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Access to Functionalized Luminescent Multi-2,2′:6′,2″-terpyridine Ligands

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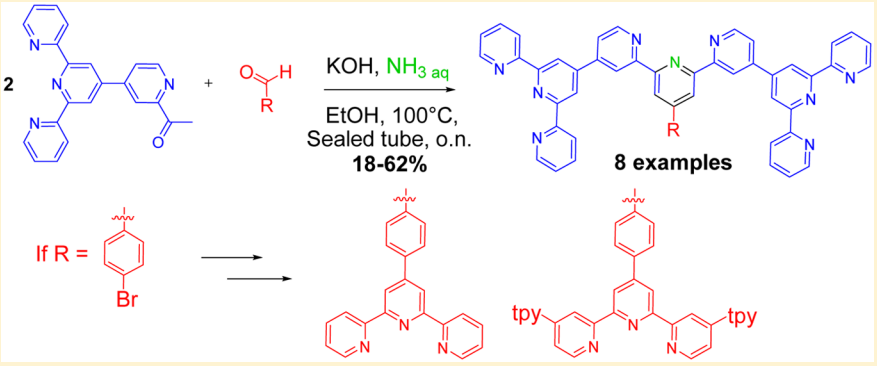
Supporting Information



ABSTRACT: A one-pot synthesis of substituted multi-2,2′:6′,2″-terpyridines (multi-tpy) has been achieved using an acetylquaterpyridine precursor with various aryl aldehydes in basic media. This strategy enables ready access to functionalized tri-terpyridines. Utilizing a Suzuki-type cross-coupling, larger structures such as tetra- or even hexa-tpy were obtained from our tri-tpy precursor. These macromolecular units are ideal building blocks for the construction of transition-metal-based supramolecular assemblies.

2,2′:6′,2″-Terpyridines (tpy) have become some of the most useful N/C-coordinating ligands for building transition-metal complexes. Indeed, interesting spectro-electrochemical, magnetic, and structural properties characterize the resulting assemblies, which can be useful in several fields of endeavor,[1] especially in supramolecular chemistry.[2] For example, supramolecular aggregates made up of metal−tpy subunits have been widely studied.[3−7] Tpy−polymer-based structures have also led to numerous applications ranging from polymer light-emitting diodes (PLED's)[8,9] to the development of advanced multiblock copolymers.[10,11] The increasing interest for tpy ligands originates from their reproducible syntheses and their ease of functionalization.[12] Numerous methods have been described and continuously improved, affording an increasing number of readily available derivatized tpy. More recently, multi-tpy-based ligands have been developed and used as luminescence sensors[13] and in self-assembled supramolecular systems (2D and 3D architectures).[13−17] Thus far, the multi-tpy systems have usually been obtained from thiol[13] or palladium cross-coupling strategies,[18−20] in which only a few functional groups were introduced.

Herein, we report an approach to overcome this issue based on a one-pot strategy using a common easily accessible precursor. Accordingly, novel tpy scaffolds bearing various substituents have been obtained and their spectroscopic properties studied. To demonstrate the strength and versatility of our synthetic approach, larger structures bearing four or six tpy units have been prepared with these new functionalized ligands. The structural and photophysical features of our new macromolecular units open doors to applications in different fields. For instance, they can be used as building blocks for the construction of transition metal-based supramolecular assemblies.

Usually, the tpy motif is obtained through a one-pot Kröhnke synthesis, in which key intermediates are required. In our case, a key precursor (**5**) for the synthesis of multi-tpy has been synthesized in five steps (Scheme 1), starting from methyl 2-acetylisonicotinate **1**. The acetal derivative **2** is then reduced by sodium borohydride in refluxing EtOH to yield the corresponding alcohol **3**. Aldehyde **4** was obtained upon treatment of **3** using a Swern oxidation. The synthesis of the key intermediate tpy **5** was adapted from a procedure developed by Schubert et al.[21] leading to the acetal−tpy **4′** followed by an aqueous acidic treatment. It is worth mentioning that this strategy was easily applied to multigram scales.

Our one-pot strategy toward functionalized luminescent multi-tpy is presented in Scheme 2. Acetylpyridine **5** reacts with aromatic aldehydes in the presence of potassium hydroxide through a Claisen-Schmidt aldol condensation and subsequent 1,4-Michael addition. The central pyridine ring is obtained from

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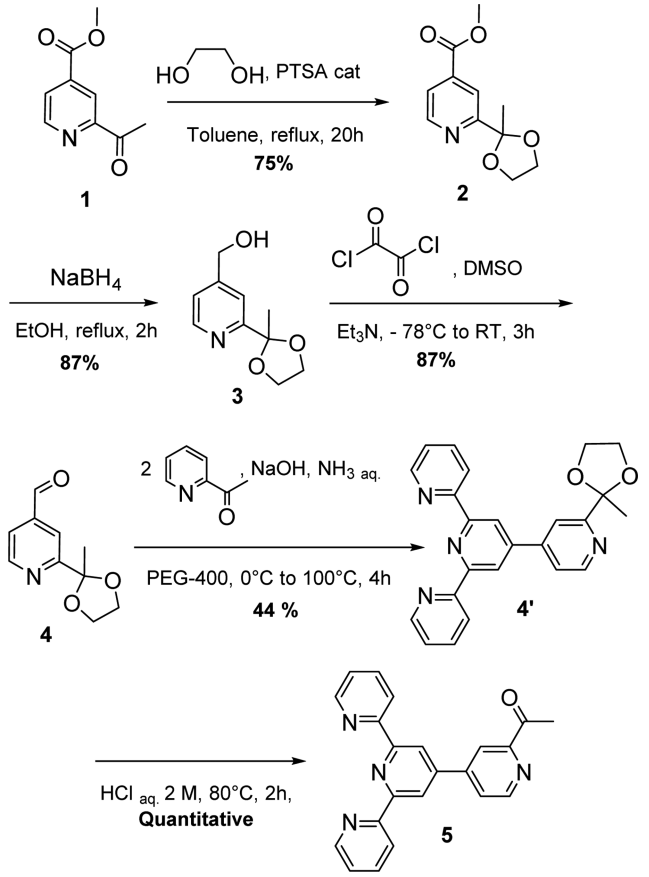
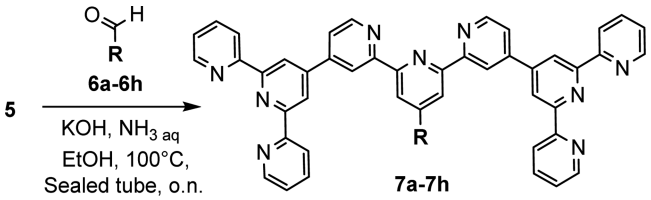
Scheme 1. Synthetic Route Followed to Yield the Intermediate 5



Scheme 2. One-Pot Synthesis of Tri-tpy



the reaction of the 1,5-dione intermediate with concentrated aqueous ammonia in a sealed tube at 100 °C in EtOH. Upon reflux at atmospheric pressure, only very low conversion was observed. The reaction also works in MeOH despite lower quantities of pure products being recovered. Typically, after 10 min of reaction, complete dissolution of tpy **5** was observed. The tri-tpy derivatives **7a−h** smoothly precipitated from the reaction mixture and were easily recovered by filtration. For purification, the crude product was suspended in large amount of EtOH, sonicated, and heated at reflux and then filtrated or purified by column chromatography depending on the nature of the substituent.

Thanks to the versatility of our synthetic approach, different substituted aromatic aldehydes (**6a−h**) can be used for the synthesis of multi-tpy (Table 1). The various pendant functional groups on the central pyridine core show the ease of structural modification and renders our method advantageous and competitive compared to multi-tpy-based strategies, which usually rely on metal-promoted cross-coupling or thiol chemistry.[18−20] It is worth mentioning that aldehydes bearing electron-rich groups (e.g., **6e,g,h**, Table 1) lead to better yields, although the reason for these results remains unclear with respect to the mechanism of the reaction. Interestingly, the solubility of the novel tri-tpy was strongly modulated by the nature of the functional groups, ranging from poorly soluble for **7a−c** (typically saturated in the 1 mmol L^{-1} range in CH_2Cl_2) to moderately soluble for **7d−i** (typically saturated in the 10 mmol L^{-1} range in CH_2Cl_2). Strikingly, a completely insoluble product was obtained when 4-carboxaldehyde pyridine was used as an aromatic aldehyde (**7j**, Table 1).

In order to gain insight into the spectroscopic behavior of our tri-tpy, their absorption and emission properties were examined. All of the compounds exhibit broad absorption bands below ca. 350 nm with a maximum close to 250 nm (ε between 50000 and 100000 M^{-1} cm^{-1}) (see Figure S1 and Table 1). These bands are attributed to $^1\pi-\pi^*$ transitions as observed for monotpy chromophores.[22] Moreover, each tri-tpy emits in CH_2Cl_2 at room temperature in air (Φ_{em} values between 0.05 and 0.27). The emission maximum is close to 370 nm except for **7d** which emits at a longer wavelength maximum ($\lambda_{max\ em}$ = 404 nm). Such a red-shifted emission has previously been reported in the literature for 4′-(4-(methylthio)phenyl)-2,2′;6′,2″-terpyridine[13] indicating that the methylthio group clearly induces a reduction in the HOMO−LUMO gap.

Based on these functionalized tri-tpy, a wide variety of multi-tpy structures become readily available. Initially, the use of terephthalaldehyde (dialdehyde) to reach a "hexa-tpy" was explored. However, a mixture of intermediates precipitated prior to completion of the reaction. As a result, another strategy relying on coupling reactions was investigated and turned out to be more successful. The Suzuki coupling was chosen due to the ease of preparation of organoboron derivatives, its usual relatively high stability, and the low toxicity of byproducts.[24] Homocoupling[17] of **7c** was achieved in good yield via a one-pot tandem Miyaura boronic ester formation and subsequent Suzuki coupling (Scheme 3). The resulting luminescent ($\lambda_{max\ em}$ = 484 nm, Φ_{em} = 0.07 in CH_2Cl_2 under air)[25] hexa-tpy product **8** possesses a unique structure. However, its poor solubility prevents its ease of use. To tackle this issue, the tetra-tpy **9** was also synthesized by a Suzuki coupling[26] between the brominated ligand **7c** and the readily available 4′-boronatophenyl-2,2′:6′,2″-terpyridine[27] with good yield (Scheme 4). Alternatively, the boronate ester **7i** was prepared upon treatment of **7c** with the commercially available bis(neopentylglycolato)diboron. Suzuki coupling of **7i** with 4′-(bromophenyl)-2,2′:6′,2″-terpyridine[28] also gave the product **9** ($\lambda_{max\ em}$ = 383 nm, Φ_{em} = 0.29 in CH_2Cl_2 under air) showing the versatility of our new synthetic protocol. As expected, this product exhibits relatively high solubility compared to the hexa-tpy **8**.

In conclusion, this paper demonstrates our efforts in expanding the classical terpyridine synthetic scheme in order to build novel multi-tpy ligands. The functionalization of these scaffolds was successfully achieved by selection of the desired aldehydes. We took advantage of this versatility to synthesize tetra- and hexa-tpy by utilizing the Suzuki−Miyaura coupling. As a result, the design and synthesis of supramolecular assemblies such as metallo-supramolecular polymers has become feasible using our synthetic methodology.

EXPERIMENTAL SECTION

Methyl 2-(2-Methyl-1,3-dioxolan-2-yl)isonicotinate (2). Ethylene glycol (0.56 mL, 10.08 mmol, 1.5 equiv) and PTSA (0.030 g,

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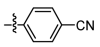
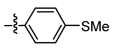
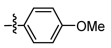
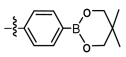
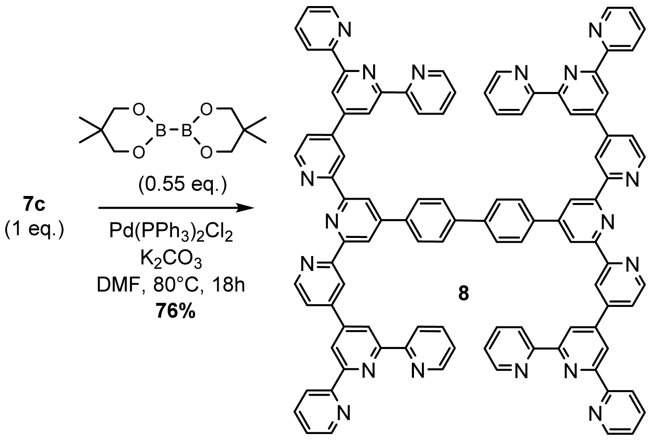
Table 1. Functionalized Tri-tpy

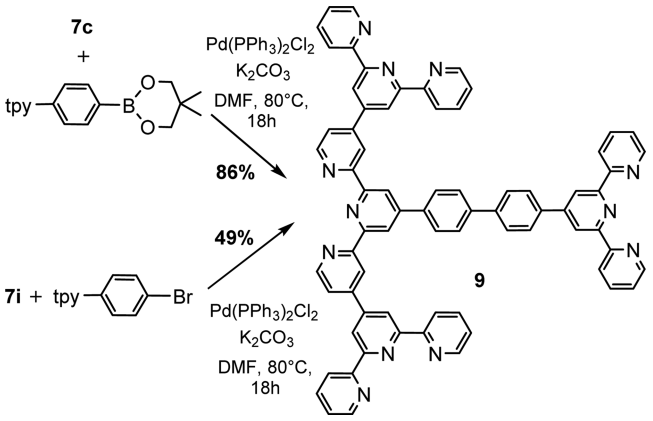
Entry	R	Yield (%)	$\lambda_{max\ abs}$ (nm - ε*10^{-3} M^{-1} cm^{-1})[a]	$\lambda_{max\ em}$ (nm)[a,b]	Φ_{em}[b]
7a		36	248 (93.6), 273 (sh, 65.4), 311 (sh, 30.6)	366	0.20
7b		18	249 (59.5), 270 (sh, 48.6), 314 (sh, 18.4)	365	0.17
7c		31	247 (75.8), 275 (sh, 59.5), 313 (sh, 26.0)	366	0.23
7d		62	241 (97.1), 282 (63.0), 295 (sh, 59.5), 310 (sh, 55.7)	404	0.05
7e		40	245 (89.4), 283 (69.7), 294 (sh, 65.0)	368	0.12
7f		25	243 (88.3), 278 (sh, 47.0), 313 (sh, 24.6)	366	0.14
7g		51	242 (90.4), 283 (54.1), 295 (sh, 49.5), 313 (sh, 35.6)	368	0.21
7h		52	250 (103.3), 269 (sh, 85.2), 294 (sh, 60.9), 315 (sh, 38.8)	374	0.27
7i[c]		68	-[d]	-[d]	-[d]
7j[e]		-[e]	-[e]	-[e]	-[e]

[a]Measured in CH_2Cl_2 at rt. [b]Quantum yield was measured under air using quinine sulfate as reference Φ_{ref} = 0.546 in aqueous 0.5 M H_2SO_4,[23] λ_{Exc} = 250 nm, 293 K. [c]**7i** was obtained upon treatment of **7c** with bis(neopentylglycolato)diboron. [d]Spectroscopic properties were not measured due to difficulties in the purification of **7i**. [e]The compound **7j** was totally insoluble in the common organic solvent; hence, no spectroscopic data could be measured.

Scheme 3. Synthetic Scheme for the Hexa-tpy



Scheme 4. Synthetic Scheme for the Tetra-tpy



0.17 mmol, 0.03 equiv) were added to methyl 2-acetylisonicotinate (**1**) (1.200 g, 6.72 mmol, 1 equiv) in anhydrous toluene (25 mL). The mixture was refluxed for 20 h with a Dean−Stark trap. A 0.05 M NaOH solution (20 mL) was added, and the aqueous layer was extracted with AcOEt (3 × 25 mL). The organic layers were combined and dried over $MgSO_4$ and solvents removed. The brown residue was purified by column chromatography on SiO_2 (eluent: cyclohexane/ethyl acetate (2/1)) to give a white powder with 75% yield (1.120 g). The ^{1}H NMR spectrum agreed with that found in the literature.[29] Mp: 61−64 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm), 8.80 (dd, 1H, J = 5.0 Hz, 0.7 Hz), 8.10 (dd, 1H, J = 1.5 Hz, 0.6 Hz), 7.78 (dd, 1H, J =

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5.0 Hz, 1.6 Hz), 4.12 (m, 2H), 3.97 (s, 3H), 3.90 (m, 2H), 1.75 (s, 3H). MS (APCI) m/z: 224.2 $[M + H]^+$.

(2-(2-Methyl-1,3-dioxolan-2-yl)pyridin-4-yl)methanol (3). Ester **2** (1.120 g, 5.02 mmol, 1 equiv) was stirred in EtOH (50 mL) until the solid dissolved. $NaBH_4$ (570 mg, 15.05 mmol, 3 equiv) was added, and the mixture was refluxed for 2 h. The reaction was quenched with water (20 mL) and EtOH removed under vacuum. The aqueous layer was extracted with CH_2Cl_2 (4 × 25 mL). The organic layers were combined and dried over $MgSO_4$, and solvent was removed. A colorless oil was obtained with 87% yield (920 mg). The ^1H NMR spectrum agreed with that found in literature.[30] ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm), 8.60 (d, 1H, J = 5.0 Hz), 7.56 (s, 1H), 7.25 (d, 1H, J = 4.9 Hz), 5.30 (s, 1H), 4.78 (s, 2H), 4.10 (m, 2H), 3.88 (m, 2H), 1.73 (s, 3H).

2-(2-Methyl-1,3-dioxolan-2-yl)isonicotinaldehyde (4). DMSO (0.87 mL, 12.20 mmol, 2.4 equiv) was added to oxalyl chloride (0.87 mL, 10.20 mmol, 2 equiv) in anhydrous CH_2Cl_2 (30 mL) at −78 °C. Alcohol **3** (1.0 g, 5.10 mmol, 1 equiv) dissolved in anhydrous CH_2Cl_2 (6 mL) was added, and the mixture was allowed to react for 45 min at −78 °C until a white salt was obtained. Et_3N (3.55 mL, 25.50 mmol, 5 equiv) was added and the reaction warmed to room temperature over 1 h 30 min. CH_2Cl_2 (50 mL) was added and the mixture washed with brine (50 mL) and water (2 × 50 mL). The organic phase was dried over $MgSO_4$ and the solvent removed under vacuum. The crude product was purified by flash chromatography on SiO_2 (cyclohexane/AcOEt (1/1)) to afford colorless oil with 87% yield (860 mg). ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm), 10.10 (s, 1H, H_g), 8.90 (d, 1H, H_a, J_{Ha-Hb} = 4.8 Hz), 7.97 (dd, 1H, H_c, J_{Hc-Hb} = 1.4 Hz, J_{Hc-Ha} = 1.0 Hz), 7.65 (dd, 1H, H_b, J_{Hb-Hc} = 4.9 Hz, J_{Hb-Ha} = 1.5 Hz), 4.14 (m, 2H, H_e), 3.91 (m, 2H, H_f), 1.96 (s, 3H, H_d). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm), 191.7, 163.4, 151.1, 142.4, 121.5, 118.5, 108.4, 77.4, 65.3, 25.5. HRMS (APCI): m/z calcd for $[C_{10}H_{12}NO_3 + H]^+$ 194.0812, found 194.0813.

4′-(2-(2-Methyl-1,3-dioxolan-2-yl)pyridin-4-yl)-2′,2′:6′,2″-terpyridine (4′). Acetal-pytpy **4′** was prepared using an adapted literature procedure.[21] 2-Acetylpyridine (2.133 g, 1.975 mL, 17.6 mmol, 2 equiv) was added to a stirred suspension of NaOH (0.704 g, 17.6 mmol, 2 equiv) in PEG-400 (10 mL) at 0 °C. After 5 min, aldehyde **4** (1.700 g, 8.8 mmol, 1 equiv) was added, and the reaction mixture was kept at 0 °C for 2 h. Then a concentrated solution of NH_3 aq (10 mL) was added, and the suspension was heated at 100 °C for 15 min. During this period, product formed as an off-white precipitate. The product was filtrated, washed with H_2O (200 mL), and recrystallized from EtOH to yield pure product (1.533 g, 44%). Mp: 177−180 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm), 8.79 (dd, 1H, H_a, J_{Ha-Hb} = 5.1 Hz, J_{Ha-Hc} = 0.7 Hz), 8.78 (s, 2H, $H_{3'}$ and $H_{5'}$), 8.75 (ddd, 2H, H_6, J_{H6-H5} = 4.8 Hz, J_{H6-H4} = 1.7 Hz, J_{H6-H3} = 0.7 Hz), 8.69 (dd, 2H, H_3, J_{H3-H4} = 8.0 Hz, J_{H3-H5} = 1.0 Hz), 8.04 (dd, 1H, H_c, J_{Hc-Hb} = 1.7 Hz, J_{Hc-Ha} = 0.7 Hz), 7.91 (td, 2H, H_4, $J_{H4-H3(H5)}$ = 7.8 Hz, J_{H4-H6} = 1.8 Hz), 7.73 (dd, 1H, H_b, J_{Hb-Ha} = 5.0 Hz, J_{Hb-Hc} = 1.8 Hz), 7.39 (ddd, 2H, H_5, J_{H5-H4} = 7.5 Hz, J_{H5-H6} = 4.8 Hz, J_{H5-H3} = 1.1 Hz), 4.15 (m, 2H, H_f), 3.95 (m, 2H, H_e), 1.81 (s, 3H, H_d). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm), 162.2, 156.5, 155.8, 150.4, 149.3, 148.0, 146.9, 137.2, 124.3, 121.6, 121.2, 119.0, 117.6, 108.8, 65.2, 25.8. HRMS (APCI): m/z calcd for $[C_{24}H_{20}N_4O_2 + H]^+$ 397.1659, found 397.1658.

1-(6′-(2-Pyridin-2-yl)[2,2′:6′,2″-terpyridin]-2″-yl]ethan-1-one (5). Acetal-pytpy **4′** (1.000 g, 2.55 mmol, 1 equiv) was dissolved in HCl_{aq} 2 M (5 mL), and the mixture was heated at 80 °C for 2 h. After the mixture was cooled, saturated $NaHCO_{3aq}$ was added to neutralize the reaction. The aqueous layer was extracted with CH_2Cl_2 (three times). The organic layers were combined and dried over $MgSO_4$, and solvent was removed to give a white powder with a quantitative yield (890 mg). Mp: 187−190 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm), 8.82 (dd, 1H, H_a, J_{Ha-Hb} = 5.1 Hz, J_{Ha-Hc} = 0.7 Hz), 8.80 (s, 2H, $H_{3'}$ and $H_{5'}$), 8.73 (ddd, 2H, H_6, J_{H6-H5} = 4.8 Hz, J_{H6-H4} = 1.7 Hz, J_{H6-H3} = 0.8 Hz), 8.66 (dd, 2H, H_3, J_{H3-H4} = 8.0 Hz, J_{H3-H5} = 1.0 Hz), 8.55 (dd, 1H, H_c, J_{Hc-Hb} = 1.8 Hz, J_{Hc-Ha} = 0.7 Hz), 7.97 (dd, 1H, H_b, J_{Hb-Ha} = 5.1 Hz, J_{Hb-Hc} = 1.8 Hz), 7.89 (td, 2H, H_4, $J_{H4-H3(H5)}$ = 7.8 Hz, J_{H4-H6} = 1.8 Hz), 7.38 (ddd, 2H, H_5, J_{H5-H4} = 7.5 Hz, J_{H5-H6} = 4.8 Hz, J_{H5-H3} = 1.2 Hz), 2.80 (s, 3H, H_d). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm), 200.1, 156.7, 155.7, 154.5, 150.0, 149.3, 147.3, 146.9, 137.1, 125.1, 124.3, 121.5, 119.8, 118.8, 26.2. IR (thin film): ν_{max} = 3053, 3011, 1697, 1583, 1566, 1537, 1468, 1410, 1389, 1352, 1283, 1267, 1248, 1213, 1124, 1092, 1072, 1041, 989, 964, 891, 845, 789, 733, 671, 660 cm^{-1}. HRMS (APCI): m/z calcd for $[C_{22}H_{17}N_4O + H]^+$ 353.1397, found 353.1396.

General Procedure for tri-tpy's 7a−h. Acetyl-pytpy **5** (200 mg, 0.568 mmol, 2 equiv) was added to a solution of the corresponding benzaldehyde **6a−c** (0.284 mmol, 1 equiv), potassium hydroxide (31.9 mg, 0.568 mmol), and aqueous ammonia (28%, 2 mL, 92.3 mmol) in absolute EtOH (10 mL). The mixture was heated for 18 h at 100 °C into a sealed tube. The off-white precipitate was filtered and washed with warm EtOH.

7a−c. A suspension of crude product was sonicated for 15 min in EtOH (100 mL) and the mixture refluxed and then filtered. This procedure was repeated three times. The resulting white powder was dried to afford the pure tri-tpy.

7d−h. The crude product was purified by chromatography column on neutral alumina with a CH_2Cl_2/MeOH (95/5) mixture as the eluent.

Compound 7a. Yield: 36% (80 mg). White powder. Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm), 9.18 (d, 2H, H_c, J_{Hc-Hb} = 1.0 Hz), 8.84 (s, 4H, $H_{3'}$ and $H_{5'}$), 8.81 (d, 2H, H_a, J_{Ha-Hb} = 5.0 Hz), 8.76 (s, 2H, H_d), 8.44 (d, 4H, H_3 and $H_{3''}$, J_{H3-H4} = 7.9 Hz), 8.37 (d, 4H, H_6 and $H_{6''}$, J_{H6-H5} = 4.7 Hz), 7.97 (dd, 2H, H_e, J_{He-Hf} = 8.5 Hz, J_{He-Hg} = 1.4 Hz), 7.80 (dd, 2H, H_b, J_{Hb-Ha} = 5.0 Hz,, J_{Hb-Hc} = 1.8 Hz), 7.74 (td, 4H, H_4 and $H_{4''}$, $J_{H4-H5(H3)}$ = 7.7 Hz, J_{H4-H6} = 1.8 Hz), 7.56 (t, 2H, H_f, $J_{Hf-He(Hg)}$ = 7.4 Hz), 7.50 (t, 1H, H_g, J_{Hg-Hf} = 7.3 Hz), 7.16 (ddd, 4H, H_5 and $H_{5''}$, J_{H5-H4} = 7.4 Hz, J_{H5-H6} = 4.7 Hz, J_{H5-H3} = 1.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm), 157.0, 156.1, 155.8, 155.7, 149.7, 149.0, 147.9, 147.0, 138.6, 137.6, 136.6, 129.1, 127.5, 123.8, 121.8, 121.0, 120.0, 119.4, 118.9. IR (thin film): ν_{max} = 1582, 1566, 1539, 1468, 1396, 1356, 1246, 1076, 1042, 988, 887, 839, 791, 735, 696 cm^{-1}. HRMS (APCI): m/z calcd for $[C_{51}H_{33}N_9 + H]^+$ 772.2932, found 772.2934.

Compound 7b. Yield: 18% (36 mg). White powder. Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm), 9.16 (d, 2H, H_c, J_{Hc-Hb} = 1.1 Hz), 8.78 (s, 4H, $H_{3'}$ and $H_{5'}$), 8.76 (d, 2H, H_a, J_{Ha-Hb} = 5.0 Hz), 8.68 (s, 2H, H_d), 8.41 (d, 4H, H_3 and $H_{3''}$, J_{H3-H4} = 7.9 Hz), 8.34 (d, 4H, H_6 and $H_{6''}$, J_{H6-H5} = 4.7 Hz), 8.01 (d, 2H, H_f, J_{Hf-He} = 8.4 Hz), 7.84 (d, 2H, H_e, J_{He-Hf} = 8.4 Hz), 7.76 (dd, 2H, H_b, J_{Hb-Ha} = 5.0 Hz,, J_{Hb-Hc} = 1.7 Hz), 7.71 (td, 4H, H_4 and $H_{4''}$, $J_{H4-H5(H3)}$ = 7.7 Hz, J_{H4-H6} = 1.7 Hz), 7.13 (ddd, 4H, H_5 and $H_{5''}$, J_{H5-H4} = 7.3 Hz, J_{H5-H6} = 4.7 Hz, J_{H5-H3} = 1.0 Hz). IR (thin film): ν_{max} = 2924, 2851, 2228, 1584, 1566, 1541, 1466, 1356, 1259, 1076, 1051, 1018, 837, 791, 733 cm^{-1}. HRMS (APCI): m/z calcd for $[C_{52}H_{32}N_{10} + H]^+$ 797.2884, found 797.2885. Note: compound **7b** was found to be too insoluble to record a carbon NMR.

Compound 7c. Yield: 31% (72 mg). White powder. Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 9.22 (d, 2H, H_c, J_{Hc-Hb} = 1.3 Hz), 8.87−8.84 (m, 6H, H_a, $H_{3'}$ and $H_{5'}$), 8.76 (s, 2H, H_d), 8.48 (d, 4H, H_3 and $H_{3''}$, J_{H3-H4} = 7.9 Hz), 8.38 (dd, 4H, H_6 and $H_{6''}$, J_{H6-H5} = 4.6 Hz, J_{H6-H4} = 0.7 Hz), 7.84 (d, 4H, H_b and H_e, J_{He-Hf} = 8.2 Hz), 7.76 (td, 4H and $H_{4''}$, H_4, $J_{H4-H5(H3)}$ = 7.7 Hz, J_{H4-H6} = 1.7 Hz), 7.69 (d, 2H, H_f, J_{Hf-He} = 8.5 Hz), 7.18 (ddd, 4H, H_5 and $H_{5''}$, J_{H5-H4} = 7.4 Hz, J_{H5-H6} = 4.7 Hz, J_{H5-H3} = 1.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm), 156.5, 156.0, 155.6, 155.5, 149.7, 148.9, 147.0, 145.7, 137.1, 136.5, 132.1, 128.9, 123.7, 121.9, 120.9, 119.9, 118.9, 118.8. IR (thin film): ν_{max} = 2928, 2843, 1582, 1566, 1541, 1466, 1394, 1354, 1259, 1074, 1038, 1018, 889, 791, 731 cm^{-1}. HRMS (APCI): m/z calcd for $[C_{51}H_{32}N_9{}^{79}Br + H]^+$ 850.2037, found 850.2034.

Compound 7d. Yield: 62% (142 mg). Clear yellow powder. Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.96 (d, 2H, H_c, J_{Hc-Hb} = 0.8 Hz), 8.62 (s, 4H, $H_{3'}$ and $H_{5'}$), 8.58 (d, 2H, H_a, J_{Ha-Hb} = 4.9 Hz), 8.49 (s, 2H, H_d), 8.25 (d, 4H, H_6 and $H_{6''}$, J_{H6-H5} = 4.1 Hz), 8.22 (d, 4H, H_3 and $H_{3''}$, J_{H3-H4} = 7.9 Hz), 7.82 (d, 2H, H_e, J_{He-Hf} = 8.3 Hz), 7.58 (td, 4H and $H_{4''}$, H_4, $J_{H4-H5(H3)}$ = 7.8 Hz, J_{H4-H6} = 1.7 Hz), 7.57 (m, 2H, H_b), 7.39 (d, 2H, H_f, J_{Hf-He} = 8.3 Hz), 7.02 (ddd,

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4H, H_5 and $H_{5''}$, J_{H5-H4} = 7.4 Hz, J_{H5-H6} = 4.9 Hz, J_{H5-H3} = 0.7 Hz), 2.61 (s, 3H, H_g). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 156.8, 155.8, 155.6, 155.5, 149.4, 148.8, 147.7, 146.9, 140.1, 136.4, 135.0, 127.7, 126.6, 123.6, 121.7, 120.9, 120.0, 118.8, 118.6, 15.7. IR (thin film): ν_{max} = 3053, 2920, 2851, 1582, 1566, 1537, 1499, 1468, 1394, 1356, 1246, 1124, 1095, 1076, 1040, 988, 887, 839, 820, 791, 735, 669 cm^{-1}. HRMS (APCI): m/z calcd for $[C_{52}H_{35}{}^{32}S_1N_9 + H]^+$ 818.28089, found 818.28088.

Compound 7e. Yield: 40% (90 mg). White powder. Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 9.00 (s, 2H, H_c), 8.68 (s, 4H, $H_{3'}$ and $H_{5'}$), 8.63 (d, 2H, H_a, J_{Ha-Hb} = 4.9 Hz), 8.54 (s, 2H, H_d), 8.32−8.26 (m, 8H, H_3, $H_{3''}$, H_6 and $H_{6''}$), 7.88 (d, 2H, H_e, J_{He-Hf} = 8.6 Hz), 7.66−7.60 (m, 6H, H_b, H_4 and $H_{4''}$), 7.08−7.04 (m, 6H, H_f, H_5 and $H_{5''}$), 3.94 (s, 3H, H_g). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 160.6, 157.0, 155.9, 155.6, 155.5, 149.5, 149.3, 148.9, 147.8, 146.9, 136.5, 130.9, 128.7, 123.7, 121.7, 121.0, 120.0, 118.8, 118.6, 114.4, 55.6. IR (thin film): ν_{max} = 3053, 3013, 2955, 2922, 2853, 1609, 1582, 1566, 1539, 1516, 1468, 1396, 1356, 1292, 1263, 1252, 1180, 1116, 1076, 1040, 987, 887, 831, 791, 735, 704, 658 cm^{-1}. HRMS (APCI): m/z calcd for $[C_{52}H_{35}O_1N_9 + H]^+$ 802.30373, found 802.30366.

Compound 7f. Yield: 25% (60 mg). White powder. Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 9.08 (d, 2H, H_c, J_{Hc-Hb} = 0.9 Hz), 8.82 (dd, 1H, H_f, J_{Hf-He} = 5.0 Hz, J_{Hf-Hg} = 0.6 Hz), 8.74 (s, 4H, $H_{3'}$ and $H_{5'}$), 8.71 (d, 2H, H_a, J_{Ha-Hb} = 5.0 Hz), 8.65 (s, 2H, H_d), 8.35 (d, 4H, H_3 and $H_{3''}$, J_{H3-H4} = 7.9 Hz), 8.31 (dd, 4H, H_6 and $H_{6''}$, J_{H6-H5} = 4.5 Hz, J_{H6-H4} = 0.6 Hz), 8.08 (dd, 1H, H_g, J_{Hg-He} = 1.7 Hz, J_{Hg-Hf} = 0.6 Hz), 7.73−7.70 (m, 3H, H_e and H_b), 7.68 (td, 4H, H_4 and $H_{4''}$, $J_{H4-H5(H3)}$ = 7.7 Hz, J_{H4-H6} = 1.7 Hz), 7.11 (ddd, 4H, H_5 and $H_{5''}$, J_{H5-H4} = 7.4 Hz, J_{H5-H6} = 4.7 Hz, J_{H5-H3} = 1.0 Hz), 4.21 (m, 2H, H_j), 4.02 (m, 2H, H_i), 1.87 (s, 3H, H_h). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 162.6, 156.6, 156.4, 156.2, 155.8, 150.8, 149.9, 149.2, 147.9, 147.6, 147.3, 147.1, 136.8, 124.0, 122.3, 121.4, 121.2, 120.4, 119.4, 119.1, 117.8, 109.2, 65.6, 26.1. IR (thin film): ν_{max} = 3053, 2955, 2928, 1582, 1566, 1539, 1468, 1445, 1394, 1356, 1265, 1200, 1123, 1076, 1040, 988, 887, 839, 791, 735, 702, 669 cm^{-1}. HRMS (APCI): m/z calcd for $[C_{54}H_{38}O_2N_{10} + H]^+$ 859.32520, found 859.32518.

Compound 7g. Yield: 51% (104 mg). White powder. Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 9.20 (d, 2H, H_c, J_{Hc-Hb} = 0.7 Hz), 8.87−8.84 (s, 4H, $H_{3'}$ and $H_{5'}$), 8.75 (s, 2H, H_a, J_{Ha-Hb} = 4.9 Hz), 8.66 (s, 2H, H_d), 8.48 (d, 4H, H_3 and $H_{3''}$, J_{H3-H4} = 7.9 Hz), 8.39 (dd, 4H, H_6 and $H_{6''}$, J_{H6-H5} = 4.5 Hz, J_{H6-H4} = 0.6 Hz), 8.09−8.06 (m, 1H, H_k), 7.99−7.95 (m, 2H, H_h and H_e), 7.80 (dd, 2H, H_b, J_{Hb-Ha} = 4.9 Hz, J_{Hb-Hc} = 1.7 Hz), 7.76 (td, 4H, H_4 and $H_{4''}$, $J_{H4-H5(H3)}$ = 7.7 Hz, J_{H4-H6} = 1.7 Hz), 7.67 (dd, 1H, H_g, J_{Hg-Hf} = 7.0 Hz, J_{Hg-He} = 1.2 Hz), 7.61 (dd, 1H, H_f, J_{Hf-He} = 7.1 Hz, J_{Hf-Hg} = 7.0 Hz), 7.63−7.58 (m, 2H, H_i and H_j), 7.17 (ddd, 4H, H_5 and $H_{5''}$, J_{H5-H4} = 7.4 Hz, J_{H5-H6} = 4.7 Hz, J_{H5-H3} = 1.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 157.1, 156.3, 155.8, 155.6, 150.0, 149.1, 148.0, 147.1, 136.8, 133.9, 133.6, 131.2, 128.9, 128.6, 127.7, 127.3, 126.8, 126.2, 125.8, 125.5, 123.9, 123.0, 122.0, 121.1, 120.0, 119.0. IR (thin film): ν_{max} = 3053, 3008, 2955, 2922, 2853, 1584, 1566, 1539, 1468, 1396, 1356, 1263, 1122, 1074, 1041, 988, 889, 839, 791, 777, 739 cm^{-1}. HRMS (APCI): m/z calcd for $[C_{55}H_{35}N_9 + H]^+$ 822.3088, found 822.3082.

Compound 7h. Yield: 52% (122 mg). Off-white powder. Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 9.01 (s, 2H, H_c), 8.66 (s, 4H, $H_{3'}$ and $H_{5'}$), 8.63 (s, 2H, H_d), 8.61 (d, 2H, H_a, J_{Ha-Hb} = 4.9 Hz), 8.36 (d, 1H, H_k, J_{Hk-He} = 1.0 Hz), 8.27−8.23 (m, 8H, H_3, $H_{3''}$, H_6 and $H_{6''}$), 8.02−7.90 (m, 4H, H_e, H_f, H_g and H_j) 7.60−7.56 (m, 4H, H_b, H_h and H_i), 7.58 (td, 4H and $H_{4''}$, H_4, $J_{H4-H5(H3)}$ = 7.6 Hz, J_{H4-H6} = 1.5 Hz), 7.02 (dd, 4H, H_5 and $H_{5''}$, J_{H5-H4} = 7.1 Hz, J_{H5-H6} = 4.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 157.1, 156.1, 155.9, 155.7, 149.8, 149.0, 147.8, 147.1, 136.6, 135.8, 133.7, 133.7, 128.9, 128.8, 127.9, 126.9, 126.8, 126.7, 125.2, 123.8, 121.9, 121.0, 120.1, 119.5, 118.9. IR (thin film): ν_{max} = 3030, 1582, 1566, 1539, 1468, 1396, 1367, 1340, 1263, 1122, 1074, 1040, 988, 887, 856, 791, 746, 737, 704, 652 cm^{-1}. HRMS (APCI): m/z calcd for $[C_{55}H_{35}N_9 + H]^+$ 822.3088, found 822.3087.

4‴-(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)-6′,6⁗-di(pyridin2-yl)-2,2′:4′,4″:2‴,2⁗:6″,2‴′:4⁗,4⁗′:2‴″,2⁗″-sepipyridine (7i). A Schlenk tube was charged with $Pd(dppf)Cl_2$ (3.4 mg, 0.0042 mmol, 0.05 equiv), KOAc (24.6 mg, 0.251 mmol, 3 equiv), **7c** (74.0 mg, 0.084 mmol, 1 equiv), and bis(neopentylglycolato)diboron (28.4 mg, 0.126 mmol, 1.5 equiv) and flushed with argon. Anhydrous DMF (8 mL) was added, and the reaction mixture was degassed by five freeze−pump−thaw cycles. The mixture was heated for 6 h at 80 °C under argon. The DMF was evaporated. The crude mixture was dissolved with dichloromethane (250 mL) and filtered over Celite. The resulting solution was washed five times with deionized water (100 mL). The dichloromethane was removed by evaporation to give an off-white product with 68% yield (50 mg). Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm), 9.17 (d, 2H, H_c, J_{Hc-Hb} = 1.4 Hz), 8.84−8.79 (m, 8H, H_a, H_f, $H_{3'}$and $H_{5'}$), 8.76 (s, 2H, H_d), 8.44 (d, 4H, H_3 and $H_{3''}$, J_{H3-H4} = 7.9 Hz), 8.36 (d, 4H, H_6 and $H_{6''}$, J_{H6-H5} = 4.9 Hz), 7.97 (d, 2H, H_e, J_{He-Hf} = 1.8 Hz), 7.79 (dd, 2H, H_b, J_{Hb-Ha} = 5.0 Hz, J_{Hb-Hc} = 1.4 Hz), 7.74 (td, 4H, H_4 and $H_{4''}$, $J_{H4-H3(H5)}$ = 7.7 Hz, J_{H4-H6} = 1.7 Hz), 7.16 (ddd, 4H, H_5 and $H_{5''}$, J_{H5-H4} = 7.7 Hz, J_{H5-H6} = 5.0 Hz, J_{H5-H3} = 1.1 Hz), 3.84 (s, 4H, H_g), 1.08 (s, 6H, H_f). ^{13}C NMR (125 MHz, CD_2Cl_2): δ (ppm), 156.0, 155.5, 155.3, 154.9, 148.9, 148.5, 147.8, 146.6, 136.2, 134.4, 126.1, 123.4, 121.4, 120.6, 119.8, 118.5, 72.6, 31.9, 21.7. IR (thin film): ν_{max} = 2964, 2928, 1584, 1566, 1541, 1468, 1420, 1394, 1356, 1315, 1308, 1261, 1132, 1076, 1040, 1020, 987, 908, 837, 791, 735 cm^{-1}. HRMS (ESI): m/z calcd for $[C_{56}H_{44}O_2N_9{}^{11}B + H]^+$ 884.3627, found 884.3634.

4,4′-Bis(6′,6‴″-di(pyridin-2-yl)-[2,2′:4′,4″:2‴,2⁗:6‴,2‴′:-4‴′,4⁗′:2‴″,2⁗″-sepipyridin]4‴-yl)-1,1′-biphenyl (8). A Schlenk tube was charged with $Pd(PPh_3)_2Cl_2$ (3.0 mg, 0.0042 mmol, 0.05 equiv), K_2CO_3 (35.2 mg, 0.254 mmol, 3 equiv), **7c** (75.0 mg, 0.085 mmol, 1 equiv), and bis(neopentylglycolato)diboron (10.5 mg, 0.046 mmol, 0.55 equiv) and flushed with argon. DMF (10 mL) was added, and the reaction mixture was degassed by five freeze−pump−thaw cycles. The mixture was heated for 18 h at 80 °C under argon. The reaction mixture was centrifuged, and the resulting solid was washed with water, ethanol, and chloroform. An off-white powder was obtained with 76% yield (32.6 mg). Mp: >280 °C. ^1H NMR ($CDCl_3$/$(CF_3)_2CHOH$:9/1, 500 MHz): δ (ppm), 8.83 (d, 4H, H_a, J_{Ha-Hb} = 5.4 Hz), 8.81 (s, 4H, H_c), 8.60 (d, 8H, H_6 and $H_{6''}$, J_{H6-H5} = 5.2 Hz), 8.53 (s, 8H, $H_{3'}$ and $H_{5'}$), 8.48 (s, 4H, H_d), 8.43 (d, 8H, H_3 an $H_{3''}$, J_{H3-H4} = 7.9 Hz), 8.07 (m, 16H, H_b, H_e or H_f, H_4 and $H_{4''}$), 7.90 (d, 4H, H_e or H_f, J_{He-Hf} = 8.3 Hz), 7.59 (dd, 4H, H_5 an $H_{5''}$, J_{H5-H6} = 5.2 Hz, J_{H5-H4} = 7.9 Hz). IR (thin film): ν_{max} = 2959, 2920, 2905, 2851, 1584, 1568, 1558, 1541, 1521, 1506, 1472, 1456, 1418, 1396, 1362, 1339, 1261, 1096, 1078, 1040, 1020, 791, 773, 669, 656 cm^{-1}. HRMS (ESI): m/z calcd for $[C_{102}H_{64}N_{18} + H]^+$ 1541.5634, found 1542.5617. Note: compound **8** was found to be too insoluble to record a carbon NMR.

4‴-(4′-([2,2′:6′,2″-Terpyridin]-4′-yl)[1,1′-biphenyl]-4-yl)-6′,6⁗-di(pyridin-2-yl)-2,2′:4′,4″:2‴,2⁗:6‴,2‴′:4‴′,4⁗′:-2⁗″,2⁗‴-sepipyridine (9). (A) A Schlenk tube was charged with $Pd(PPh_3)_2Cl_2$ (3.1 mg, 0.0043 mmol, 0.05 equiv), K_2CO_3 (36.1 mg, 0.261 mmol, 3 equiv), **7c** (77.0 mg, 0.087 mmol, 1 equiv), and 4′-(boronatophenyl)-2,2′:6′,2″-terpyridine (55.0 mg, 0.131 mmol, 1.5 equiv) and flushed with argon. DMF (10 mL) was added, and the reaction mixture was degassed by five freeze−pump−thaw cycles. The mixture was heated for 18 h at 80 °C under argon. The DMF was removed by rotary evaporation. The crude mixture was washed successively with water and ethanol and centrifuged. An off-white powder was obtained with 86% yield (78 mg). Mp: >280 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm), 9.12 (s, 2H, $H_{c'}$), 8.80 (m, 10H, H_a, $H_{a'}$, $H_{e'}$, $H_{3'}$ and $H_{5'}$), 8.68 (d, 2H, $H_{d'}$, $J_{Hd'-Hc'}$ = 8.1 Hz), 8.36 (d, 4H, $H_{3'}$ and $H_{3''}$, J_{H3-H4} = 7.8 Hz), 8.33 (d, 4H, H_6 and $H_{6''}$, J_{H6-H5} = 4.7 Hz), 8.05 (dd, 4H, H_f and $H_{g'}$, J_{Hf-He} = 8.2 Hz, $J_{Hf-Hg'}$ = 1.8 Hz), 7.88 (td, 2H, $H_{c'}$, $J_{Hc'-Hb'(d')}$ = 7.7 Hz, $J_{Hc'-Ha'}$ = 1.6 Hz), 7.84 (d, 4H, H_e and $H_{f'}$, J_{He-Hf} = 8.3 Hz), 7.72 (dd, 2H, H_b, J_{Hb-Ha} = 5.1 Hz, $J_{Hb-Hc'}$ = 1.8 Hz), 7.68 (td, 4H, H_4 and $H_{4''}$, $J_{H4-H3(5)}$ = 7.8 Hz, J_{H4-H6} = 1.8 Hz), 7.36 (ddd, 2H, $H_{b'}$, $J_{Hb'-Hc'}$ = 7.7 Hz, $J_{Hb'-Ha'}$ = 4.6 Hz, $J_{Hb'-Hd'}$ = 1.2 Hz), 7.36 (ddd, 2H, $H_{b'}$, $J_{Hb'-Hc'}$ = 7.7 Hz, $J_{Hb'-Ha'}$ = 4.6 Hz, $J_{Hb'-Hd'}$ = 1.2 Hz), 7.10 (ddd, 4H, H_5 and $H_{5''}$, J_{H5-H4} = 7.8 Hz, $J_{H5-H6'}$ = 4.6 Hz, J_{H5-H3} = 1.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm), 157.3, 156.6, 156.4, 156.3, 156.1, 155.9, 150.0, 149.6, 149.2, 148.1, 147.3, 137.3, 136.8, 128.2, 128.0, 124.2, 124.0, 122.1, 121.8, 121.3, 120.3,

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119.4, 119.2, 119.1. IR (thin film): ν_{max} = 3055, 3005, 2922, 1584, 1566, 1539, 1506, 1466, 1394, 1356, 1265, 1123, 1074, 988, 885, 837, 818, 789, 764, 745, 733 cm^{-1}. HRMS (ESI): *m/z* calcd for $[C_{72}H_{46}N_{12} + H]^+$ 1079.4041, found 1079.4030.

(B) A Schlenk tube was charged with $Pd(PPh_3)_2Cl_2$ (2.0 mg, 0.0028 mmol, 0.05 equiv), K_2CO_3 (23.6 mg, 0.171 mmol, 3 equiv), **7i** (50.4 mg, 0.057 mmol, 1 equiv), and 4′-(bromophenyl)-2,2′:6′,2″-terpyridine (3320 mg, 0.085 mmol, 1.5 equiv) and flushed with argon. DMF (10 mL) was added, and the reaction mixture was degassed by five freeze−pump−thaw cycles. The mixture was heated for 18 h at 80 °C under argon. The DMF was removed by rotary evaporation. The crude mixture was washed successively with water and ethanol and centrifuged. An off-white powder was obtained with 49% yield (30 mg).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01897.

^1H and ^{13}C NMR and $^1H-^1H$ COSY NMR spectra; absorption and emission spectra of tri-tpy, tetra-tpy and hexa-tpy (PDF)

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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