Synthesis of Methylene- and Methine-Bridged Oligopyridines

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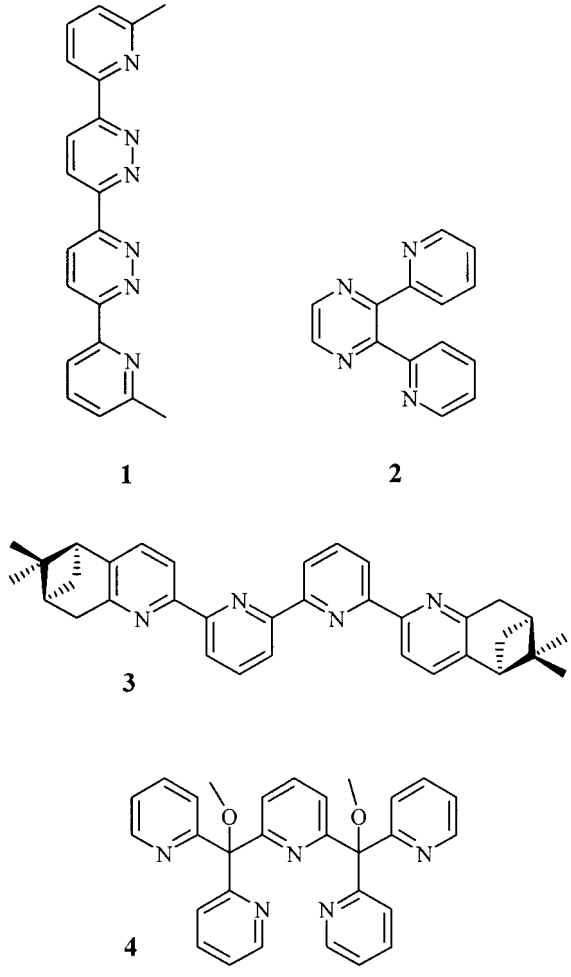
A variety of methylene- and methine-bridged oligopyridines are conveniently accessible through stepwise nucleophilic aromatic substitution with fluoro-substituted pyridines. The yields achieved are regularly above 90%.

Introduction

Oligo(azaheterocyclic) compounds are excellent ligands for building up large polymetallic complexes.[1] The structures **1**−**3** are rather rigid because of the direct connection of the hetarene units and have been used to study self-organization to gridlike complexes[2,3] and even to helicates.[4]

However, structural rigidity is not at all a prerequisite to a rich supramolecular chemistry with the formation of oligonuclear complexes featuring fascinating architectures. Far more flexible oligopyridines,[5] with the pyridine units linked by methylene groups or even longer alkanediyl chains, can also take part in such self-organization processes as Lehn et al.[6,7] impressively demonstrated with the synthesis of heteroduplex and circular helicates. Moreover, the structural diversity of these flexible oligopyridines also includes branched structures such as the pentadentate ligand **4**, which has been proven to form stable complexes with a variety of metal ions.[8] This ligand is capable of stabilizing Fe^{II} and Mn^{II} centers,[9] thus modeling intermediates in the oxygenation cycle with lipoxygenase[10,11] and promising the development of novel biomimetic catalysts. The simplest representative of this type of flexible oligopyridines, 2-(2-pyridylmethyl)pyridine (**11**), is commonly synthesized by nucleophilic aromatic substitution with lithiated 2-methylpyridine as nucleophile and either pyridine or 2-bromopyridine as electrophilic component.[12] Vedernikov et al. developed a synthesis for substituted 2,6-bis(2-pyridylmethyl)pyridine with 2,6-dimethylpyridine-dilithium as bis(nucleophile) and pyridine as electrophile.[13] According to our own results, nucleophilic substitutions of this type with pyridine as well as with 2-bromopyridine as reactants lead to rather impure crude products, which necessitate tedious separation procedures and result in at best moderate yields of the final products. In order to develop an improved general method for the synthesis of methylene- and methine-linked oligopy-



Scheme 1

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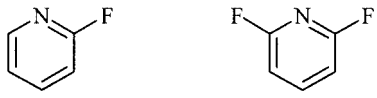
ridines, we tested 2-fluoropyridine (**5**) and 2,6-difluoropyridine (**6**) as reactants.



5 **6**

Results and Discussion

The methylene-linked bis(pyridine) **11** was synthesized in 96% yield by lithiation of 2-methylpyridine (**8**) in dry THF and addition of 0.5 equivalents of 2-fluoropyridine (**5**) as nucleophilic component. Using an excess of the lithiated 2-methylpyridine (**8**) is crucial, since the product **11** contains an acidic methylene unit, leading to the consumption of one equivalent of lithiated **8**. As a result, the negative charge of lithiated **11** is stabilized by the two conjugated pyridyl units,[14] and the formation of branched byproducts is somewhat suppressed.

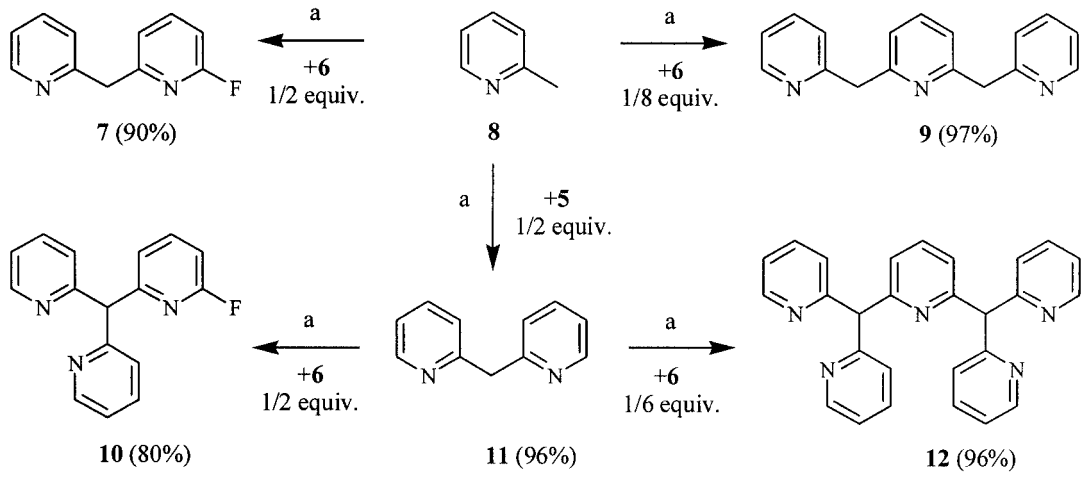
The synthesis of 2-fluoro-6-(2-pyridylmethyl)pyridine (**7**, 90% yield) starts from lithiated 2-methylpyridine (**8**) and 0.5 equivalents of 2,6-difluoropyridine (**6**). Again, excess nucleophile is necessary because of the consumption by product **7** (see above). To replace both the 2- and the 6-position of 2,6-difluoropyridine, it is necessary to use at least four equivalents (actually up to eight equivalents) of lithiated **8**, leading to an excellent yield of the tris(pyridine) product **9**.

After deprotonation with *n*-butyllithium, the methylene-linked bis(pyridine) **11** is a suitable nucleophile for the reaction with **6**, forming the monofluoro-functionalized tris(pyridine) compound **10**. For a double nucleophilic substitution at **6**, six equivalents of lithiated **11** have to be applied, again because of the increased acidity of the final product. In this case a remarkable yield of 96% of the pentakis(pyridine) compound **12** is obtained.

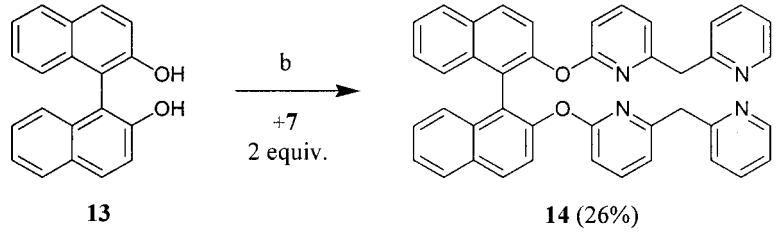
The versatility of fluoropyridines as building blocks in nucleophilic substitution reactions was further demonstrated by the successful synthesis of the chiral tetradentate ligand **14** from **7** and binaphthol **13**.

Conclusion

The family of methylene- and methine-bridged oligopyridines is efficiently accessible through stepwise nucleophilic aromatic substitution with 2-fluoropyridine (**5**) or 2,6-difluoropyridine (**6**) in yields of 90% and more. Especially bis- and tris-pyridine units with one remaining fluorine functionality, such as **7** and **10**, are valuable building blocks for further transformations. This straightforward entry to a broad variety of multidentate ligands is currently under investigation.



Scheme 2. a: 1. *n*BuLi, dry THF at −78 °C; 2. addition of **5** or **6** at −20 °C, then reflux



Scheme 3. b: KO*t*Bu, 18-crown-6, xylene, reflux, 3 days

Experimental Section

General Remarks: Melting points (uncorrected values) were determined with a Reichert Thermovar. Infrared spectroscopy was performed with a Perkin−Elmer 983 instrument. UV/Vis spectra were recorded with a Perkin−Elmer Lambda 40 apparatus. ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX 500 by use of $CDCl_3$ as solvent and TMS as the internal standard. Assignments of the NMR signals are based on CH COSY spectra and chemical shift considerations. Mass spectroscopy was performed with a Varian MAT 311A ITD (70 eV). For analytical TLC, POLYGRAM SIL G/UV254 precoated plastic sheets from Macherey−Nagel were used. Elemental analyses were performed with an Euro Elemental Analyzer 3000.

2-(2-Pyridylmethyl)pyridine (11): A solution of 2-methylpyridine (7.46 g, 80.0 mmol) in dry THF (80 mL) was cooled to −78 °C, and *n*-butyllithium (40 mL, 80.0 mmol, 2.0 M in pentane) was added within 15 min. The reaction mixture was stirred for 45 min at −78 °C and then warmed up to −20 °C. 2-Fluoropyridine (3.88 g, 40.0 mmol) was added within 5 min, and the reaction mixture was heated to reflux for 25 min and hydrolyzed with ice (75 g). The water layer was extracted three times with CH_2Cl_2 (50 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated, and the residue was distilled bulb-to-bulb (0.8 mbar, 150 °C). Yield: 6.51 g (38.2 mmol, 96%) of **11** as a slightly yellow oil. ^1H NMR (300.1 MHz, $CDCl_3$): δ = 4.34 (s, 2 H, *CH*$_2$), 7.12 (m, 2 H, 5/5′-H), 7.26 (d, *J* = 7.8 Hz, 2 H, 3/3′-H), 7.60 (td, *J* = 7.7, 1.9 Hz, 2 H, 4/4′-H), 8.55 (ddd, *J* = 4.9, 1.8, 0.8 Hz, 2 H, 6/6′-H) ppm.

2-Fluoro-6-(2-pyridylmethyl)pyridine (7): A solution of 2-methylpyridine (1.86 g, 20.0 mmol) in dry THF (20 mL) was cooled to −78 °C, and *n*-butyllithium (10 mL, 20.0 mmol, 2.0 M in pentane) was added within 5 min. The reaction mixture was stirred at −78 °C for 45 min and then warmed up to −20 °C. 2,6-Difluoropyridine (1.15 g, 10.0 mmol) was added within 5 min, and the reaction mixture was heated to reflux for 25 min and hydrolyzed with ice (20 g). The water layer was extracted three times with CH_2Cl_2 (25 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated, and the residue was distilled bulb-to-bulb (0.7 mbar, 150 °C). Yield: 1.70 g (9.0 mmol, 90%) of **7** as a slightly yellow oil. IR (film): $\tilde{\nu}$ = 3078 (w), 3014 (w), 2927 (w), 1607 (s), 1592 (s), 1577 (s), 1475 (s), 1435 (s), 1264 (s), 1226 (s), 1149 (m), 998 (s), 974 (m), 797 (s), 751 (s), 723 (m), 668 (w), 552 (w) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 204 (3.73), 262 (3.61), 268 (3.49, sh), 330 (1.72) nm. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 4.27 (s, 2 H, *CH*$_2$), 6.76 (ddd, *J* = 8.2, 2.8, 0.5 Hz, 1 H, 3-H), 7.14 (m, 2 H, 5/5′-H), 7.29 (dm, *J* = 7.8 Hz, 1 H, 3′-H), 7.62 (td, *J* = 7.7, 1.9 Hz, 1 H, 4′-H), 7.69 (m, 1 H, 4-H), 8.54 (ddd, *J* = 4.9, 1.8 , 0.9 Hz, 1 H, 6′-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 46.4 (t, *CH*$_2$), 107.0 (dd, $J_{C,F}$ = 36.9 Hz, C-3), 120.7 (dd, $J_{C,F}$ = 4.0 Hz, C-5), 121.7 (d, C-5′), 123.7 (d, C-3′), 136.6 (d, C-4′), 141.4 (dd, $J_{C,F}$ = 7.5 Hz, C-4), 149.4 (d, C-6′), 158.4 (d, $J_{C,F}$ = 13.0 Hz, C-6), 158.5 (s, C-2′), 163.0 (d, $J_{C,F}$ = 238.9 Hz, C-2) ppm. MS (EI, 70 eV): *m*/*z* (%) = 188 (29) [M^+], 187 (100), 186 (15). $C_{11}H_9FN_2$ (188.20): calcd. C 70.20, H 4.82, N 14.88; found C 70.26, H 4.87, N 15.01.

2,6-Bis(2-pyridylmethyl)pyridine (9): A solution of 2-methylpyridine (7.45 g, 80.0 mmol) in dry THF (40 mL) was cooled to −78 °C, and *n*-butyllithium (40 mL, 80.0 mmol, 2.0 M in pentane) was added within 15 min. The reaction mixture was stirred at −78 °C for 45 min and then warmed up to −20 °C. 2,6-Difluoropyridine (1.15 g, 10.0 mmol) was added within 15 min, and the reaction mixture was heated to reflux for 3 h. After cooling to room temperature overnight, water was added (25 mL), and after separation the water layer was extracted three times with CH_2Cl_2 (25 mL). The combined organic layers were dried with Na_2SO_4. The solvent was evaporated, and the residue was distilled bulb-to-bulb (0.5 mbar, 190 °C). Yield: 2.53 g (9.7 mmol, 97%) of **9** as a light yellow oil, which crystallizes after longer standing to give a slightly yellow solid, m.p. 46 °C. IR (KBr): $\tilde{\nu}$ = 3086 (w), 3057 (w), 2998 (m), 2962 (w), 2931 (w), 1589 (s), 1473 (s), 1459 (s), 1439 (s), 1328 (m), 1309 (w), 1211 (m), 1097 (w), 1052 (w), 997 (m), 793 (m), 767 (m), 756 (s), 608 (m), 586 (m), 573 (m) cm^{-1}. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 4.34 (s, 4 H, *CH*$_2$), 7.05 (d, *J* = 7.7 Hz, 2 H, 3/ 5-H), 7.10 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 2 H, 5′/5′′-H), 7.23 (dm, *J* = 7.8 Hz, 2 H, 3′/ 3′′-H), 7.49 (t, *J* = 7.6 Hz, 1 H, 4-H), 7.56 (dt, *J* = 7.7, 1.8 Hz, 2 H, 4′/ 4′′-H), 8.53 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 2 H, 6′/ 6′′-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 47.1 (t, *CH*$_2$), 121.1 (d, C-3/ 5), 121.3 (d, C-5′/ 5′′), 123.6 (d, C-3′/ 3′′), 136.3 (d, C-4′/4′′), 137.0 (d, C-4), 149.2 (d, C-6′/ 6′′), 158.9 (s), 159.5 (s) ppm. MS (EI): *m*/*z* (%) = 261 (43) [M^+], 260 (100), 183 (76), 169 (99), 168 (37), 129 (15), 123 (12), 106 (17), 93 (12), 79 (4), 78 (11). $C_{17}H_{15}N_3$ (261.33): calcd. C 78.13, H 5.79, N 16.08; found C 77.99, H 5.75, N 16.18.

2-Fluoro-6-[bis(2-pyridyl)methyl]pyridine (10): A solution of 2-(2-pyridylmethyl)pyridine (**11**) (1.70 g, 10.0 mmol) in dry THF (50 mL) was cooled to −78 °C, and *n*-butyllithium (5 mL, 10.0 mmol, 2.0 M in pentane) was added within 2 min. The reaction mixture was stirred at −78 °C for 30 min and then warmed up to −20 °C. 2,6-Difluoropyridine (0.58 g, 5.00 mmol) was added within 5 min, and the reaction mixture was heated to reflux for 25 min and hydrolyzed with ice (20 g). The water layer was extracted three times with CH_2Cl_2 (25 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was evaporated, and the residue was distilled bulb-to-bulb (0.5 mbar, 200 °C). Yield: 1.06 g (4.0 mmol, 80%) of **10** as a light orange sticky oil which crystallizes after longer standing to give a slightly yellow solid, m.p. 81 °C. IR (KBr): $\tilde{\nu}$ = 3049 (w), 3000 (w), 1603 (s), 1590 (s), 1469 (s), 1449 (s), 1273 (w), 1238 (m), 1221 (m), 1152 (w), 995 (m), 971 (w), 800 (m), 760 (s), 668 (m), 613 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 207 (4.08), 262 (3.98), 268 (3.89) nm. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 5.91 (s, 1 H, *CH*), 6.79 (ddd, *J* = 8.2, 2.9, 0.4 Hz, 1 H, 3-H), 7.15 (m, 2 H, 5′/5′′-H), 7.21 (dd, *J* = 7.4, 2.5 Hz, 1 H, 5-H), 7.33 (dm, *J* = 7.9 Hz, 2 H, 3′/3′′-H), 7.63 (td, *J* = 7.7, 1.9 Hz, 2 H, 4′/ 4′′-H), 7.72 (dt, *J* = 8.3, $J_{H,F}$ = 7.5 Hz, 1 H, 4-H), 8.57 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 2 H, 6′/6′′-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 63.3 (d, 1 H, *CH*), 107.5 (dd, $J_{C,F}$ = 36.9 Hz, C-3), 121.4 (dd, $J_{C,F}$ = 4.0 Hz, C-5), 121.9 (d, C-5′/5′′), 124.1 (d, C-3′/3′′), 136.6 (d, C-4′/4′′), 141.4 (dd, $J_{C,F}$ = 7.5 Hz, C-4), 149.5 (d, C-6′/6′′), 159.9 (d, $J_{C,F}$ = 13.0 Hz, C-6), 160.3 (s, C-2′/ 2′′), 162.9 (d, $J_{C,F}$ = 239.4 Hz, C-2) ppm. MS (EI, 70 eV): *m*/*z* (%) = 265 (68) [M^+], 264 (83), 187 (43), 186 (27), 170 (13), 169 (100), 168 (16), 78 (9). $C_{16}H_{12}FN_3$ (265.29): calcd. C 72.44, H 4.56, N 15.84; found C 72.08, H 4.63, N 15.97.

2,6-Bis[bis(2-pyridyl)methyl]pyridine (12): A solution of 2-(2-pyridylmethyl)pyridine (**11**) (1.02 g, 6.00 mmol) in dry THF (30 mL) was cooled to −78 °C, and *n*-butyllithium (3 mL, 6.0 mmol, 2.0 M in pentane) was added within 3 min. The reaction mixture was stirred at −78 °C for 30 min and then warmed up to −20 °C. 2,6-Difluoropyridine (115 mg, 1.00 mmol) was added within 5 min, and the reaction mixture was heated to reflux for 24 h and cooled to room temperature. Water (20 mL) was added, and after separation the water layer was extracted three times with CH_2Cl_2 (25 mL). The combined organic layers were dried with Na_2SO_4. The solvent was

removed, and the crude product was recrystallized from acetone. Yield: 400 mg (0.96 mmol, 96%) of **12** as slightly yellow crystals, m.p. 146 °C. IR (KBr): $\tilde{\nu}$ = 3046 (w), 3007 (w), 1585 (s), 1564 (s), 1465 (s), 1429 (s), 1328 (w), 1148 (m), 1088 (m), 1050 (m), 995 (m), 775 (m), 754 (s), 703 (w), 624 (m), 603 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 204 (4.91, sh), 207 (4.88, sh), 257 (4.60, sh), 263 (4.65), 269 (4.59, sh), 401 (2.23) nm. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 5.93 (s, 2 H, *CH*), 7.10 (m, 4 H, 5′/5′′/5′′′/5′′′′-H), 7.19 (m, 6 H, 3′/3′′/3′′′/3′′′′-H, 3/5-H), 7.50 (td, *J* = 7.8, 1.9 Hz, 4 H, 4′/ 4′′/ 4′′′/4′′′′-H), 7.58 (t, ^3J = 7.7 Hz, 1 H, 4-H), 8.53 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 4 H, 6′/6′′/6′′′/6′′′′-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 63.9 (d, *CH*), 121.5 (d, C-5′/5′′/5′′′/ 5′′′′), 122.1 (d, C-3/5), 124.1 (d, C-3′/ 3′′/ 3′′′/ 3′′′′), 136.1 (d, C-4′/ 4′′/ 4′′′/ 4′′′′), 137.2 (d, C-4), 149.1 (d, C-6′/ 6′′/ 6′′′/ 6′′′′), 160.2 (s, C-2/ 6), 161.4 (s, C-2′/ 2′′/ 2′′′/ 2′′′′) ppm. MS (EI, 70 eV): *m*/*z* (%) = 415 (67) [M^+], 414 (60), 337 (56), 258 (13), 247 (38), 246 (100), 169 (52), 168 (22). $C_{27}H_{21}N_5$ (415.50): calcd. C 78.05, H 5.09, N 16.86; found C 78.12, H 5.04, N 16.72.

2,2′-Bis[6-(2-pyridylmethyl)-2-pyridyloxy]-1,1′-binaphthalene (14): A solution of 1,1′-bi(2-naphthol) (**13**) (286 mg, 1.00 mmol), 18-crown-6 (530 mg, 2.00 mmol), and K-O*tBu* (225 mg, 2.00 mmol) in dry xylene (5 mL) under argon was stirred for 15 min. 2-Fluoro-6-(2-pyridylmethyl)pyridine (**7**) (376 mg, 2.00 mmol) was added, and the reaction mixture was heated at reflux for three days. After cooling to room temperature water (10 mL) was added, and the mixture was extracted three times with CH_2Cl_2 (25 mL). The combined organic layer was dried with Na_2SO_4. Evaporation of the solvent and flash chromatography (silica, ethyl acetate) yielded **14** (160 mg, 0.26 mmol, 26%) as a light brown glassy solid. R_f = 0.23 (silica, ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3056 (w), 3007 (w), 1590 (s), 1574 (s), 1508 (m), 1474 (m), 1443 (s), 1359 (w), 1258 (s), 1228 (s), 1147 (m), 1074 (w), 1002 (s), 821 (w), 798 (w), 755 (m) cm^{-1}. UV/Vis (CH_3CN): $\lambda_{max.}$ (lg ε) = 223 (4.41), 274 (3.87), 323 (2.90) nm. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.98 (”q”, *J* = 14.5 Hz, 4 H, CH_2), 6.34 (d, *J* = 8.1 Hz, 2 H, Py-5′′/5′′′-H), 6.70 (d, *J* = 7.4 Hz, Py-3′′/3′′′-H), 7.05−7.28 (m, 12 H, Ar/Py-H), 7.37 (tm, *J* = 7.5 Hz, 2 H), 7.44 (td, *J* = 7.7, 1.9 Hz, 2 H), 7.85 (m, 4 H, 4/4′/5/ 5′-H), 8.47 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 2 H, 6′′′′/6′′′′′-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 46.6 (t, CH_2), 108.7 (d, C-5′′/5′′′), 117.5 (d, C-3′′/3′′′), 121.4 (d), 121.8 (d), 123.4 (s), 124.0 (d), 124.9 (d), 126.2 (d), 126.5 (d), 127.7 (d), 129.1 (d), 130.9 (s), 134.1 (s), 136.3 (d), 139.2 (d), 149.1 (d), 150.3 (s), 157.4 (s), 159.2 (s), 163.1 (s) ppm. MS (EI, 70 eV): *m*/*z* (%) = 622 (15) [M^+], 437 (9), 213 (10), 186 (13), 169 (9), 155 (24), 127 (14), 100 (29), 79 (31). $C_{42}H_{30}N_4O_2$ (622.72): calcd. C 81.01, H 4.86, N 8.99; found C 80.76, H 4.74, N 9.12.

Acknowledgments

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