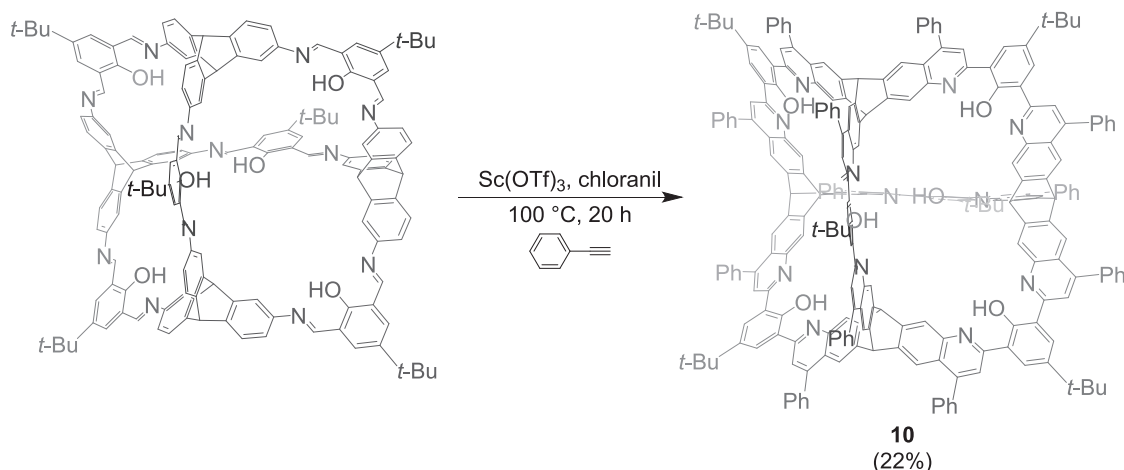
Synthesis of chiral molecules

The use of chiral acid catalysts in the Povarov reaction affords chiral molecules that exhibit circularly polarized luminescence (CPL) (Fig. 2). Li et al. developed an enantioselective Povarov reaction using a chiral phosphoric acid and DDQ (Fig. 2a). The resulting quinohelicenes

exhibited interesting chiroptical properties (Fig. 2b), including CPL with dissymmetry factors (g_{lum}) up to 5.1×10^{-3} (M-5ac) at 465 nm and 3.8×10^{-3} (M-5a) at 457–465 nm among the various derivatives (Fig. 2c) [48]. Additionally, Yang and co-workers have also reported enantioselective Povarov reactions that afford chiral quinoline motifs with generally good yields and high enantioselectivities [49,50].

Synthesis of π -extended molecules via the Povarov reaction

The Povarov reaction yields substituted molecules that can be post-functionalized to afford π -extended aza-PAHs. For instance, 1,6-anthrazoline precursors with Cl substituents, which are versatile precursors for further π -extension, are readily synthesized via the Povarov reaction (Scheme 9) [51]. Subsequent regioselective C–C bond formation via base-mediated cyclodehydrohalogenation produced the nitrogen-doped tetrabenzopentacene 12. Alternatively, Pd-catalyzed C–H/C–Cl intra-molecular coupling in the presence of Pd(OAc)₂, PCy₃, and DBU achieves π -extension through aryl–aryl bond formation, affording nitrogen-



Scheme 8. 12-Fold Povarov reaction for the synthesis of a quinoline cage.

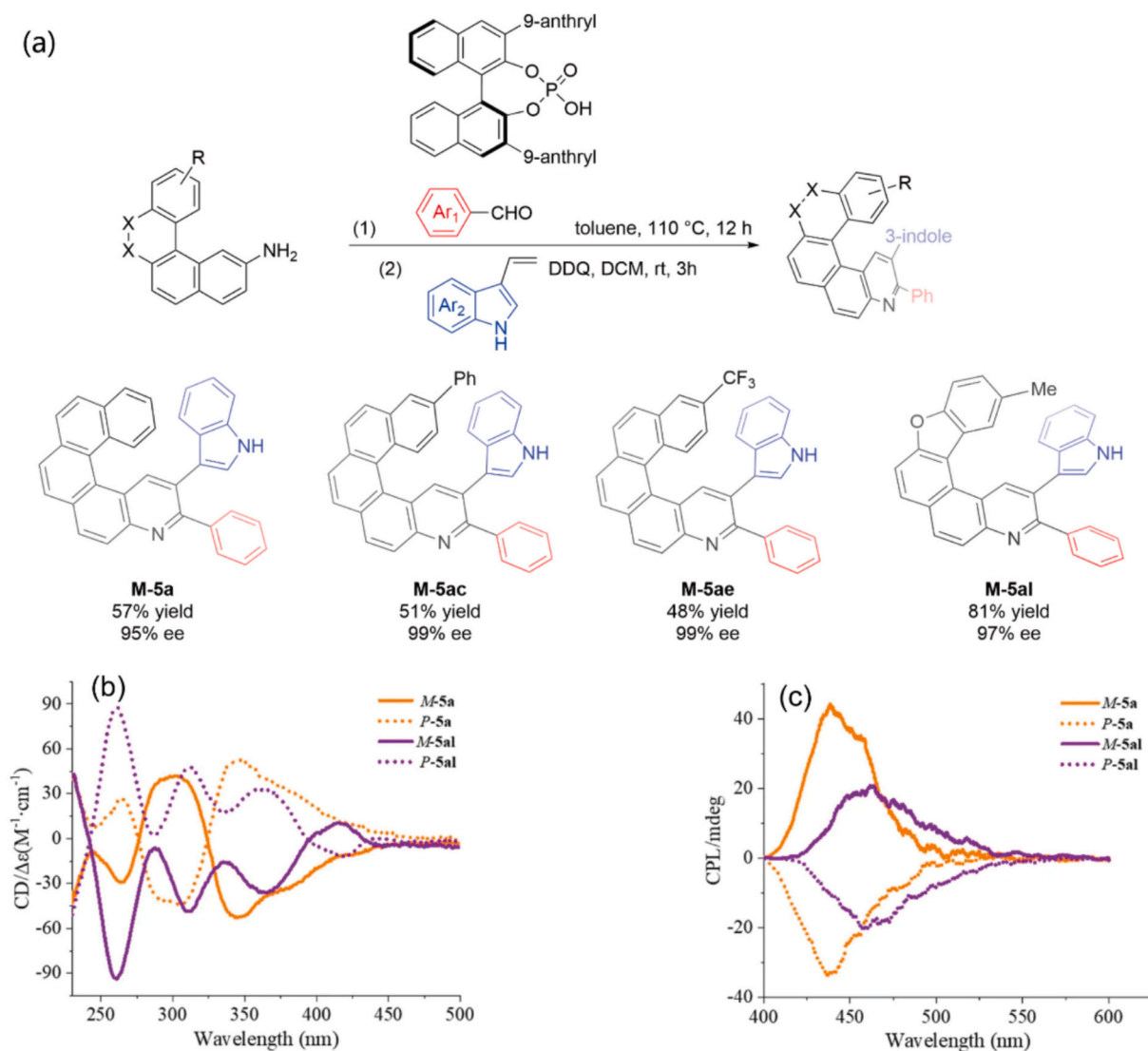
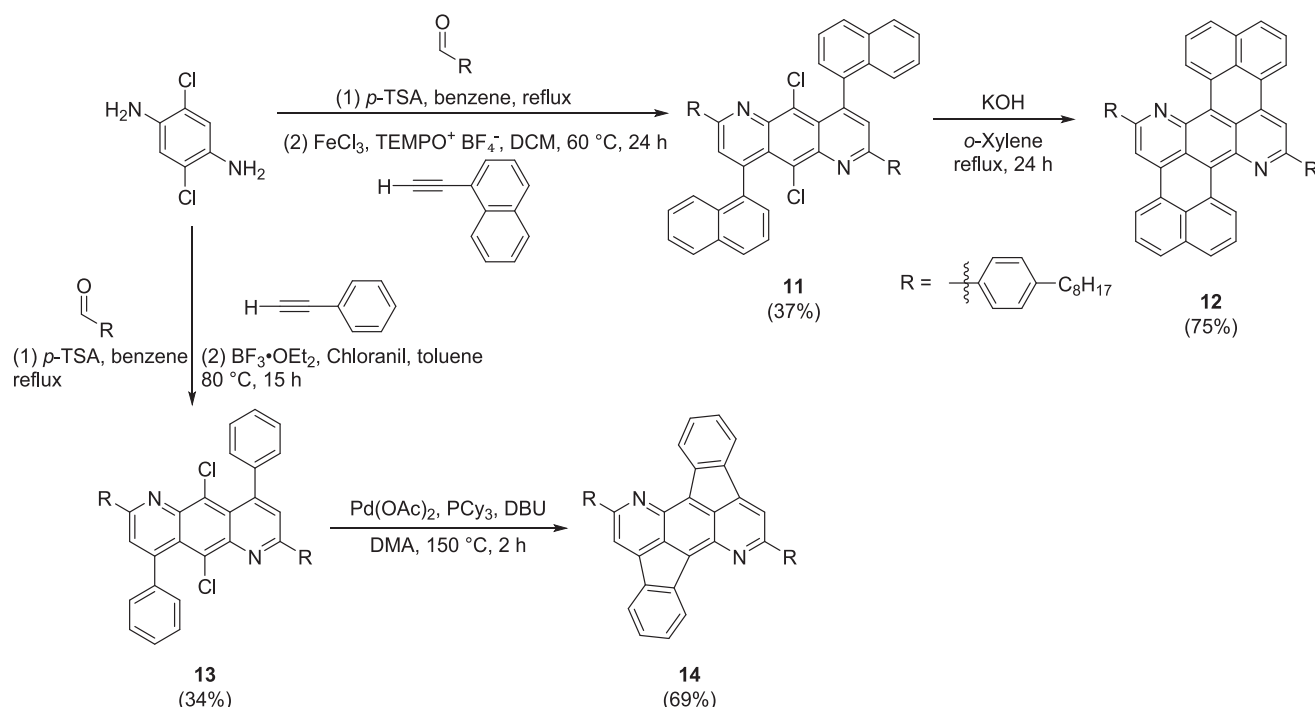


Fig. 2. (a) Chiral quinothelicene derivatives; (b) Circular dichroic absorption (CD) of **M/P-5a** and **M/P-5al**; (c) Circular polarization luminescence (CPL) of **M/P-5a** and **M/P-5al** (P/M are enantiomers). Figure reproduced from ref. 48, under CC BY 4.0 license.

doped rubicene **14**. These π -extended architectures exhibited tunable electronic properties, with lowest unoccupied molecular orbital (LUMO) energies ranging from -3.01 to -3.77 eV, as demonstrated by cyclic voltammetry and DFT calculations. These electron-deficient heterocycles are promising candidates for n-type semiconductors in OLEDs and OFETs.

A double Povarov reaction was effectively employed in the synthesis of 4,10-diazachrysene derivatives, which were further transformed to afford a π -extended condensed azaperylene framework via intramolecular direct C—H arylation (Scheme 10) [52]. This strategy yields highly planar 4,10-diazachrysene derivatives with π - π stacking interactions. The single-crystal X-ray diffraction analysis of compound **15** revealed π - π stacking distances of 3.539 Å in the diazachrysene core. These π - π interactions cause pronounced red-shifts in the absorption and emission spectra of their films relative to those measured in solution. Compound **15** readily formed thin films and is therefore suitable for applications in optoelectronics. Compound **17** underwent

intramolecular cyclization via Pd-catalyzed direct C—H arylation, in which the aryl bromide moieties selectively coupled with adjacent C—H bonds to form new C—C bonds, affording the π -extended product **18**. DFT calculations were performed to better understand the conjugated structure of compound **18**. Nucleus-independent chemical shift (NICS) calculations reveal that compound **18** is a condensed azaperylene structure. The absorption and emission spectra of compound **18** exhibited significant redshifts relative to those of compounds **15** and **16**, which was attributed to the extended π -system formed through cyclization and is particularly pronounced in the solid state, likely owing to strong π - π stacking interactions in the extended conjugated framework. Furthermore, compound **18** possesses a markedly higher highest occupied molecular orbital (HOMO) energy level than compounds **15** and **16**, while retaining a similar LUMO energy (Table 1), resulting in a narrower optical bandgap and underscoring the electronic impact of π -extension via direct arylation.



Scheme 9. Synthesis of intermediates **11** and **13** via the Povarov reaction, tetrabenzopentacene **12** via base-mediated cyclodehydrohalogenation, and rubicene **14** via Pd-catalyzed intramolecular coupling.

Regioselectivity in the double Povarov reaction

The regioselectivity of the double Povarov reaction was studied in detail, with a particular focus on the double Povarov reaction of 1,4-diaminobenzene with 4-tert-butylbenzaldehyde and phenylacetylene in the presence of BF₃·OEt₂ and DDQ (Scheme 11) [53,54]. The reaction predominantly afforded the 4,7-phenanthroline derivative (**19**) over the 1,6-anthrazoline isomer (**20**), despite strong steric repulsion between the phenyl groups of compound **19**. Single-crystal X-ray diffraction analysis that the phenanthroline core of **19** is distorted owing to the steric repulsion of the phenyl groups. To determine the mechanism of selective formation of compound **19**, the properties of the quinoline intermediate were calculated using DFT. The HOMO distribution of the quinoline intermediate was higher on the α -position than on the β -position. The preferential cyclization at the α -position can therefore be attributed to this large HOMO distribution at the α -position. Electronic effects, therefore, play a dominant role at this stage and override the influence of steric repulsion. This study provides critical insights into the regioselectivity and mechanism of the Povarov reaction, enabling the precise design of aza-PAHs.

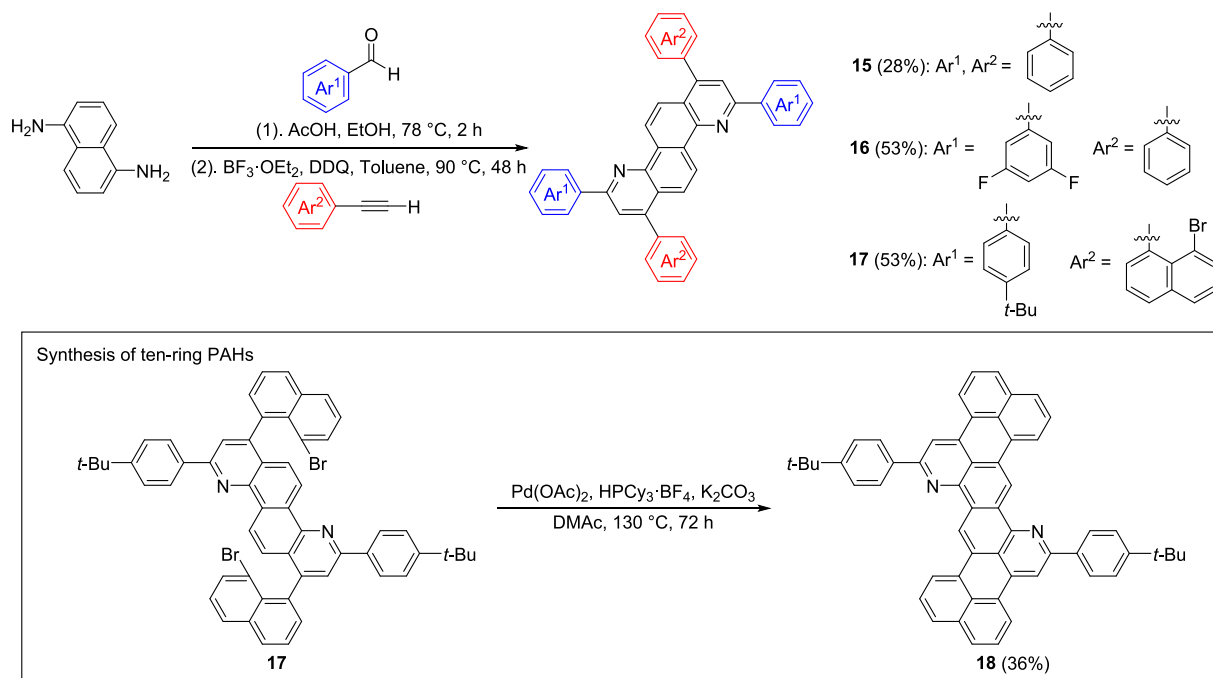
Synthesis and properties of 1,7-phenanthrolines

1,7-phenanthrolines with various substituents were synthesized via the Povarov reaction of 1,3-diaminobenzene with various benzaldehyde and phenylacetylene derivatives in a straightforward manner, demonstrating the versatility of the method (Fig. 3a). Owing to the relatively low HOMO energies of the 1,7-phenanthroline derivatives (−6.28 to −6.75 eV), the application of these compounds as hole-blocking and electron-transporting materials in OLEDs was evaluated (Fig. 3b, c). Devices with **H-mP** and **F₂-mP** demonstrated external quantum efficiencies (EQEs) of approximately 2.4 % [55], approaching the theoretical maximum of the selected emitting materials and device configuration (2.7 %), suggesting an appropriate charge balance. Conversely, **tBu-mP**, which exhibits the highest HOMO energy (−6.28

eV), exhibited the lowest EQE owing to its poor hole-blocking capability. Devices with **CF₃-mP** showed elevated resistance and reduced efficiency despite their favorable HOMO energy, owing to their low electron mobility. Notably, **F₂-mP** outperformed **H-mP** in devices with an emitter with a lower HOMO energy (Super Yellow). This was attributed to the deeper HOMO level of **F₂-mP** (−6.71 eV), which more effectively inhibits the passage of holes. Overall, the study demonstrates the utility of **F₂-mP** as a hole-blocking material in emitters with a low HOMO energy.

Triple Povarov reaction

Several studies have demonstrated the efficient synthesis of triaza-triphenylene derivatives via a one-pot, multicomponent triple Povarov reaction involving 1,3,5-triaminobenzene, arylaldehydes, and alkynes. This approach offers rapid access to aza-PAHs with a three-fold symmetry (Fig. 4a). Arylaldehydes substituted with electron-donating substituents (*t*-Bu) promote imine formation and cyclization, thereby improving the yield of the product, whereas electron-withdrawing groups inhibit the reaction [56]. Single-crystal X-ray diffraction confirmed that substituents significantly influence the molecular conformation. These compounds exhibit high glass transition temperatures (*T_g*), which improves the thermal stability of the devices. Although **tBu-TaT** has a higher *T_g* (176 °C) than **H-TaT** (140 °C), **H-TaT** shows superior performance as a hole-blocking and electron-transporting material in OLEDs (Fig. 4b). The device with **H-TaT** exhibited a higher maximum luminance of 5400 cd/m², superior external quantum efficiency, and lower turn-on and drive voltages than the device with **tBu-TaT** (Fig. 4c). This superior performance was attributed to deeper HOMO (−6.48 eV) and LUMO (−3.08 eV) energy levels of **H-TaT**, as well as its enhanced charge transport properties. Despite the high thermal stability conferred by the *t*-Bu groups of **tBu-TaT**, its steric bulk may prevent charge transport. These findings demonstrate the utility of the triple-Povarov strategy for the development of functional nitrogen-containing semiconductors for optoelectronic applications.

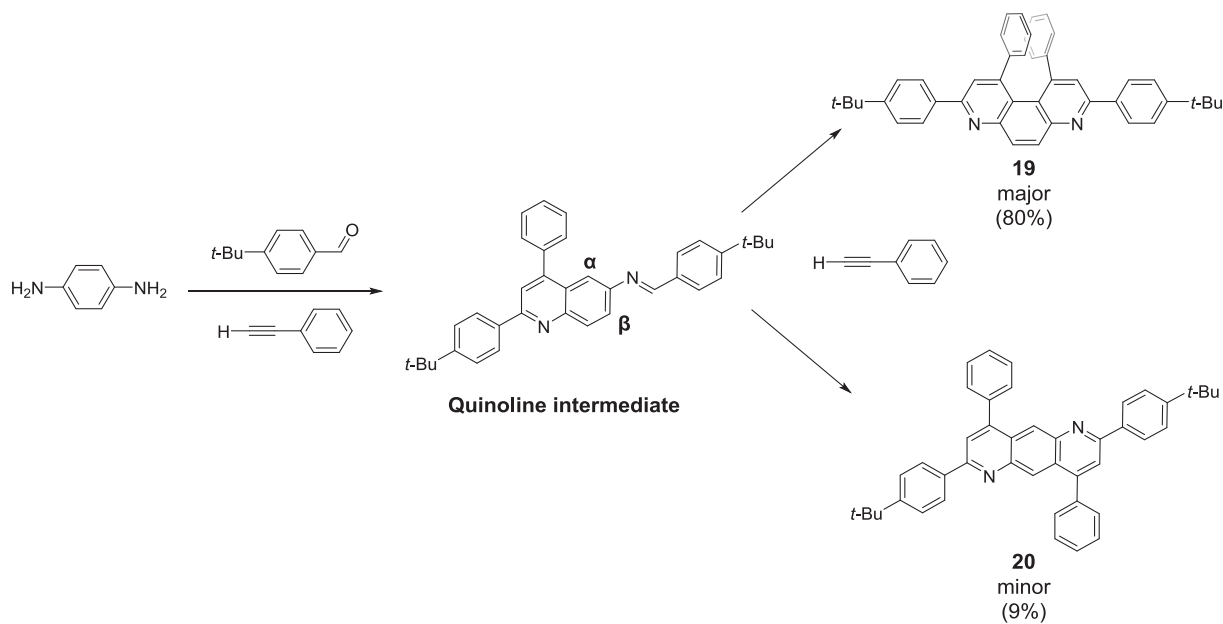


Scheme 10. Synthesis of 4,10-diazachrysene derivatives.

Table 1

Physical properties of 4,10-diazachrysene derivatives.

—	Solution state ^a		Thin-film state				
	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$E_{\text{g, opt}}/\text{eV}^{\text{b}}$	HOMO/eV ^c	LUMO/eV ^d
15	348	395	394	457	3.03	−6.03	−3.00
16	387	395	394	461	3.03	−6.42	−3.39
18	496	533	521	563	2.07	−5.04	−2.97

^a in toluene, 5.0×10^{-6} M.^b Optical bandgap obtained from the absorption edge.^c Obtained by photoelectron yield spectroscopy.^d $E_{\text{LUMO}} = E_{\text{g, opt}} + E_{\text{HOMO}}$.

Scheme 11. Regioselectivity in the double Povarov reaction.

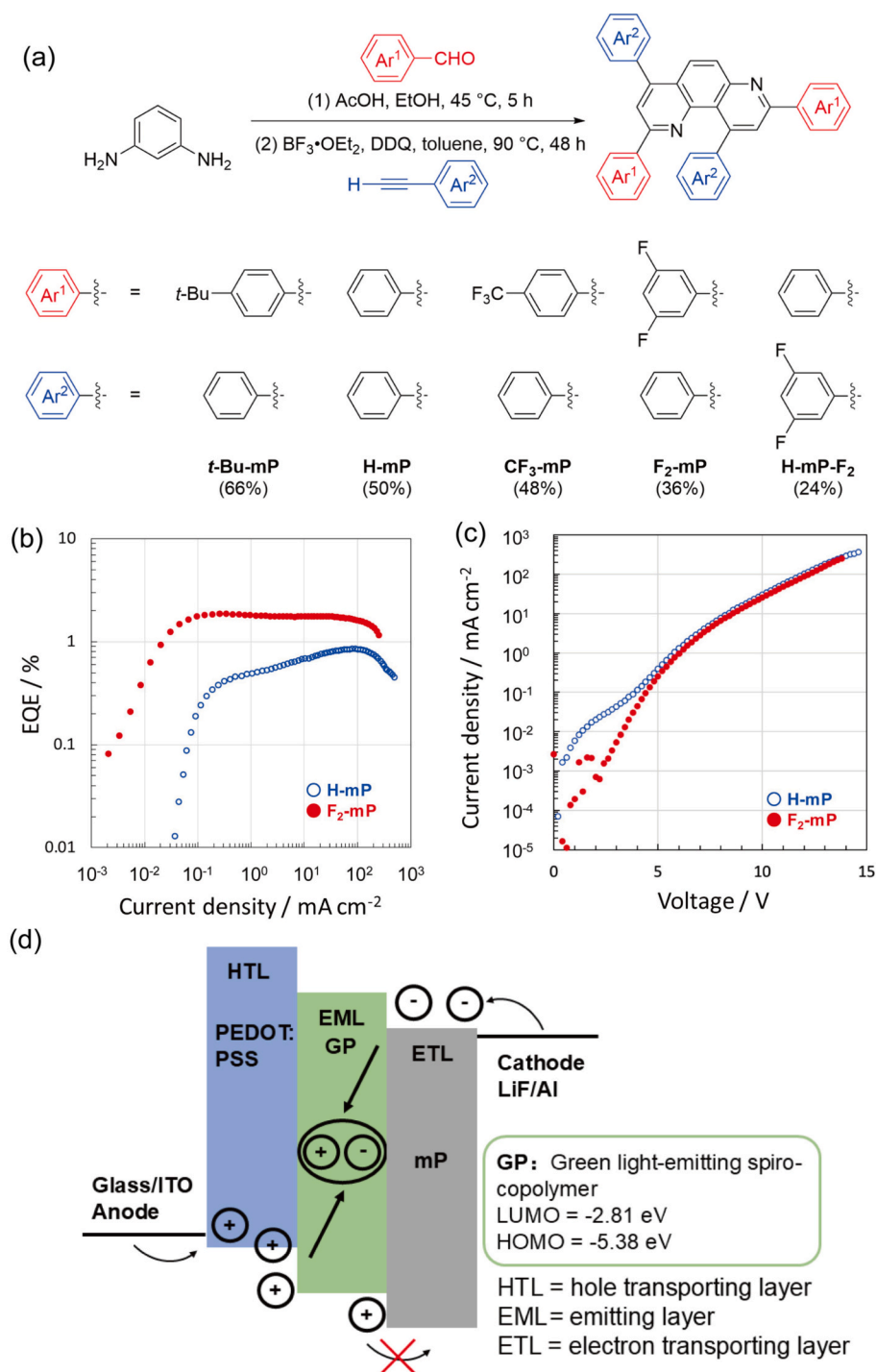


Fig. 3. (a) Synthesis of 1,7-phenanthroline derivatives; (b) EQE-current density characteristics and (c) Current density-voltage plots of OLEDs fabricated with **mP** derivatives. Configuration: ITO/PEDOT:PSS (40 nm)/Green light-emitting spirocopolymer (31 nm)/**mP** (40 nm)/LiF (1 nm)/Al (100 nm). (d) OLED device structure. Reproduced with permission from ref. [55]. Copyright 2022 Oxford University Press. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

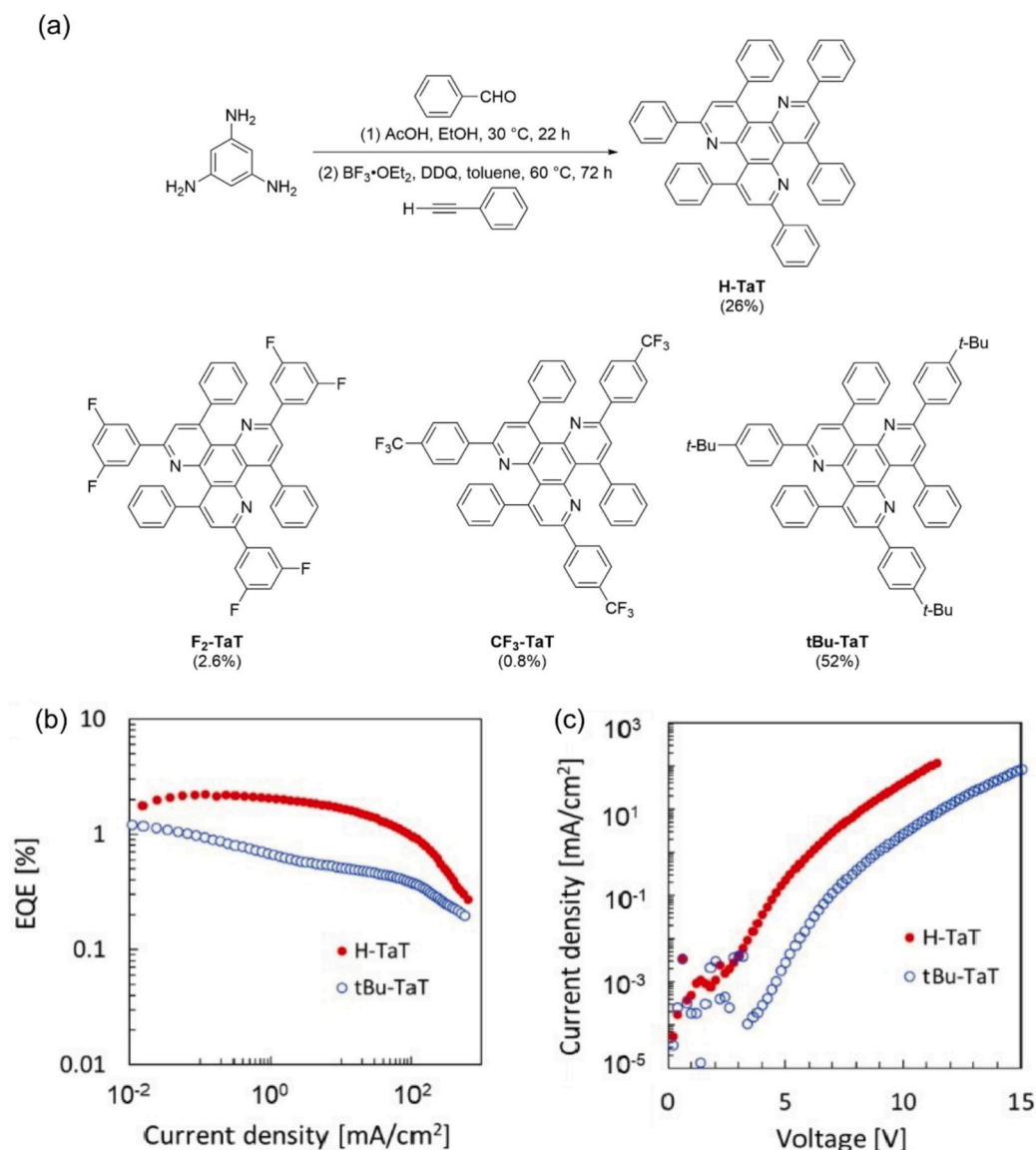


Fig. 4. (a) 1,3,5-triaminobenzene derivatives; (b) EQE–current density characteristics. (c) Current density–voltage characteristics. Configuration: ITO/PEDOT:PSS (40 nm)/Green light-emitting spirocopolymer (31 to 33 nm)/H-TaT or tBu-TaT (40 nm)/LiF (1 nm)/Al (100 nm). Figure adapted from, ref. [56], ©2023 Wiley-VCH. Reproduced with permission. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Conclusions

Over six decades of research have elevated the Povarov reaction, a classical imine–alkene [4+2] cycloaddition, to a highly adaptable synthetic platform for the synthesis of aza-PAHs. Mechanistic studies have enabled the prediction of the regioselectivity of multiple Povarov reactions and facilitated programmable multi-annulation pathways. Concurrent advancements in catalysis using homogeneous Lewis/Brønsted acids, heterogeneous solids, ionic liquids, and metal-organic frameworks have streamlined the synthetic procedure using one-pot cascade methodologies while significantly broadening the substrate scope of the Povarov reaction and improving its environmental sustainability. The Povarov reaction affords new materials including quinoline-based polymers, a cage molecule, π -extended aza-PAHs, and COFs, which exhibit photoluminescence, redox behaviors, charge transport, CPL emitting, and sensing properties. Combined computational and experimental studies building on these achievements will accelerate catalyst development and improve the modularity of these methods for further exploitation in the construction of hierarchical frameworks and

multifunctional optoelectronics. Next-generation Povarov-inspired approaches are expected to facilitate the development of nitrogen-doped materials capable of meeting the performance and eco-efficiency standards of modern energy and electronic technologies.

CRediT authorship contribution statement

Yuanrong Shan: Writing – original draft. **Takaki Kanbara:** Writing – review & editing. **Junpei Kuwabara:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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