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Palladium-Catalyzed Multialkynyl Cross-Coupling Reactions with Tetraalkynylindates

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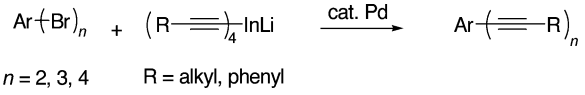
Dedicated to the memory of Professor Chi Sun Hahn

Keywords: Cross-coupling / Indium / Alkynes / Palladium

An efficient Pd-catalyzed multialkynyl cross-coupling reaction performed with tetraalkynylindates generated in situ from the reaction of 1 equiv. of indium trichloride with 4 equiv. of organometallic reagents has been developed to produce symmetric as well as unsymmetric multialkynyl-substituted aromatic compounds in good-to-excellent yields. In these reactions, the four acetylide groups in the tetraalkynylindates transferred effectively to a variety of aryl bromides.

Introduction

Pd-catalyzed alkynylation is one of the most general and reliable methods for the synthesis of alkynes.[1] Much attention has recently been focused on multialkynyl-substituted aromatic compounds owing to their potential as nonlinear optical materials,[2] liquid crystals,[3] core structures for light-harvesting,[4] as well as dendritic materials[5] and building blocks for two-dimensional carbon networks.[6] During the last two decades a variety of transition-metal-catalyzed multialkynyl cross-coupling reactions have been reported.[1] Of these, metalated alkynes, especially those containing Zn,[1c,7] Sn,[8] B,[9] Cu,[10] and Au[11] have generally been used in multialkynyl cross-coupling reactions. Although these reactions show wide applicability, convenience, and overall excellence, new and efficient transition-metal-catalyzed multialkynyl reactions are strongly required to overcome some of their limitations, such as the use of organometallic reagents in excess, the dimerization of the alkynes, and the toxicity of the metals. In recent years, organoindium reagents have become a favorite in organic reactions mainly due to their reactivity, selectivity, ease of preparation and handling, operational simplicity, and low toxicity.[12,13] On the basis of these properties, Sarandeses and co-workers reported efficient Pd-catalyzed cross-coupling reactions using triorganoindiums.[14] Recently we reported the Pd-catalyzed cross-coupling reactions of allylindiums,[15] allenylindiums,[16] 1,3-butadien-2-ylindiums,[17] tetraorganoindates,[18] and indium tris(organothiolate)s[19] with a variety of electrophiles. As a continuation of our organic-conjugated materials chemistry program,[20] we envisioned the possibility of extending the scope of transition-metal-catalyzed multialkynyl cross-coupling reactions by using tetraorganoindates. Herein, we report the efficient Pd-catalyzed multialkynyl cross-coupling reactions of tetraalkynylindates with various aryl bromides with high atom efficiency, producing symmetric as well as unsymmetric multialkynyl-substituted aromatic compounds (Scheme 1).



Scheme 1. Pd-catalyzed multialkynyl cross-coupling reactions performed with tetraalkynylindates.

Results and Discussion

Our initial study focused on the Pd-catalyzed two-fold alkynyl cross-coupling reactions of lithium tetrakis(phenylethynyl)indate (**2a**) with 2,5-dibromopyridine (**1a**) due to its possible applications in materials science.

Because the reaction of 2,5-dibromopyridine with tetrakis(phenylethynyl)indate generated in situ from 1 equiv. of indium trichloride and 4 equiv. of lithium phenylacetylide required a long time (17 h) in THF at 70 °C and produced 5-bromo-2-(phenylethynyl)pyridine in 5% yield (entry 2, Table 1), various Pd catalysts were re-examined with a view

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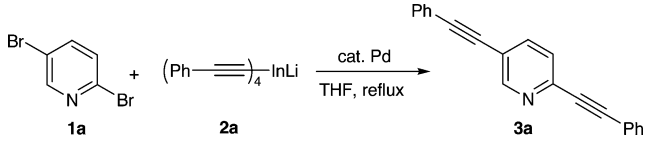
to accelerating the reaction rate and suppressing the formation of side-products. Of the catalysts screened, [Pd(dppf)-Cl_2] was the most satisfactory in terms of product yield and reaction rate (entry 3). The use of other ligands such as Ph_3P, $(4\text{-}CF_3C_6H_4)_3P$, and $(4\text{-}MeOC_6H_4)_3P$ required long reaction times (24 h, entries 1, 4, and 5) or, as in the case of entry 4, also gave a low yield of the product **3a**. The use of 0.6 equiv. of **2a** gave the best result, which indicates that the four phenylethynyl groups attached to the indium transferred effectively to **1a** with high atom efficiency.

Table 1. Optimization of Pd-catalyzed two-fold alkynyl cross-coupling reactions.[a]



1a 2a 3a

Entry	Pd/Ligand	*t* [h]	Yield [%][b]
1	2 mol-% $[Pd_2dba_3CHCl_3]$ 16 mol-% PPh_3	24	89
2	4 mol-% $[Pd(PPh_3)_4]$	17	92(5)
3	4 mol-% $[Pd(dppf)Cl_2]$	8	95
4	2 mol-% $[Pd_2dba_3CHCl_3]$ 16 mol-% $P(4\text{-}CF_3C_6H_4)_3$	24	11
5	2 mol-% $[Pd_2dba_3CHCl_3]$ 16 mol-% $P(4\text{-}MeOC_6H_4)_3$	24	64

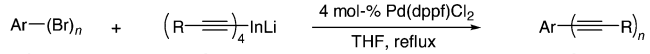
[a] The reaction was performed with 4 mol-% $[Pd(dppf)Cl_2]$ and 0.6 equiv. of indate. [b] Isolated yield. The number in parentheses represents the yield of 5-bromo-2-(2-phenylethynyl)pyridine.

With these results in hand, the Pd-catalyzed multialkynyl cross-coupling reactions of various indates with 2,5-dibromopyridine (**1a**) were investigated. The results are summarized in Table 2. 2,5-Di(1-heptynyl)pyridine (**3b**) was obtained in 96% yield by using 0.6 equiv. of lithium tetra(1-heptynyl)indate (**2b**) under the optimum reaction conditions (entry 1). Lithium tetrakis(*tert*-butylethynyl)indate (**2c**) produced the cross-coupling product **3c** in a lower yield of 77%, presumably due to steric considerations and its basicity (entry 2). In addition, the use of 0.6 equiv. of lithium tetrakis(1-cyclohexenylethynyl)indate (**2d**), lithium tetrakis(5-chloro-1-pentynyl)indate (**2e**), and indate **2f** with a THP ether group participated well as nucleophiles in the Pd-catalyzed cross-coupling reactions, producing the corresponding di(alkynyl) compounds (**3d**, **3e**, and **3f**) in good-to-excellent yields (entries 3, 4, and 5). These results imply that the four acetylide groups in the tetraalkynylindates transferred effectively to the 2,5-dibromopyridine with high atom efficiency and that the double bond, chloride, and THP ether were tolerated in the cross-coupling reactions. The addition of 0.6 equiv. of lithium tetrakis(phenylethynyl)-indate (**2a**) to 4,4′-dibromobiphenyl (**1b**) resulted in all of the phenylethynyl groups attached to indium being transferred to **1b** to afford 4,4′-bis(phenylethynyl)biphenyl (**3g**) in 85% yield (entry 7). 9,10-Dibromoanthracene (**1c**) was treated with **2e** to provide the desired product **3j** in 88% yield (entry 10). The use of 0.9 equiv. of **2e** may have been required because of the low solubility of **1c**. The reactions of various indates (0.6 equiv., **2c**, **2a**, and **2b**) with 2,7-dibromo-9*H*-fluorene (**1d**) and 9-ethyl-3,6-dibromo-9*H*-carbazole (**1e**) afforded the desired dialkynylated products **3k**, **3l**, and **3m** in good-to-excellent yields (entries 11–13). Treatment of 2,4-dibromoanisole with indates **2a** and **2g** (0.6 equiv.) gave the corresponding 2,4-di(alkynyl)anisoles **3n** and **3o** in 95 and 92% yields, respectively (entries 14 and 15). We were pleased to obtain di(alkynyl)thiophenes **3p** and **3q**, respectively, from the reactions of 2,3- and 3,4-dibromothiophene with the corresponding indates (1.2 equiv., entries 16 and 17). The thermal instability of di(alkynyl)-thiophenes required the use of 1.2 equiv. of **2a**. Under the optimum reaction conditions, the reaction of indate complex **2e** with 5,5′-dibromo-2,2′-bithiophenyl (**1i**) produced the desired di(alkynyl) product **3r** in 91% yield (entry 18). Encouraged by these results, the treatment of 1,3,5-tribromobenzene (**1j**) and 1,2,4,5-tetrabromobenzene (**1k**) with **2a** (1.2 equiv.) and **2e** (2 equiv.) furnished tri- and tetraalkynylbenzene derivatives (**3s** and **3t**) in 84 and 72% yields, respectively (entries 19 and 20).

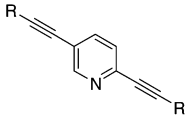
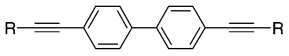
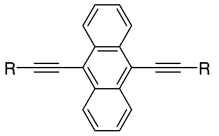
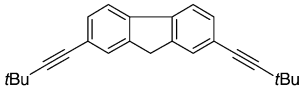
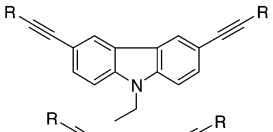
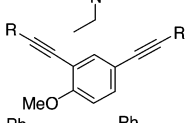
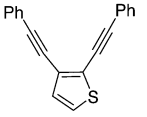
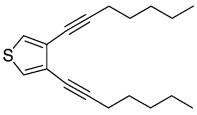
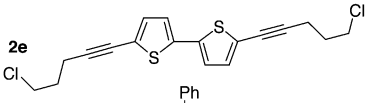
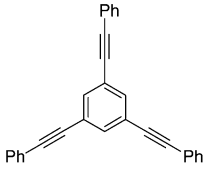
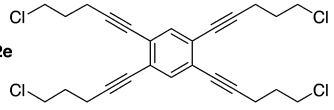
Next, Pd-catalyzed multialkynyl cross-coupling reactions using different kinds of tetraorganoindate were examined for the preparation of unsymmetric alkynes. For example, consecutive two-fold Pd-catalyzed cross-coupling reactions using different indates (0.3 equiv. of **2c** and 0.3 equiv. of **2a**) occurred chemo- and regioselectively in one-pot to afford unsymmetric dialkyne **3u** in 81% yield, which indicates that all the ligands attached to the indium transferred to the electrophilic reagent (Scheme 2). The unsymmetric dialkyne derivative **3v** with two pyridyl groups was obtained in 70% yield from the reaction of 2,5-dibromopyridine and 0.3 equiv. of the indate generated in situ from (2-pyridyl) acetylene and indium trichloride and subsequent treatment with 0.45 equiv. of the indate derived from 6-chloro-1-pentyne. Side-products such as reduced halide compounds, two-fold cross-coupling products arising from reaction with the same alkynyl group, and homocoupling products were not observed in the preparation of alkynes **3u** and **3v**.

Although the mechanism for Pd-catalyzed cross-coupling reactions with lithium tetraalkynylindate has not been firmly established, the details of these reactions can be described in connection with the mechanism generally accepted for these kinds of reactions.[21] In this mechanism we accept that R_3In, R_2InX, and $RInX_2$ are all leaving groups in a catalytic cycle and that these groups can be re-involved in a new catalytic cycle and effectively transfer groups attached to indium to an electrophilic coupling partner (Scheme 3). This plausible mechanism is supported by the fact that $n Bu_3In$, $n Bu_2InCl$, and $n BuInCl_2$ have been effectively used in Pd-catalyzed and carbonylative cross-coupling reactions.[14c,22] The efficient transfer of four organic groups attached to the indium to the electrophile can be explained by the weak In–C bond strength. In addition, the large difference between the heats of formation of In–C and In–X supports the present mechanism.[23]

Table 2. Pd-catalyzed multialkynyl cross-coupling reactions with tetraalkynylindate.[a]



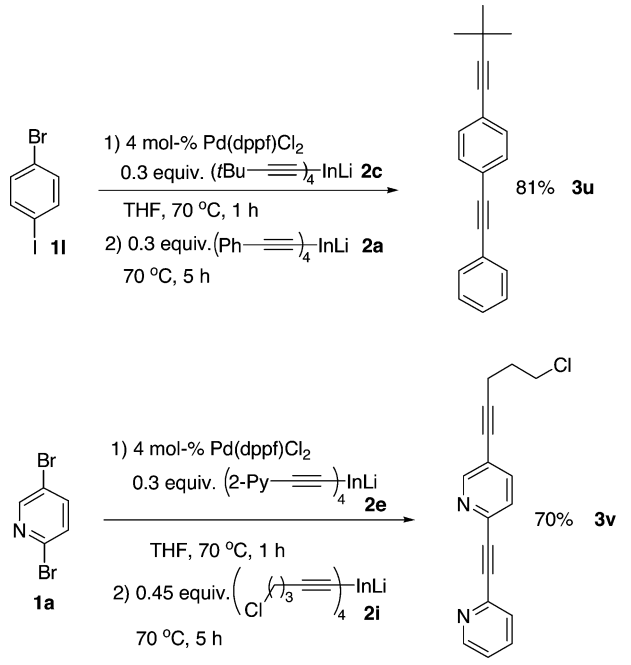
1 2 3

Entry	Aryl bromide	R		Product		t [h]	Yield [%]
1	**1a**	*n*Pent	**2b**		**3b**	6	96
2	**1a**	*t*Bu	**2c**		**3c**	7	77
3	**1a**	1-Cyclohexenyl	**2d**		**3d**	8	86
4	**1a**	$Cl(CH_2)_2CH_2$	**2e**		**3e**	4	99
5	**1a**	$THPOCH_2$	**2f**		**3f**	7	81
6	**1a**	Ph	**2a**		**3a**	8	95
7	**1b**	Ph	**2a**		**3g**	10	85
8	**1b**	$PhCH_2CH_2CH_2$	**2g**		**3h**	5	97
9	**1c**	Ph	**2a**		**3i**	24	71[b]
10	**1c**	$Cl(CH_2)_2CH_2$	**2e**		**3j**	20	88[b]
11	**1d**	*t*Bu	**2c**		**3k**	2	90
12	**1e**	Ph	**2a**		**3l**	15	87
13	**1e**	*n*Pent	**2b**		**3m**	4	93
14	**1f**	Ph	**2a**		**3n**	8	95
15	**1f**	$PhCH_2CH_2CH_2$	**2g**		**3o**	8	92
16	**1g**	Ph	**2a**		**3p**	15	85[c]
17	**1h**	Ph	**2a**		**3q**	6	85[c]
18	**1i**	$Cl(CH_2)_2CH_2$	**2e**		**3r**	7	91[c]
19	**1j**	Ph	**2a**		**3s**	15	84[c]
20	**1k**	$Cl(CH_2)_2CH_2$	**2e**		**3t**	12	72[d]

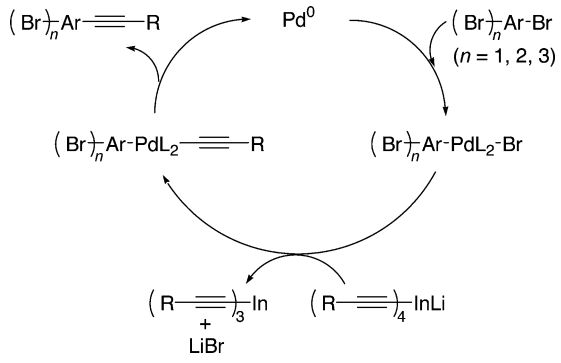
[a] The reactions were performed with 4 mol-% [$Pd(dppf)Cl_2$] and 0.6 equiv. of indate in THF (70 °C). [b] 0.9 equiv. of indate were used. [c] 1.2 equiv. of indate were used. [d] 2.0 equiv. of indate were used.

Conclusions

We have developed an efficient Pd-catalyzed multialkynyl cross-coupling reaction with tetraalkynylindates generated in situ from the reaction of 1 equiv. of indium trichloride with 4 equiv. of an organometallic reagent for the preparation of symmetric as well as unsymmetric multialkynyl-substituted aromatic compounds. In these reactions the four acetylide groups in the tetraalkynylindates transferred effectively to a variety of aryl bromides with high atom efficiency. These novel features make tetraalkynylindates highly useful alternatives to other organometallic reagents used in transition-metal-catalyzed multialkynyl cross-coupling reactions and also mark them out as promising reagents for organic synthesis.



Scheme 2. Pd-catalyzed multialkynyl cross-coupling reactions using different tpes of tetraalkynylindates.



Scheme 3. Plausible mechanism for the Pd-catalyzed multialkynyl cross-coupling reactions using tetraalkynylindates.

Experimental Section

General: Reactions were carried out in oven-dried glassware under nitrogen. All commercial reagents were used without purification and all solvents were of reagent grade. DMF was freshly distilled from CaH_2 and dried with molecular sieves (4 Å). All reactions were monitored by TLC using glass plates precoated with silica gel, purifications were performed by column chromatography with silica gel (0.04–0.063 mm, 230–400 mesh). ^1H and ^{13}C NMR spectra were recorded with a 400 MHz spectrometer using deuteriated chloroform as the solvent. Chemical shift values (δ) are reported in parts per million relative to TMS as an internal standard (δ = 7.24 ppm for ^1H and δ = 77.0 ppm for ^{13}C). Infrared spectra were recorded with a FTIR spectrometer; samples were either measured as thin films pressed between two sodium chloride plates or as solids suspended in potassium bromide disks. High-resolution mass spectra were recorded with a JEOL JMS 700 high-resolution mass spectrometer. Melting points were determined in an open capillary tube.

Typical Procedure for the Synthesis of Tetrakis(phenylethynyl)-indate:[18] *n*BuLi (1.2 mmol, 1.6 M in hexane) was slowly added to a solution of phenylacetylene (132 μL, 1.2 mmol) in THF (1 mL) at –78 °C. After stirring for 10 min, the cooling bath was removed and the reaction mixture was warmed to room temperature, producing lithium (2-phenyl)ethynylide. The resulting solution was slowly added to a solution of $InCl_3$ (66.3 mg, 0.3 mmol) in THF (1 mL) at –78 °C. After stirring the mixture for 30 min, the cooling bath was removed and the reaction mixture was warmed to room temperature over 30 min.

2,5-Bis(phenylethynyl)pyridine (3a):[24] A solution of tetrakis(phenylethynyl)indate (0.3 mmol, ca. 0.15 M in dry THF) was added to a mixture of [Pd(dppf)Cl_2] (16.3 mg, 4 mol-%) and 2,5-dibromopyridine (118.4 mg, 0.5 mmol) in THF (1 mL) under nitrogen. The reaction mixture was heated at reflux for 8 h. After cooling to room temperature, the reaction mixture was quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic phases were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane = 1:30) to give 2,5-bis(phenylethynyl)pyridine (132.7 mg, 95%). Brown solid, m.p. 170–172 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.76 (s, 1 H), 7.78 (d, J = 10.14 Hz, 1 H), 7.62–7.60 (m, 2 H), 7.56 (m, 2 H), 7.50 (d, J = 8.02 Hz, 1 H), 7.37 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.5, 141.9, 138.4, 132.1, 131.7, 129.2, 129.0, 128.5, 126.4, 122.4, 122.4, 122.1, 119.2, 94.3, 91.2, 88.6, 86.0 ppm. IR (film): $\tilde{\nu}$ = 3049, 2215, 1594, 1494, 1464, 1364, 1021, 751 cm^{-1}.

2,5-Di-1-heptynylpyridine (3b):[25] ^1H NMR (400 MHz, $CDCl_3$25 °C): δ = 8.46 (s, 1 H), 8.75 (d, J = 8.05 Hz, 1 H), 7.20 (d, J = 8.05 Hz, 1 H), 2.35 (q, J = 7.23 Hz, 4 H), 1.59–1.50 (m, 4 H), 1.39–1.22 (m, 8 H), 0.86–0.81 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.7, 142.3, 138.7, 126.3, 120.0, 95.8, 93.0, 80.7, 77.8, 31.5, 31.5, 28.6, 28.4, 22.6, 19.9, 19.8, 14.35, 14.33 ppm. IR (film): $\tilde{\nu}$ = 2932, 2859, 2225, 1584, 1537, 1467, 1363, 840 cm^{-1}.

2,5-Bis(3,3-dimethyl-1-butynyl)pyridine (3c): White solid, m.p. 149–151 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.52 (s, 1 H), 7.57 (d, J = 8.04 Hz, 1 H), 7.27 (d, J = 8.04 Hz, 1 H), 1.34 (s, 9 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.6, 142.3, 138.8, 126.4, 120.0, 103.6, 100.5, 79.3, 76.4, 31.2, 31.1, 28.5, 28.4 ppm. IR (film): $\tilde{\nu}$ = 3324, 2965, 2240, 1583, 1536, 1458, 1359, 1278, 1174 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{21}N$ 239.1674; found 239.1676.

2,5-Bis(cyclohexenyl-1-ethynyl)pyridine (3d): Pale-yellow solid, m.p. 78–80 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.58 (s, 1 H), 7.61 (d, J = 8.09 Hz, 1 H), 7.32 (d, J = 8.09 Hz, 1 H), 6.33 (s, 1 H), 6.26 (s, 1 H), 2.24–2.22 (m, 4 H), 2.16–2.15 (m, 4 H), 1.71–1.61 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.6, 142.3, 138.5, 138.0, 137.0, 126.4, 120.7, 120.5, 120.0, 96.4, 93.4, 86.7, 84.0, 29.4, 29.2, 26.3, 26.2, 22.62, 22.60, 21.79, 21.78 ppm. IR (film): $\tilde{\nu}$ = 3384, 2933, 2858, 2203, 1579, 1538, 1467, 1348, 1263, 918 cm^{-1}. HRMS (EI): calcd. for $C_{21}H_{21}N$ 287.1674; found 287.1674.

2,5-Bis(5-chloro-1-pentynyl)pyridine (3e): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.55 (s, 1 H), 7.61 (d, J = 8.41 Hz, 1 H), 7.30 (d, J = 8.41 Hz, 1 H), 3.73–3.69 (m, 4 H), 2.67–2.63 (m, 4 H), 2.12–2.04 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.3, 141.7, 138.5, 126.1, 119.5, 93.3, 90.4, 81.0, 78.2, 43.7, 43.6, 31.2, 31.0, 17.0, 16.9 ppm. IR (film): $\tilde{\nu}$ = 2960, 2230, 1584, 1539, 1469, 1439, 1270, 1173, 1035 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{15}Cl_2N$ 279.0582; found 279.0583.

2,5-Bis[(tetrahydropyran-2-yloxy)ethynyl]pyridine (3f): Pale-yellow solid, m.p. 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.63 (s, 1 H), 7.68 (d, J = 8.06 Hz, 1 H), 7.39 (d, J = 8.06 Hz, 1 H), 4.90–4.87 (m, 2 H), 4.54 (dd, J = 15.58, J = 2.38 Hz, 2 H), 4.48 (dd, J = 16.09, J = 8.99 Hz, 2 H), 3.91–3.85 (m, 2 H), 3.60–3.54 (m, 2 H), 1.89–1.73 (m, 4 H), 1.70–1.53 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.0, 142.1, 139.1, 126.8, 119.5, 97.5, 97.4, 90.8, 87.7, 85.1, 82.6, 62.4, 55.0, 54.9, 30.6, 25.7, 19.4 ppm. IR (film): $\tilde{\nu}$ = 3475, 2942, 2869, 2244, 1584, 1540, 1469, 1363, 1267, 1120, 1027, 902 cm^{-1}. HRMS (EI): calcd. for $C_{21}H_{25}NO_4$ 355.1784; found 355.1780.

4,4′-Bis(phenylethynyl)biphenyl (3g):[26] Pale-yellow solid, m.p. 249–250 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.61 (s, 8 H), 7.53–7.59 (m, 4 H), 7.33–7.40 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 139.0, 131.1, 130.6, 127.4, 127.3, 125.9, 122.2, 121.5, 88.6, 87.9 ppm. IR (film): $\tilde{\nu}$ = 3051, 2919, 1914, 1568, 1438, 1400, 1136, 822 cm^{-1}.

4,4′-Bis(5-phenyl-1-pentynyl)biphenyl (3h): White solid, m.p. 52–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.52–7.45 (m, 8 H), 7.31–7.27 (m, 4 H), 7.23–7.17 (m, 6 H), 2.79 (t, J = 7.29 Hz, 4 H), 2.43 (t, J = 7.29 Hz, 4 H), 1.97–1.89 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 142.1, 140.0, 132.5, 129.0, 128.9, 127.2, 126.4, 123.6, 91.3, 81.5, 35.3, 30.8, 19.4 ppm. IR (film): $\tilde{\nu}$ = 3061, 3026, 2938, 2222, 1602, 1493, 1454, 1261, 822 cm^{-1}. HRMS (EI): calcd. for $C_{34}H_{30}$ 438.2348; found 438.2348.

9,10-Bis(phenylethynyl)anthracene (3i):[27] Orange solid, m.p. 229–230 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.72–8.69 (m, 4 H), 7.80–7.78 (m, 4 H), 7.67–7.63 (m, 4 H), 7.49–7.43 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 132.5, 132.1, 129.1, 129.0, 127.7, 127.2, 123.8, 118.9, 102.8, 86.9 ppm. IR (film): $\tilde{\nu}$ = 3476, 1635, 1489, 1261, 1174, 1036, 764 cm^{-1}.

9,10-Bis(5-chloro-1-pentynyl)anthracene (3j): Orange solid, m.p. 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.54–8.50 (m, 4 H), 7.58–7.54 (m, 4 H), 3.84 (t, J = 6.29 Hz, 4 H), 2.95 (t, J = 6.88 Hz, 4 H), 2.28–2.21 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 132.6, 127.6, 127.0, 118.8, 101.4, 78.6, 44.3, 32.1, 18.1 ppm. IR (film): $\tilde{\nu}$ = 3397, 1634, 1395, 1261, 1173, 1036, 765 cm^{-1}. HRMS (EI): calcd. for $C_{24}H_{20}Cl_2$ 378.0942; found 378.0945.

2,7-Bis(3,3-dimethyl-1-butynyl)-9*H*-fluorene (3k): Yellow solid, m.p. 180–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.64 (d, J = 8.22 Hz, 2 H), 7.57 (s, 2 H), 7.41 (d, J = 8.22 Hz, 2 H), 3.82 (s, 2 H), 1.36 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.7, 141.0, 130.9, 128.5, 122.8, 120.1, 99.1, 80.0, 36.8, 31.5, 28.5 ppm. IR (film): $\tilde{\nu}$ = 3479, 2967, 1609, 1464, 1361, 1260, 1173, 1036, 827 cm^{-1}. HRMS (EI): calcd. for $C_{25}H_{26}$ 326.2034; found 326.2036.

9-Ethyl-3,6-bis(phenylethynyl)-9*H*-carbazole (3l):[28] Pale-yellow solid, m.p. 161–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.30 (s, 2 H), 7.68 (d, J = 8.48 Hz, 2 H), 7.62 (d, J = 8.04 Hz, 4 H), 7.41–7.35 (m, 8 H), 4.33 (q, J = 7.19 Hz, 2 H), 1.44 (t, J = 7.19 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 140.4, 131.9, 130.2, 128.8, 128.3, 124.6, 124.3, 123.0, 114.3, 109.2, 91.1, 88.3, 38.2, 14.3 ppm. IR (film): $\tilde{\nu}$ = 3433, 2207, 1628, 1592, 1492, 1380, 1260, 1231, 1173, 1036 cm^{-1}.

9-Ethyl-3,6-di(1-heptynyl)-9*H*-carbazole (3m): (1-Heptynyl)lithium (1.2 mmol, 1.0–1.2 M in THF) was added to a solution of $InCl_3$ (66.3 mg, 0.3 mmol) in THF (1 mL) at –78 °C under nitrogen. After stirring the mixture for 30 min, the cooling bath was removed and the reaction mixture was warmed to room temperature over 30 min. The tetra(1-heptynyl)indate solution (0.3 mmol, ca. 0.15 M in THF) was added to a mixture of [Pd(dppf)Cl_2] (16.3 mg, 4 mol-%) and 9-ethyl-3,6-dibromo-9*H*-carbazole (176.6 mg, 0.5 mmol) in THF (1 mL) under nitrogen. The reaction mixture was heated at reflux until consumption of the starting material (4 h). After cooling to room temperature, the reaction mixture was quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic phases were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane = 1:100) to give 9-ethyl-3,6-di(1-heptynyl)-9*H*-carbazole (178.4 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.10 (t, J = 11.66 Hz, 2 H), 7.52–7.48 (m, 2 H), 7.26–7.19 (m, 2 H), 4.29–4.22 (m, 2 H), 2.45 (t, J = 7.14 Hz, 4 H), 1.69–1.61 (m, 4 H), 1.52–1.43 (m, 4 H), 1.41–1.34 (m, 7 H), 0.94 (t, J = 7.21 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 140.4, 131.9, 130.2, 128.8, 128.3, 124.6, 124.3, 123.0, 114.3, 109.2, 91.1, 88.3, 38.2, 14.3 ppm. IR (film): $\tilde{\nu}$ = 3055, 2955, 2857, 1862, 1626, 1482, 1378, 1290, 1229, 804 cm^{-1}. HRMS (EI): calcd. for $C_{23}H_{33}N$ 383.2613; found 383.2618.

1-Methoxy-2,4-bis(phenylethynyl)benzene (3n): White solid, m.p. 123–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.71 (s, 1 H), 7.59–7.56 (m, 2 H), 7.54–7.52 (m, 2 H), 7.50–7.47 (m, 1 H), 7.38–7.33 (m, 6 H), 6.89 (d, J = 8.62 Hz, 1 H), 3.94 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.2, 137.1, 133.5, 132.1, 131.9, 128.8, 128.72, 128.71, 128.5, 123.8, 123.7, 116.0, 113.3, 111.2, 94.3, 88.9, 85.2, 56.4 ppm. IR (film): $\tilde{\nu}$ = 3055, 2964, 2839, 2210, 1591, 1502, 1441, 1281, 1248, 1179, 1024 cm^{-1}. HRMS (EI): calcd. for $C_{23}H_{16}O$ 308.1201; found 308.1196.

1-Methoxy-2,4-bis(5-phenyl-1-pentynyl)benzene (3o): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.45 (s, 1 H), 7.31–7.27 (m, 5 H), 7.24–7.27 (m, 6 H), 6.77 (d, J = 8.59 Hz, 1 H), 5.14 (s, 3 H), 2.83–2.76 (m, 4 H), 2.46 (t, J = 7.00 Hz, 2 H), 2.39 (t, J = 7.00 Hz, 2 H), 1.97–1.87 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 159.8, 142.1, 137.1, 132.7, 129.05, 129.00, 128.8, 126.32, 126.31, 11.6, 113.7, 110.9, 94.9, 56.3, 35.3, 35.2, 30.8, 19.6, 19.2 ppm. IR (film): $\tilde{\nu}$ = 3024, 2939, 2858, 1599, 1454, 1268, 1243, 1177, 1034, 894 cm^{-1}. HRMS (EI): calcd. for $C_{29}H_{28}O$ 392.2140; found 392.2142.

2,3-Bis(phenylethynyl)thiophene (3p): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.57–7.54 (m, 4 H), 7.35–7.33 (m, 6 H), 7.20 (d, J = 5.25 Hz, 1 H), 7.10 (d, J = 5.25 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 132.1, 131.9, 129.4, 129.1, 128.9, 128.8, 127.1, 126.7, 126.6, 123.6, 123.3, 98.0, 94.0, 84.4, 82.5 ppm. IR (film): $\tilde{\nu}$ = 3105, 3078, 2198, 1950, 1595, 1492, 1442, 1259, 1175 cm^{-1}. HRMS (EI): calcd. for $C_{20}H_{12}S$ 284.0660; found 284.0661.

3,4-Di(1-heptynyl)thiophene (3q): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.26 (s, 2 H), 2.42 (t, J = 7.08 Hz, 4 H), 1.65–1.58 (m, 4 H), 1.49–1.42 (m, 4 H), 1.40–1.31 (m, 4 H), 0.92 (t, J = 7.21 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 127.3, 126.0, 92.7, 74.9, 31.5, 28.9, 22.7, 19.9, 14.4 ppm. IR (film): $\tilde{\nu}$ = 3477, 3106, 2956, 2857, 2233, 1465, 1260, 1173, 1036 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{24}S$ 272.1599; found 272.1598.

5,5′-Bis(5-chloro-1-pentynyl)-2,2′-bithiophenyl (3r): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.00 (d, J = 3.38 Hz, 2 H), 6.96 (d, J = 3.88 Hz, 2 H), 3.68 (t, J = 6.39 Hz, 4 H), 2.63 (t, J = 6.82 Hz, 4 H), 2.08–2.01 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 137.6, 132.6, 124.0, 123.2, 94.1, 75.0, 44.1, 31.7, 17.7 ppm. IR (film): $\tilde{\nu}$ = 3071, 2958, 2221, 1605, 1512, 1440, 1284, 1037, 796 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{16}Cl_2S_2$ 366.0070; found 366.0073.

1,3,5-Tris(phenylethynyl)benzene (3s):[14f] White solid, m.p. 141–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.66 (s, 3 H), 7.55–7.53 (m, 6 H), 7.38–7.35 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 134.5, 132.1, 129.0, 128.8, 124.4, 123.2, 90.9, 88.2 ppm. IR (film): $\tilde{\nu}$ = 3476, 3078, 2211, 1598, 1581, 1489, 1260, 1173, 1036 cm^{-1}. HRMS (EI): calcd. for $C_{30}H_{18}$ 378.1409; found 378.1411.

1,2,4,5-Tetrakis(5-chloro-1-pentynyl)benzene (3t): (5-Chloropentynyl)lithium (4.0 mmol, 1.0–1.2 M in dry THF) was added to a solution of $InCl_3$ (221.2 mg, 1.0 mmol) in THF (1 mL) at –78 °C under nitrogen. After stirring the mixture for 30 min, the cooling bath was removed and the reaction mixture was warmed to room temperature over 30 min. The solution of tetrakis(5-chloropentynyl)indate (1.0 mmol, ca. 0.15 M in THF) was added to a mixture of [Pd(dppf)Cl_2] (16.3 mg, 4 mol-%) and 1,2,3,5-tetrabromobenzene (196.9 mg, 0.5 mmol) in THF (1 mL) under nitrogen. The reaction mixture was heated at reflux until consumption of the starting material (4 h). After cooling to room temperature, the reaction mixture was quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic phases were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane = 1:60) to give 1,2,4,5-tetrakis(5-chloro-1-pentynyl)benzene (173.0 mg, 72%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.40 (s, 2 H), 3.76 (t, J = 6.44 Hz, 8 H), 2.66 (t, J = 6.71 Hz, 8 H), 2.10–2.03 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 135.6, 125.5, 94.0, 80.1, 44.0, 31.7, 17.5 ppm. IR (film): $\tilde{\nu}$ = 2958, 2231, 1486, 1428, 1289, 1173, 902 cm^{-1}. HRMS (EI): calcd. for $C_{26}H_{26}Cl_4$ 478.0789; found 478.0788.

1-(3,3-Dimethyl-1-butynyl)-4-phenylethynylbenzene (3u): White solid, m.p. 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.53 (m, 2 H), 7.44 (d, J = 8.15 Hz, 2 H), 7.37–7.33 (m, 5 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 132.0, 131.9, 131.8, 128.8, 124.4, 123.6, 122.6, 101.0, 91.1, 89.6, 79.3, 31.4, 28.5 ppm. IR (film): $\tilde{\nu}$ = 3396, 2969, 2866, 2231, 1593, 1511, 1362, 1288, 915 cm^{-1}. HRMS (EI): calcd. for $C_{20}H_{18}$ 258.1409; found 258.1410.

2-[5-(5-Chloro-1-pentynyl)pyridin-2-ylethynyl]pyridine (3v): A solution of tetrakis(pyridin-2-ylethynyl)indate (0.15 mmol, ca. 0.15 M in THF) was added to a mixture of [Pd(dppf)Cl_2] (16.3 mg, 4 mol-%) and 2,5-dibromopyridine (118.4 mg, 0.5 mmol) in THF (1 mL) under nitrogen. After stirring for 1 h at 70 °C, a solution of tetrakis(5-chloro-1-pentynyl)indate (0.25 mmol, ca. 0.15 M in THF) was added. The reaction mixture was heated at reflux until consumption of the starting material (5 h). After cooling to room temperature, the reaction mixture was quenched with satd. aq. $NaHCO_3$. The aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic phases were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane = 1:2) to give 2-[5-(5-chloro-1-pentynyl)pyridin-2-ylethynyl]pyridine (98.3 mg, 70%). Brown solid, m.p. 44 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.65 (s, 1 H), 8.64 (d, J = 1.82 Hz, 1 H), 7.74–7.67 (m, 2 H), 7.62 (d, J = 7.88 Hz, 1 H), 7.55 (d, J = 8.04 Hz, 1 H), 7.31–7.27 (m, 1 H), 3.75 (t, J = 6.28 Hz, 2 H), 2.66 (t, J = 6.84 Hz, 2 H), 2.08 (quintet, J = 6.56 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.6, 150.2, 142.6, 140.8, 138.7, 136.3, 127.8, 127.0, 123.5, 120.4, 94.0, 89.3, 87.6, 78.2, 43.6, 31.1, 17.0 ppm. IR (film): $\tilde{\nu}$ = 3420, 3049, 2959, 2227, 1581, 1471, 1428, 778 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{13}ClN_2$ 280.0767; found 280.0770.

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