Indacenodipyrene containing small molecules and ladder polymers

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ABSTRACT

A series of s-indaceno[1,2,3-cd:5,6,7-c'd']dipyrene-containing small molecules and ladder polymers were prepared using a palladium catalyzed arylation reaction. Precursor polymers and their resulting ladder polymers with molecular weights up to 13 kDa were prepared. The rigid, planar materials possessed highest occupied molecular orbital (HOMO) energies of −5.39 to −5.23 eV, lowest unoccupied molecular orbitals (LUMO) energies of −2.42 eV to −2.98 eV, and optical gaps of 1.68–2.03 eV. Organic field effect transistors were prepared with derivatives giving hole mobilities up to 2.5 X 10^{-5} $cm^2V^{-1}s^{-1}$.

1. Introduction

The demand of renewable and sustainable energy has grown exponentially due to industrialization, urbanization, geopolitical changes, and environmental concerns [1–3]. Robust organic semiconducting materials that are thermally and oxidatively stable while possessing high charge carrier mobilities are worthy targets for advancing technologies including organic field effect transistors and solar cells [4,5]. Among the variety of organic materials possible for adaptation to these technologies, conjugated ladder polymer based semiconductors offer opportunities for improved thermal stability and greater interchain pi-stacking interactions owing to the lack of bond rotation along the polymer backbone [6–25]. The defining feature of a ladder polymer is the linkage between monomer units consists of two or more separate bonds instead of a single linkage location. The result of this bonding motif is ring-like structures linking aromatic segments along the polymer backbone. The rigid-coplanar structures often offer higher thermal stability and extended conjugation lengths and electron delocalization [26]. New synthetic pathways that enable the synthesis of unique carbon backbones in conjugated ladder polymers can provide opportunities to probe the structure-function properties and enable advancement in this field.

In this contribution, we have synthesized a series of rigid conjugated small molecules and conjugated ladder polymers based on an indacenodipyrene skeleton (Fig. 1). The pyrene chromophores provide a large surface area aromatic chromophore that is well-studied in its monomeric form. In addition, this work builds upon a different pyrene-fused s-indacene regioisomer recently reported [27]. A palladium-catalyzed arylation reaction was employed as an efficient rigidification reaction that ultimately forms five-membered rings as the new ladder rungs
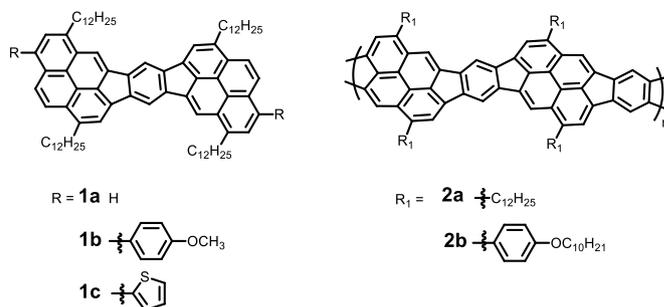

Fig. 1. Conjugated small molecules and conjugated ladder polymers based on indacenodipyrene.

linking the pyrene chromophores in the small molecules as well as polymeric materials.

2. Results and discussion

To optimize reaction conditions for the preparation of the conjugated ladder polymers, small molecule derivatives were first prepared. Initial attempts to access the fused indacenodipyrene scaffold followed a Scholl cyclodehydrogenation strategy (Scheme 1) [28,29]. Singly borylated pyrene **3** was cross-coupled with 1,4-dibromo-2,5-bis(dodecyloxy)benzene **4** to give precursor **5** in good yields. However, Scholl cyclodehydrogenation reactions utilizing either FeCl$_3$ [30] or DDQ [31] with strong organic acids (triflic acid and methyl sulfonic acid) were found to not give the desired product **6**, but instead resulted in retrieval of starting
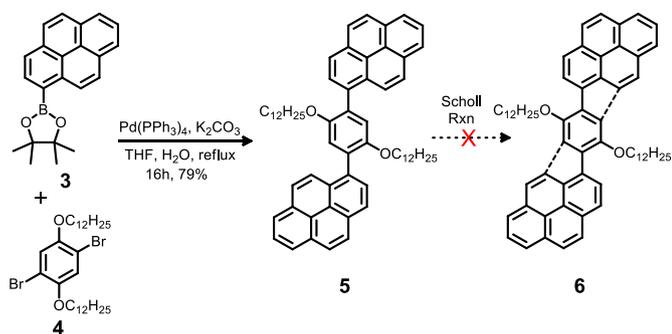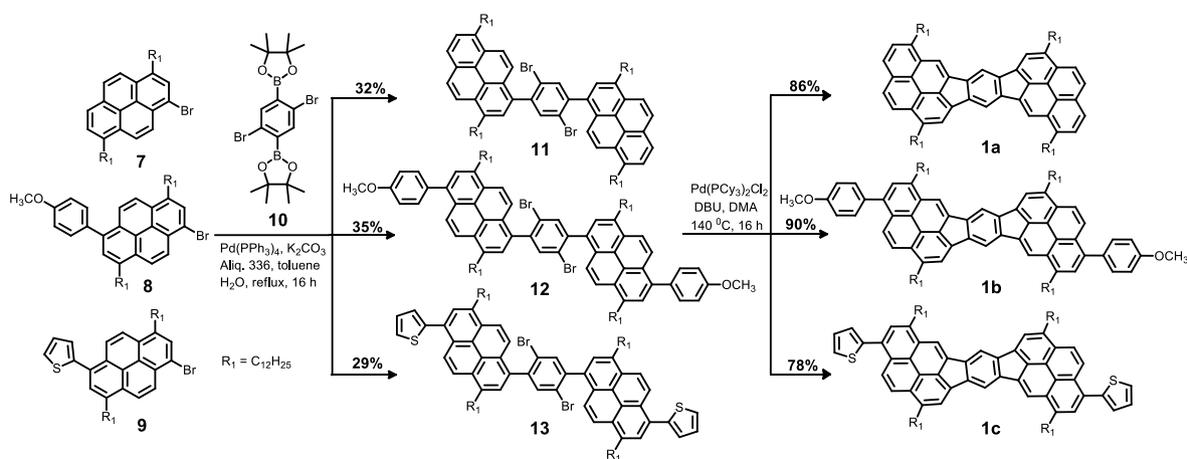
Scheme 1. Synthesis of small molecule precursor via Suzuki cross coupling.

material. As an alternative, we prepared brominated precursors to enable a palladium-catalyzed arylation reaction strategy [32,33]. Mono-brominated pyrene derivatives **7–9** with varying substituents on the pyrene core were prepared (Supporting Information) and reacted with 2,2'-(2,5-dibromo-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3, 2-dioxaborolane) **10** [34] to give precursors **11–13** in modest yields of 29–35% (Scheme 2). Here, [Pd(PCy$_3$)$_2$Cl$_2$] as the catalyst and DBU as base was employed to create the five-membered ring bridges to give **1a-c** in isolated yields of 78–90%. It should be noted that a preliminary route to build up a library of diverse substituted structures from a common precursor was investigated. For example, attempts were made to

brominate **1a**, which would have provided a scaffold to easily build a library of structures through cross-coupling chemistry (e.g., **1b** and **1c**). However, these attempts were unsuccessful in preparing pure brominated materials for further utilization as an intractable mixture of products were found during chromatography. This preliminary difficulty led to the less convenient, yet operational method, of stepwise functionalization we report here.

With the small molecule derivatives prepared, the reaction chemistry was applied to preparing ladder conjugated polymers. Pyrene precursors were modified from the single bromine containing monomers **7–9** to dibromo-containing monomers **14** and **15** (Scheme 3). Polymerization conditions utilized the same Suzuki-Miyaura conditions with monomer **10** to build up the pyrene containing materials. Recycling preparative gel permeation chromatography (GPC) was used to exclude lower molecular weight material and resulted in collected samples of 10 kDa and 13 kDa (based on GPC with polystyrene standards), for **16** and **17**, respectively (supporting information). The palladium-catalyzed arylation reaction was applied to **16** and **17** to form the laddered polymers **2a** and **2b**. As expected, the solubility of the resulting materials was significantly reduced owing to the extended planarized surfaces. Ladder polymer **2a** was found to be totally insoluble in common organic solvents such as toluene, chloroform, dichloromethane, tetrahydrofuran and dichloroethane at higher temperatures. However, **2b** was found to give some solubility (~0.05 mg/mL) in hot chloroform for limited processing and characterization.

Solution based UV/Vis absorption spectra of the indacenodipyrene

Scheme 2. Synthesis of small molecule derivatives via Suzuki cross coupling and Heck reaction.
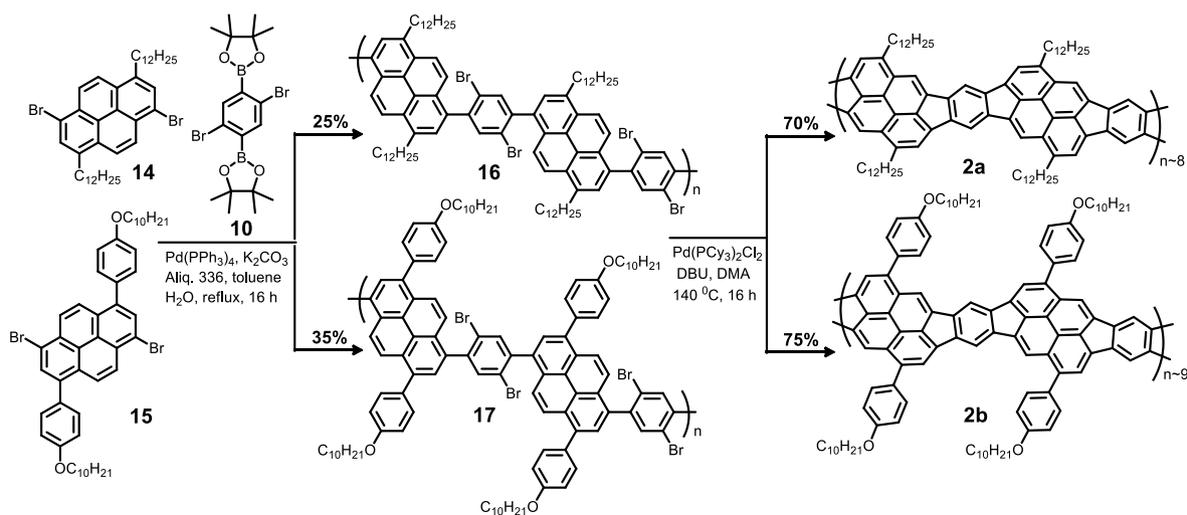
Scheme 3. Synthesis of conjugated ladder polymers via Suzuki cross coupling and arylation reaction.

based materials are shown in Fig. 2. Overall, the three small molecule derivatives (**1a-c**) were similar, but with small bathochromic shifts with substitutions consisting of the anisole (8 nm) and thiophene (18 nm). The optical band gaps of the pyrene-based materials, as determined by the onset of film-based absorption from the diffuse reflectance absorption spectra (supporting information) were 2.03 eV, 1.98 eV and 1.90 eV for **1a**, **1b** and **1c,** respectively. The precursor polymer **17** onset is significantly hypsochromically shifted in relation to the ring closed compounds **1a-c.** However, upon the arylation reaction, polymer **2b** shows significant bathochromic shift with an onset of 693 nm in solution with the lowest energy transition (470–600 nm) overlapping with the small molecule analogs. The absorption tails to lower energies and suggests expanded delocalization along the polymer backbone in relation to the dimeric pyrene small molecule derivatives.

To further probe the electronic properties of **1a-c**, **17**, and **2b**, cyclic voltammograms (CV) of the solid films were obtained. Organic films for
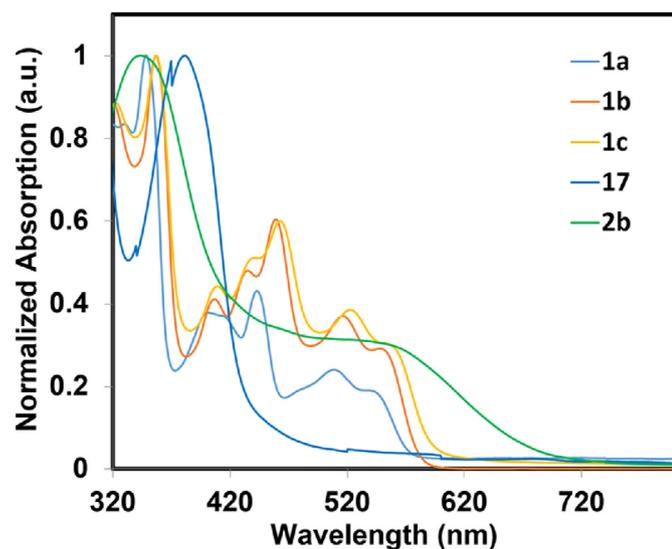
Table 1
Summary of molecular weight and optoelectronic properties of compounds **1a-c**, **17** and **2b**.

Cmpd	$E_{ox/onset}$ (V)	$E_{red/onset}$ (V)	HOMO	LUMO	E-chem	λ_{onset}	Optical
			(eV)	(eV)	gap (eV)	(nm)	gap (eV)
1a	0.59	−2.36	−5.39	−2.44	2.95	610	2.03
1b	0.43	−2.38	−5.23	−2.42	2.81	625	1.98
1c	0.48	−2.01	−5.28	−2.79	2.49	651	1.90
17	0.58	−2.31	−5.38	−2.49	2.89	471	2.63
2b	0.58	−1.82	−5.38	−2.98	2.40	739	1.68

[a] Potentials measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Fig. 3). $E_{ox/onset}$ is the onset of oxidation potential, $E_{red/onset}$ is the onset of reduction potential. HOMO and LUMO values calculated on the basis of the oxidation of the ferrocene reference in vacuum (−4.8 eV). Optical gap taken from λ_{onset} of film (SI).

CV were prepared by drop casting chloroform solutions on a glassy carbon electrode. Analysis of the CV shows the materials have both irreversible oxidation and reduction signals (Fig. 3). The most significant oxidation was found in **1c**, which would arise from thiophene radical cation electropolymerization at the open 2-position [35]. It is unknown the exact reactive radical species that leads to the irreversibility in these system, however, the dimerization of pyrene and quinone formation are known pathways in other pyrene systems [36]. Utilizing ferrocene as an internal standard, the highest occupied molecular level (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the materials were evaluated. The HOMO levels ranged from −5.28 eV to −5.39 eV, while the LUMO energies varied between −2.42 to −2.98 eV (Table 1). The optical and electrochemical gaps diverged in absolute value and is presumably owing to the exciton binding energies being considerably different in these systems [37].

The newly prepared materials were then evaluated in regard to their charge carrier mobilities. Organic field effect transistors with bottom gate and bottom contact arrangements were prepared. Traditional gold contacts deposited on octadecyltrichlorosilane functionalized Si/SiO$_2$ substrates were utilized. Films were cast by spin-coating chloroform solutions at 3000 rpm onto the prepared substrates. Typical output and transfer plots of the resulting devices can be found in Fig. 4 and Fig. 5. The average (n = 5) charge carrier mobilities **1b** and **1c**, as tested in air, were found to be an average of 2.5X10^{-5} ($\pm$2.1X10^{-6}) and 7.4X10^{-5} ($\pm$1.7 X10^{-5}) cm^2 V^{-1} s^{-1}, respectively. No appreciable current was observed for **1a** or polymer **2b**, and were presumed to be owing to inconsistent film formation resulting from poor solubilities. Although the charge carrier mobilities in these systems are relatively small, they do demonstrate the materials are active as charge carriers.

Fig. 2. Absorption spectra of small molecules **1a-c** and polymers **17** and **2b** in chloroform.
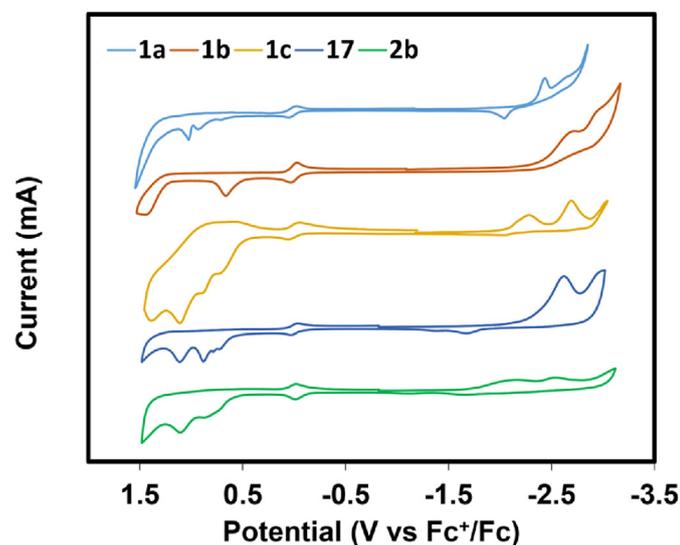

Fig. 3. Thin film cyclic voltammetry of **1a-c**, **17** and **2b** in acetonitrile with 0.05 M tetrabutyl ammonium hexafluorophosphate, glassy carbon working electrode, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 100 mV/s. Ferrocene was added as an internal standard and referenced to 0 V.
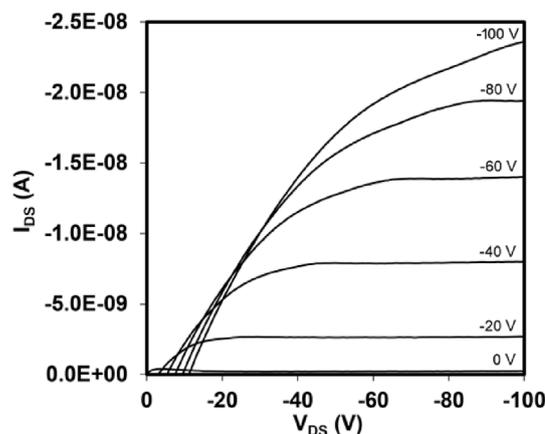

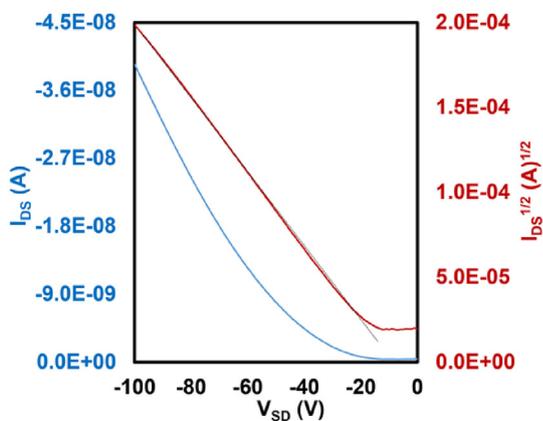**Fig. 4.** Typical output curves for **1b** showing p-type semiconductor behavior.

Fig. 5. Typical transfer plot for the p-type semiconductor **1b**. $V_G = -80$ V. Average mobility ($h^+ = 2.5 \times 10^{-5}$ cm^2 V^{-1} s^{-1} $\pm$ 2.1×10^{-6}).

In conclusion, we have synthesized a series of new indacenodipyrene based small molecule and conjugated ladder polymers by an efficient palladium catalyzed arylation of a dipyrenyl benzene precursor. The small molecule reaction optimization was applied to make conjugated-ladder polymers that possessed bathochromically shifted optical properties and less soluble materials in comparison to the small molecule analogs. While the conjugated polymers in this study did not show charge conduction, the small molecule derivatives did show modest charge carrier mobilities.

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.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tchem.2022.100019.

References

[1] D. Griggs, M. Stafford-Smith, O. Gaffney, J. Rockström, M.C. Öhman, P. Shyamsundar, W. Steffen, G. Glaser, N. Kanie, I. Noble, Sustainable development goals for people and planet, Nature 495 (7441) (2013) 305–307, https://doi.org/10.1038/495305a.

[2] L. Lu, T. Zheng, Q. Wu, A.M. Schneider, D. Zhao, L. Yu, Recent advances in bulk heterojunction polymer solar cells, Chem. Rev. 115 (23) (2015) 12666–12731, https://doi.org/10.1021/acs.chemrev.5b00098.

[3] Polman, A.; Knight, M.; Garnett, E. C.; Ehrler, B.; Sinke, W. C. Photovoltaic materials: present efficiencies and future challenges. Science 352 (6283), 307–317.

[4] J.E. Anthony, Functionalized acenes and heteroacenes for organic electronics, Chem. Rev. 106 (12) (2006) 5028–5048, https://doi.org/10.1021/cr050966z.

[5] J. Wu, W. Pisula, K. Müllen, Graphenes as potential material for electronics, Chem. Rev. 107 (3) (2007) 718–747, https://doi.org/10.1021/cr068010r.

[6] A.-D. Schlüter, Ladder polymers: the new generation, Adv. Mater. 3 (6) (1991) 282–291, https://doi.org/10.1002/adma.19910030603.

[7] U. Scherf, K. Müllen, Polyarylenes and poly(arylenevinylenes), 7. A soluble ladder polymer via bridging of functionalized poly(p-phenylene)-precursors, Makromol. Chem., Rapid Commun. 12 (8) (1991) 489–497, https://doi.org/10.1002/marc.1991.030120806.

[8] A.-D. Schlüter, M. Löffler, V. Enkelmann, Synthesis of a fully unsaturated all-carbon ladder polymer, Nature 368 (6474) (1994) 831–834, https://doi.org/10.1038/368831a0.

[9] M.B. Goldfinger, T.M. Swager, Fused polycyclic aromatics via electrophile-induced cyclization reactions: application to the synthesis of graphite ribbons, J. Am. Chem. Soc. 116 (17) (1994) 7895–7896, https://doi.org/10.1021/ja00096a056.

[10] U. Scherf, K. Müllen, The synthesis of ladder polymers, in: Synthesis and Photosynthesis; Advances in Polymer Science, Springer, Berlin, Heidelberg, 1995, pp. 1–40, https://doi.org/10.1007/3-540-58908-2_1.

[11] M.B. Goldfinger, K.B. Crawford, T.M. Swager, Directed electrophilic cyclizations: efficient methodology for the synthesis of fused polycyclic aromatics, J. Am. Chem. Soc. 119 (20) (1997) 4578–4593, https://doi.org/10.1021/ja9642673.

[12] K. Ohashi, T. Kubo, T. Masui, K. Yamamoto, K. Nakasuji, Y. Takui, Y. Kai, I. Murata, 4,8,12,16-Tetra-Tert-Butyl-s-Indaceno[1,2,3-Cd:5,6,7-c'd']Diphenalene: a four-stage amphoteric redox system, J. Am. Chem. Soc. 120 (9) (1998) 2018–2027, https://doi.org/10.1021/ja970961m.

[13] A. Babel, S.A. Jenekhe, High electron mobility in ladder polymer field-effect transistors, J. Am. Chem. Soc. 125 (45) (2003) 13656–13657, https://doi.org/10.1021/ja0371810.

[14] C. Xu, A. Wakamiya, S. Yamaguchi, Ladder oligo(p-phenylenevinylene)s with silicon and carbon bridges, J. Am. Chem. Soc. 127 (6) (2005) 1638–1639, https://doi.org/10.1021/ja042964m.

[15] Z. Chen, J.P. Amara, S.W. Thomas, T.M. Swager, Synthesis of a novel poly(iptycene) ladder polymer, Macromolecules 39 (9) (2006) 3202–3209, https://doi.org/10.1021/ma052451f.

[16] A.L. Briseno, S.C.B. Mannsfeld, P.J. Shamberger, F.S. Ohuchi, Z. Bao, S.A. Jenekhe, Y. Xia, Self-assembly, molecular packing, and electron transport in n-type polymer semiconductor nanobelts, Chem. Mater. 20 (14) (2008) 4712–4719, https://doi.org/10.1021/cm8010265.

[17] X. Yang, X. Dou, A. Rouhanipour, L. Zhi, H.J. Räder, K. Müllen, Two-dimensional graphene nanoribbons, J. Am. Chem. Soc. 130 (13) (2008) 4216–4217, https://doi.org/10.1021/ja710234t.

[18] J.D. Plumhof, T. Stöferle, L. Mai, U. Scherf, R.F. Mahrt, Room-temperature bose–einstein condensation of cavity exciton–polaritons in a polymer, Nat. Mater. 13 (3) (2014) 247–252, https://doi.org/10.1038/nmat3825.

[19] J. Lee, B.B. Rajeeva, T. Yuan, Z.-H. Guo, Y.-H. Lin, M. Al-Hashimi, Y. Zheng, L. Fang, Thermodynamic synthesis of solution processable ladder polymers, Chem. Sci. 7 (2) (2016) 881–889, https://doi.org/10.1039/C5SC02385H.

[20] W. Yang, A. Lucotti, M. Tommasini, W.A. Chalifoux, Bottom-up synthesis of soluble and narrow graphene nanoribbons using alkyne benzannulations, J. Am. Chem. Soc. 138 (29) (2016) 9137–9144, https://doi.org/10.1021/jacs.6b03014.

[21] J. Gao, F.J. Uribe-Romo, J.D. Saathoff, H. Arslan, C.R. Crick, S.J. Hein, B. Itin, P. Clancy, W.R. Dichtel, Y.-L. Loo, Ambipolar transport in solution-synthesized graphene nanoribbons, ACS Nano 10 (4) (2016) 4847–4856, https://doi.org/10.1021/acsnano.6b00643.

[22] J. Lee, A.J. Kalin, T. Yuan, M. Al-Hashimi, L. Fang, Fully conjugated ladder polymers, Chem. Sci. 8 (4) (2017) 2503–2521, https://doi.org/10.1039/C7SC00154A.

[23] W. Zeng, H. Phan, T.S. Herng, T.Y. Gopalakrishna, N. Aratani, Z. Zeng, H. Yamada, J. Ding, J. Wu, Rylene ribbons with unusual diradical character, Chem 2 (1) (2017) 81–92, https://doi.org/10.1016/j.chempr.2016.12.001.

[24] Cao, Z.; Leng, M.; Cao, Y.; Gu, X.; Fang, L. How Rigid Are Conjugated Non-Ladder and Ladder Polymers? Journal of Polymer Science n/a (n/a). https://doi.org/10.1002/pol.20210550.

[25] Y. Wang, Y. Huang, T. Huang, J. Zhang, T. Luo, Y. Ni, B. Li, S. Xie, Z. Zeng, Perylene-based linear nonalternant nanoribbons with bright emission and ambipolar redox behavior, Angew. Chem. Int. Ed. 61 (21) (2022), e202200855, https://doi.org/10.1002/anie.202200855.

[26] Y.C. Teo, H.W.H. Lai, Y. Xia, Synthesis of ladder polymers: developments, challenges, and opportunities, Chem. Eur. J. 23 (57) (2017) 14101–14112, https://doi.org/10.1002/chem.201702219.

[27] J. Melidonie, J. Liu, Y. Fu, J.J. Weigand, R. Berger, X. Feng, Pyrene-Fused s-Indacene, J. Org. Chem. 83 (12) (2018) 6633–6639, https://doi.org/10.1021/acs.joc.8b00925.

[28] B.T. King, J. Kroulík, C.R. Robertson, P. Rempala, C.L. Hilton, J.D. Korinek, L.M. Gortari, Controlling the Scholl reaction, J. Org. Chem. 72 (7) (2007) 2279–2288, https://doi.org/10.1021/jo061515x.

[29] M. Grzybowski, K. Skonieczny, H. Butenschön, D.T. Gryko, Comparison of oxidative aromatic coupling and the Scholl reaction, Angew. Chem. Int. Ed. 52 (38) (2013) 9900–9930, https://doi.org/10.1002/anie.201210238.

[30] T. Horibe, S. Ohmura, K. Ishihara, Structure and reactivity of aromatic radical cations generated by FeCl3, J. Am. Chem. Soc. 141 (5) (2019) 1877–1881, https://doi.org/10.1021/jacs.8b12827.

[31] L. Zhai, R. Shukla, S.H. Wadumethrige, R. Rathore, Probing the arenium-ion (ProtonTransfer) versus the cation-radical (electron transfer) mechanism of Scholl reaction using DDQ as oxidant, J. Org. Chem. 75 (14) (2010) 4748–4760, https://doi.org/10.1021/jo100611k.

[32] J.E. Rice, Z.W. Cai, An intramolecular arene-triflate coupling reaction for the regiospecific synthesis of substituted benzofluoranthenes, J. Org. Chem. 58 (6) (1993) 1415–1424, https://doi.org/10.1021/jo00058a023.

[33] H.A. Reisch, M.S. Bratcher, L.T. Scott, Imposing curvature on a polyarene by intramolecular palladium-catalyzed arylation reactions: a simple synthesis of dibenzo[a,g]corannulene, Org. Lett. 2 (10) (2000) 1427–1430, https://doi.org/10.1021/ol005755p.

[34] T. Higashino, K. Ishida, T. Sakurai, S. Seki, T. Konishi, K. Kamada, K. Kamada, H. Imahori, Pluripotent features of doubly thiophene-fused benzodiphospholes as

organic functional materials, Chem. Eur J. 25 (25) (2019) 6425–6438, https://doi.org/10.1002/chem.201900661.

[35] J. Roncali, Conjugated poly(thiophenes): synthesis, functionalization, and applications, Chem. Rev. 92 (4) (1992) 711–738, https://doi.org/10.1021/cr00012a009.

[36] L. Jeftic, R.N. Adams, Electrochemical oxidation pathways of benzo[a]Pyrene, J. Am. Chem. Soc. 92 (5) (1970) 1332–1337.

[37] N.S. Sariciftci, Primary Photoexcitations in Conjugated Polymers: Molecular Excitons vs Semiconductor Band Model, World Scientific, Singapore, 1997.