Chapter 2

Synthesis and characterization of nitrogen donor ligands: 2,2’:6’,2”-terpyridines
2. Synthesis and characterization of nitrogen donor ligands: 2,2'6',2''-terpyridines

2.1 General

Oligopyridines have attracted special interest in coordination chemistry. Although 2,2'-bipyridine (bpy) has been announced to be “the most used ligand in coordination chemistry” [1], 2,2':6',2''-Terpyridine (tpy) also has a rich chemistry. Almost 70 years ago, Burstall and Morgan reported the first synthesis of 2,2':6',2''-Terpyridine [2,3]. 2,2':6',2''-Terpyridines are among the N-heterocycles which have very high binding affinity towards transition metal ions due to dπ-pπ* backbonding of the metal to the pyridine rings and the chelate effect. In this context, we have synthesized 2,2':6',2''-terpyridines and used for complexation with copper(II) metal ion.

2.1.1 Methods for the synthesis of terpyridines

The two general methodologies used in the synthesis of 2,2':6',2''-terpyridines involve either the synthesis of the central ring or the coupling of the three pyridine rings.

a) Cross-coupling methods: Early attempts for terpyridine synthesis using coupling procedures included either an Ullmann synthesis with 2-bromopyridine and 2,6-dibromopyridine with metallic copper or an oxidative route with pyridine and 2,2'-bipyridine with iodine leading to yield < 10% [3]. More recently, modern Pd-catalyzed Stille [4], Suzuki [5] and Negishi [6] cross-coupling reactions with good yield (50–90%) and simple procedures have contributed greatly to terpyridine synthesis.

b) Ring assembly methods: Terpyridines are prepared by variety of ring assembly approach; Kröhnke, Potts, Jameson, Adrian and Sauer methods. Constable and Ward suggest the route for terpyridine by forming triketone from
ethyl–2-picolinate and acetone, which on addition of NH₄OAc produced 4’-hydroxyterpyridine (enol tautomer of 4-terpyridone)[8]. This 4’-hydroxyterpyridine was subsequently functionalized with alkoxy groups, by an Sₘ₂-type nucleophilic substitution with primary alkyl bromides or converted to 4’-chloroterpyridine by reacting it with PCl₅/POCl₃.

Jameson and Guise reported an alternate synthetic route for terpyridine in 1991 [9]. They prepared N,N-dimethylaminoenone by the reaction of N,N-dimethylformamide dimethyl acetal with 2-acetylpyridine. Ketone was reacted with potassium enolate of 2-acetylpyridine to give the 1,5-diketone intermediate (not isolated) with loss of dimethylamine. Terpyridine was formed upon ring-closure of 1,5-diketone with NH₄OAc in a moderate overall yield (47%).

Adrian et al., reported a high yield (73–93%) synthesis of terpyridines in 1998 [10]. He synthesized 2,6-bis(N-cyclohexylacetimidoyl)pyridine by treating 2,6-diacetylpyridine with cyclohexylamine. Then, cyclization of Si-protected 3-bromopropylamines with the bisimine gave the tetrahydropyridines, which were reacted with N-chlorosuccinimide (NCS) in CCl₄ to afford the tetrachloro adducts and lastly treatment with NaOMe yielded the desired substituted terpyridines.

![Scheme 2.1.1](image)

**Scheme 2.1.1**: Synthesis of 4-aryl–2,2′:6′,2″-terpyridines by modified Kröhnke method

The methodology of condensation procedures leading to oligopyridines has been developed by F. Kröhnke [11]. The starting point of this reaction is the aldol condensation of 2-acetylpyridine (or a substituted derivatives) with an aldehyde in basic aqueous or alcoholic media to give an α,β-unsaturated ketone or enone. Michael addition of a suitable enolate then affords a 1,5-diketone. Ring closure with ammonium acetate results in the formation of a dihydropyridine which undergoes oxidation to the desired terpyridine (Scheme 2.1.1).
Symmetrical and unsymmetrical 2,2’:6’,2’”-terpyridines were prepared in moderate to good yields by this route, a major advantage.

2.2 Materials and methods

2–Acetylpyridine, pyridine-2-carbaldehyde, pyridine-3-carbaldehyde, 3-benzyloxybenzaldehyde, 4-benzyloxybenzaldehyde, 4-bromobenzaldehyde, 4-fluorobenzaldehyde, 4-methoxybenzaldehyde, 4-chlorobenzaldehyde, benzaldehyde, 4-methylbenzaldehyde, 3-chlorobenzaldehyde, 3-bromobenzaldehyde, thiophene-2-carbaldehyde (thc) and 9-anthraldehyde were purchased from Spectrochem (Mumbai, India). The elemental analysis (C, H and N) of the ligands were performed with a model 240 Perkin Elmer elemental analyzer. Infrared spectra were recorded on a FT–IR ABB Bomen MB 3000 spectrophotometer as KBr pellets in the range 4000–400 cm⁻¹. The ¹H and ¹³C NMR were recorded on a Bruker Avance (400 MHz).

2.3 Synthesis of ligands

2.3.1 4’–Substituted-2,2’:6’,2’”-terpyridines

2–Acetylpyridine (20.0 mmol) has been added to an ethanolic solution of various aldehydes (10.0 mmol in 70 mL EtOH). KOH pellets (26 mmol) and aqueous NH₃ (25%, 0.425 mol) have been added to the solution and has been stirred at room temperature for 8 hours. An off–white solid formed which has been collected by filtration, followed by washing with H₂O (3 × 10 mL) and EtOH (2 × 5 mL). Crystallization from CHCl₃–MeOH system gives a white crystalline solid. General synthesis of various 4’–substituted–2,2’:6’,2’”–terpyridines is shown in Scheme 2.3.1.

![Scheme 2.3.1: General synthesis of 4’–substituted–2,2’:6’,2’”–terpyridine](image-url)
Table 2.3.1 represents the various substituted aldehydes used for the synthesis of 4′-substituted-2,2′:6′,2′′-terpyridines via second route of modified Kröhnke method.

**Table 2.3.1:** Various substituted aldehyde used for the synthesis of terpyridines

<table>
<thead>
<tr>
<th>Aldehydes (R–CHO)</th>
<th>Resulting terpyridines</th>
</tr>
</thead>
<tbody>
<tr>
<td>4–Chlorobenzaldehyde</td>
<td>4–cptpy (L¹)</td>
</tr>
<tr>
<td>4–Bromobenzaldehyde</td>
<td>4–bptpy (L²)</td>
</tr>
<tr>
<td>4–Fluorobenzaldehyde</td>
<td>4–fptpy (L³)</td>
</tr>
<tr>
<td>4–Methylbenzaldehyde</td>
<td>4–ttpy (L⁴)</td>
</tr>
<tr>
<td>Pyridine–2–carbaldehyde</td>
<td>2′′′–pytpy (L⁵)</td>
</tr>
<tr>
<td>Thiophene–2–carbaldehyde</td>
<td>2–tptpy (L⁶)</td>
</tr>
<tr>
<td>4–Benzyloxybenzaldehyde</td>
<td>4–boptpy (L⁷)</td>
</tr>
<tr>
<td>4–Methoxybenzaldehyde</td>
<td>4–mptpy (L⁸)</td>
</tr>
<tr>
<td>3–Chlorobenzaldehyde</td>
<td>3–cptpy (L⁹)</td>
</tr>
<tr>
<td>3–Bromobenzaldehyde</td>
<td>3–bptpy (L¹⁰)</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>ptpy (L¹¹)</td>
</tr>
<tr>
<td>Pyridine–3–carbaldehyde</td>
<td>3′′′–pytpy (L¹²)</td>
</tr>
<tr>
<td>9–Anthraldehyde</td>
<td>9–atpy (L¹³)</td>
</tr>
<tr>
<td>3–Benzyloxybenzaldehyde</td>
<td>3–boptpy (L¹⁴)</td>
</tr>
</tbody>
</table>
2.3.2 4’-(4-Chlorophenyl)-2,2’;6,2″-terpyridine (4–cptpy) (L₁)

Yield: 1.48 g, 43%
Melting point: 168–169 °C
Molecular formula (mol. wt.): C₂₁H₁₄ClN₃ (343.81 g/mol)

Microanalysis data:
Calc. (%): C, 73.36; H, 4.10; N, 12.22
Found (%): C, 73.12; H, 4.24; N, 12.06

IR (KBr, 4000–400 cm⁻¹): 3042, ν(C–H); 1540, 1409, ν(C=C); 1460, ν(C=N); 1385, 1351, (pyridine skeleton band); 1277, δ(C–Cl); 1035, ν(C–Cl); 1090, 1055, 812, (p–substituted aromatic ring)

¹H NMR (CDCl₃, 400 MHz) δ/ppm: 8.753–8.744, (complex, 4H, H₃,3′,5′,3″); 8.697, (d, 2H, H₆,6″); 7.939–7.859, (complex, 4H, H₄,4′,H₆₅,6); 7.495, (d, 2H, H₅,5″); 7.390, (dd, 2H, H₅,5″)
2.3.3 4′-(4-Bromophenyl)-2,2′:6′,2″-terpyridine (4-bptpy) (L²)

Yield: 1.84 g, 47.54%
Melting point: 125 °C
Molecular formula (mol. wt.): C₂₁H₁₄N₃Br (388.26 g/mol)

Microanalysis data:
Calc. (%): C, 64.96; H, 3.63; N, 10.82
Found (%): C, 64.76; H, 3.83; N, 10.67

IR (KBr, 4000–400 cm⁻¹): 3066, ν(C–H); 1499, 1461, ν(C=C); 1396, ν(C=N); 1396, 1339, (pyridine skeleton band); 1232, δ(C–Br); 1114, 1052, 801, (p-substituted aromatic ring); 1017, ν(C–Br)
\( ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz} \) \( \delta/\text{ppm}: 8.721–8.591, \) (complex, 6H); 7.984, \( t, 2H, H_{4,4''} \); 7.802, \( d, 2H, H_{ph2,6} \); 7.710, \( d, 2H, H_{ph3,5} \); 7.486, \( d, 2H, H_{5,5''} \) 

\( ^13C \text{ NMR (CDCl}_3, 100 \text{ MHz} \) \( \delta/\text{ppm}: 156.15, \) (C_{2,6}); 155.27, \( (C_{2,2'}) \); 149.67, \( (C_{6,6''}) \); 148.53, \( (C_{4'}) \); 137.77, \( (C_{ph1}) \); 137.08, \( (C_{4,4''}) \); 132.66, \( (C_{3,3''}) \); 129.35, \( (C_{ph2,6}) \); 124.89, \( (C_{5,5''}) \); 123.08, \( (C_{ph4}) \); 121.34, \( (C_{ph3,5}) \); 118.14, \( (C_{3,5'}) \) 

### 2.3.4 4’-(4-Fluorophenyl)–2,2’:6’,2”-terpyridine (4-fptpy) \( (L^3) \)

**Yield:** 1.32 g, 40.49%  
**Melting point:** 182 °C  
**Molecular formula (mol. wt.):** C_{21}H_{14}N_{3}F (327.35 g/mol)  
**Microanalysis data:**  
**Calc. (%):** C, 77.05; H, 4.31; N, 12.84  
**Found (%):** C, 77.24; H, 4.09; N, 12.71
IR (KBr, 4000–400 cm⁻¹): 2988, ν(C–H); 1522, 1466, ν(C=C); 1390, ν(C=N); 1362, 1341, (pyridine skeleton band); 1210, ν(C–F); 1099, 1062, 820, (p-substituted aromatic ring)

1H NMR (CDCl₃, 400 MHz) δ/ppm: 8.743–8.691, (complex, 6H); 7.918–7.902, (complex, 4H, H₆₄,₃,₅,₆); 7.391, (t, 2H, H₄₄,₄₄); 7.215, (t, 2H, H₅₅⁻⁻)

13C NMR (CDCl₃, 100 MHz) δ/ppm: 162.29, (C₄₄); 155.96, (C₂₆,₆'); 155.73, (C₂₂'); 149.40, (C₄); 148.94, (C₆₆⁺); 137.18, (C₄₄'); 129.22, (C₃₃'); 129.12, (C₆₆); 123.97, (C₅₅'); 121.52, (C₄₄); 118.91, (C₃₃'); 115.82, (C₆₆)
2.3.5 4′-(4-Tolyl)-2,2′:6′,2″-terpyridine (4-ttpy) (L^4)

Yield: 1.26 g, 39%
Melting point: 151–152 °C
Molecular formula (mol. wt.): C_{22}H_{17}N_{3} (323.39 g/mol)
Microanalysis data:
Calc. (%): C, 81.71; H, 5.30; N, 12.99
Found (%): C, 81.96; H, 5.13; N, 13.12

IR (KBr, 4000–440 cm^{-1}): 3082, \nu(C–H); 2973, \nu(C–H); 1590, \nu(C=C); 1420, \nu(C=N); 1395, 1322, (pyridine skeleton band); 718, 694, \delta(C–H)

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \delta/ppm: 8.798, (s, 2H, H\textsubscript{3′,5′}); 8.776, (d, 2H, H\textsubscript{3,3″}); 8.721, (d, 2H, H\textsubscript{5,5″}); 7.924, (dd, 2H, H\textsubscript{4,4″}); 7.869, (d, 2H, H\textsubscript{ph2,6}); 7.404, (dd, 2H, H\textsubscript{5,5″}); 7.344, (d, 2H, H\textsubscript{ph3,5}); 2.453, (s, 3H, CH\textsubscript{3})
$^{13}$C NMR (CDCl$_3$, 100 MHz) δ/ppm: 156.26, (C$_2$,6'); 155.75, (C$_{2',2''}$); 150.18, (C$_4'$); 148.98, (C$_{6,6''}$); 139.1, (C$_{ph1}$); 136.92, (C$_{4,4''}$); 135.45, (C$_{ph4}$); 129.66, (C$_{ph3,5}$); 127.15, (C$_{ph2,6}$); 123.75, (C$_{5,5''}$); 121.42, (C$_{3,3''}$); 118.7, (C$_{3',5'}$); 21.25, (CH$_3$)

2.3.6 4’-(2′′Pyridyl)-2,2':6',2''-terpyridine (2′′Pytpy) (L$_5$)

Yield: 1.04 g, 33.5%
Melting point: 224–225 °C
Molecular formula (mol. wt.): C$_{20}$H$_{14}$N$_4$ (310.35 g/mol)
Microanalysis data:
Calc. (%): C, 77.4; H, 4.55; N, 18.05
Found (%): C, 77.13; H, 4.64; N, 17.93

IR (KBr, 4000–400 cm$^{-1}$): 3092 ν(C–H); 1590, 1499, 1450, ν(C=C); 1340, 1395, (pyridine skeleton band); 1418, (C=N); 710, 1030, 670, (o–substituted aromatic ring)
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$/ppm: 9.15, (s, 2H, H$_{3',5'}$); 8.81, (dd, 1H, H$_{6'''}$); 8.78, (dd, 2H, H$_{3,3''}$); 8.71, (d, 2H, H$_{6,6''}$); 8.13, (d, 1H, H$_{3'''}$); 7.92, (dt, 2H, H$_{4,4''}$); 7.85, (dt, 1H, H$_{4'''}$); 7.37, (complex, 3H, H$_{5,5',5'''}$)

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$/ppm: 155.76, (C$_{2',6'}$); 155.71, (C$_{2,2''}$); 154.84, (C$_{2'''}$); 150.00, (C$_4$); 148.78, (C$_{6'''}$); 148.76, (C$_{6,6''}$); 137.33, (C$_{4'''}$); 136.93, (C$_{4,4''}$); 123.95, (C$_{5,5'}$); 123.79, (C$_{5'''}$); 121.56, (C$_{3,3''}$); 121.39, (C$_{3'''}$); 118.9, (C$_{3',5'}$)

2.3.7  $^{4'}$-(2-Thiophenyl)-2,2':6',2''-terpyridine (2-tptpy) ($L^6$)

Yield: 1.17 g, 37%
Melting point: 211–213 °C
Molecular formula (mol. wt.): $C_{19}H_{13}N_3S$ (315.39 g/mol)
Microanalysis data:
Calc. (%): C, 72.36; H, 4.15; N, 13.32
Found (%): C, 72.57; H, 4.03; N, 13.18
IR (KBr, 4000–625 cm⁻¹): 3068, ν(C–H); 1482, 1408, ν(C=C); 1408, 1335, (pyridine skeleton band); 778, ν(C=S); 1042, 637, (o–substituted aromatic ring)

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz) } \delta/\text{ppm:} \ 8.748, (d, 2H, H_{3,3''}); 8.714, (s, 2H, H_{3',5'}); 8.643, (d, 2H, H_{6,6''}); 7.873, (dd, 2H, H_{4,4''}); 7.796, (d, 1H, H_{Th3}); 7.448, (d, 1H, H_{Th5}); 7.358, (dd, 2H, H_{5,5'}); 7.172, (t, 1H, H_{Th4}) \]

\[ ^{13}C \text{ NMR (CDCl}_3, 100 \text{ MHz) } \delta/\text{ppm:} \ 155.8, (C_{2,2',6,6''}); 148.89, (C_{6,6''}); 143.48, (C_4); 141.79, (C_{Th2}); 137.08, (C_{4,4''}); 128.33, (C_{Th5}); 127.16, (C_{Th4}); 125.97, (C_{Th3}); 123.94, (C_{5,5'}); 121.44, (C_{3,3''}); 117.28, (C_{3,5'}) \]
2.3.8 4′-(4-Benzylxylophenyl)-2,2′:6′,2″-terpyridine(4-boptpy) (L7)

Yield: 1.33 g, 32.4%
Melting point: 160–162 °C
Molecular formula (mol. wt.): C28H21N3O (415.49 g/mol)
Microanalysis data:
Calc. (%): C, 80.94; H, 5.09; N, 10.11
Found (%): C, 81.17; H, 4.82; N, 10.37

IR (KBr, 4000–500 cm⁻¹): 3088, ν(C–H)Ar; 2922, ν(C–H)Al; 1525, 1496, ν(C=C); 1452, ν(C=N); 1395, 1322, (pyridine skeleton band); 1210, ν(C–O–C)sym; 1052, ν(C–O–C)asym; 1080, (monosubstituted benzene); 1110, 780, (p–substituted benzene)

1H NMR (CDCl3, 400 MHz) δ/ppm: 8.79, (s, 2H, H3′,5′); 8.76, (dd, 2H, H3,3′); 8.69, (d, 2H, H6,6′); 7.91, (dt, 2H, H4,4′); 7.55, (d, 2H, HPh2,6); 7.48–7.37, (complex, 7H); 7.15, (d, 2H, HPh3,5); 5.17, (s, 2H, CH2)
\[ ^{13}\text{C} \text{NMR (CDCl}_3, \text{ 100 MHz)} \delta/\text{ppm:} \ 160.58, \text{ (C}_{\text{Ph}4}); \ 156.15, \text{ (C}_{2',6'}; \ 155.57, \text{ (C}_{2,2''}); \ 149.8, \text{ (C}_4; \ 148.94, \text{ (C}_{6,6''}; \ 137.27, \text{ (C}_{\text{Bz}1}); \ 137.13, \text{ (C}_{4,4''}; \ 130.75, \text{ (C}_{\text{Ph}1}); \ 128.86, \text{ (C}_{\text{Bz}3,5}); \ 128.64, \text{ (C}_{\text{Ph}2,6}); \ 127.58, \text{ (C}_{\text{Bz}4}); \ 127.13, \text{ (C}_{\text{Bz}2,6}); \ 123.73, \text{ (C}_{5,5''}); \ 121.58, \text{ (C}_{3,3''}); \ 118.12, \text{ (C}_{3',5'}); \ 114.64, \text{ (C}_{\text{Ph}3,5}); \ 70.7, \text{ (CH}_2) \]

2.3.9 4’-(4-Methoxyphenyl)-2,2’:6’,2”-terpyridine (4–mptpy) (L\(^8\))

Yield: 1.16 g, 34.31%
Melting point: 158 °C
Molecular formula (mol. wt.): C\(_{22}\)H\(_{17}\)N\(_3\)O (339.39 g/mol)
Microanalysis data:
Calc. (%): C, 77.86; H, 5.05; N, 12.38
Found (%): C, 77.65; H, 4.78; N, 12.53

IR (KBr, 4000–425 cm\(^{-1}\)): 3122, \(\nu(C–H)_{\text{Ar}}\); 2955, \(\nu(C–H)_{\text{Al}}\); 1543, 1511, \(\nu(C=C); \ 1440, \nu(C=N); \ 1412, 1341, \) (pyridine skeleton band); 1264, \(\nu(C–O–C)_{\text{sym}}\); 1054, \(\nu(C–O–C)_{\text{asym}}\); 1110, 780, (\(p\)–substituted benzene); 780, \(\nu(C–H)\) out of plane; 717, 620, (\(m\)–substituted aromatic ring)
1H NMR (CDCl₃, 400 MHz) δ/ppm: 8.795–8.76, (complex, 4H, H₆₃,₅₅₃'); 8.71, (d, 2H, H₆₆'); 7.940–7.913, (complex, 4H); 7.396, (d, 2H, Hₚ₃₅₃); 7.055, (dd, 2H, H₅₅₃'); 3.90, (s, 3H, OCH₃)

13C NMR (CDCl₃, 100 MHz) δ/ppm: 160.57, (Cₚ₄); 156.15, (C₂₆'); 155.59, (C₂₂'); 149.81, (C₄); 148.88, (C₆₆'); 137.08, (C₄₄'); 130.63, (Cₚ₃); 128.55, (Cₚ₂₆); 123.81, (C₅₅₃'); 121.48, (C₃₃'); 118.41, (C₃₅₅'); 114.35, (Cₚ₃₅₃); 55.38, (OCH₃)

2.3.10 4’-(3-Chlorophenyl)-2,2′:6′,2″-terpyridine (3-cptpy) (L⁹)

Yield: 1.44 g, 42%
Melting point: 152–153 °C
Molecular formula (mol. wt.): C₂₁H₁₄ClN₃ (343.81 g/mol)
Microanalysis data:
Calc. (%): C, 73.36; H, 4.10; N, 12.22
Found (%): C, 73.12; H, 4.21; N, 12.36
IR (KBr, 4000–400 cm⁻¹): 3017, ν(C–H); 1543, 1442, ν(C=C); 1477, ν(C=N); 1368, 1350, (pyridine skeleton band); 1280, δ(C–Cl); 1154, 871, 790, (m-substituted aromatic ring); 1043, ν(C–Cl)

¹H NMR (CDCl₃, 400 MHz) δ/ppm: 8.775–8.699, (complex, 6H); 7.948–7.917, (m, 3H, Hₘₜ₂, H₄₄‴); 7.826, (d, 1H, H₆ₚ₆); 7.471, (complex, 2H, Hₕ₄ₕ₅ₚ₅₆); 7.404, (dd, 2H, H₅₅‴)

¹³C NMR (CDCl₃, 100 MHz) δ/ppm: 155.5, (C₂₂‴, C₆₆‴); 149.14, (C₄); 140.16, (C₆₆‴); 137.61, (Cₚₘ₁); 135.00, (C₄₄‴); 130.27, (Cₚ₄); 129.16, (Cₚ₄); 127.42, (Cₚ₅); 125.68, (Cₚ₂); 124.13, (Cₚ₆); 121.70, (C₅₅‴); 119.24, (C₃₃‴); 117.36, (C₃₃‴)
2.3.11 4′-(3-Bromophenyl)–2,2′:6′,2″-terpyridine (3-bptpy) (L₁₀)

Yield: 1.82 g, 47%
Melting point: 167–168 °C
Molecular formula (mol. wt.): C₂₁H₁₄BrN₃ (388.26 g/mol)
Microanalysis data:
Calc. (%): C, 64.96; H, 3.63; N, 10.82
Found (%): C, 65.16; H, 3.52; N, 10.96

IR (KBr, 4000–400 cm⁻¹): 3092, ν(C–H); 1538, 1448, ν(C=C); 1487, ν(C=N); 1358, 1305, (pyridine skeleton band); 1238, δ(C–Br); 1142, 849, 782, (m-substituted aromatic ring); 1002, ν(C–Br)

¹H NMR (CDCl₃, 400 MHz) δ/ppm: 8.789–8.719, (complex, 6H); 8.081, (s, 1H, Hₘₕ₂); 7.955, (dd, 2H, H₄,₄″); 7.892, (d, 1H, Hₖₕ₆); 7.612, (d, 1H, Hₖ₅₄); 7.436–7.397, (complex, 3H, Hₕ₅, Hₕ₅₅″)
2.3.12 4′-Phenyl-2,2′:6′,2″-terpyridine (ptpy) (L11)

Yield: 1.11 g, 36%
Melting point: 202–204 °C
Molecular formula (mol. wt.): C_{21}H_{15}N_{3} (309.36 g/mol)

Microanalysis data:
Calc. (%): C, 81.53; H, 4.89; N, 13.58
Found (%): C, 81.32; H, 4.71; N, 13.41

IR (KBr, 4000–600 cm\(^{-1}\)): 3099, ν(C–H); 1620, 1495, ν(C=C); 1474, ν(C=N); 1390, 1320, (pyridine skeleton band); 761, δ(C–H)
1H NMR (CDCl$_3$, 400 MHz) $\delta$/ppm: 8.802, (s, 2H, H$_{3',5'}$); 8.771, (d, 2H, H$_{3,3''}$); 8.72, (d, 2H, H$_{6,6''}$); 7.959–7.910, (complex, 4H, H$_{4,4''}$, H$_{ph2,6}$); 7.556–7.456, (m, 3H, H$_{ph3,4,5}$); 7.395, (dd, 2H, H$_{5,5''}$)

13C NMR (CDCl$_3$, 100 MHz) $\delta$/ppm: 155.88, (C$_{2',6'}$); 155.55, (C$_{2,2''}$); 150.47, (C$_{4'}$); 148.78, (C$_{6,6''}$); 138.31, (C$_{ph1}$); 137.32, (C$_{4,4''}$); 129.11, (C$_{ph2,6}$); 127.39, (C$_{ph3,4,5}$); 123.94, (C$_{5,5''}$); 121.6, (C$_{3,3''}$); 119.2, (C$_{3',5'}$)

2.3.13 4'–(3'’–Pyridyl)–2,2':6',2''–terpyridine (3''–pytpy) (L$^{12}$)

Yield: 1.13 g, 36.4%
Melting point: 203–204 °C
Molecular formula (mol. wt.): C$_{20}$H$_{14}$N$_{4}$ (310.35 g/mol)
Microanalysis data:
Calc. (%): C, 77.4; H, 4.55; N, 18.05
Found (%): C, 77.25; H, 4.69; N, 18.18
IR (KBr, 4000–400 cm\(^{-1}\)): 3126, ν(C–H); 1540, 1500, ν(C=C); 1435, ν(C=N); 1400, 1360, (pyridine skeleton band); 717, 620, (m–substituted aromatic ring)

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta/\text{ppm}\): 9.13, (d, 1H, H\(_{2''''}\)); 8.742–8.702, (complex, 5H, H\(_{3,3',5',3',6'}\)); 8.66, (d, 2H, H\(_{6,6'}\)); 8.20, (d, 1H, H\(_{4''''}\)); 7.89, (t, 2H, H\(_{4,4'}\)); 7.46, (q, 1H, H\(_{5''''}\)); 7.37, (dt, 2H, H\(_{5,5'}\))

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta/\text{ppm}\): 156.09, (C\(_{2',6'}\)); 155.64, (C\(_{2''}\)); 149.73, (C\(_{2''''}\)); 149.02, (C\(_{6,6'}\)); 148.05, (C\(_{6''}\)); 147.03, (C\(_{4'}\)); 137.10, (C\(_{4,4'}\)); 135.00, (C\(_{4''}\)); 134.35, (C\(_{3''}\)); 124.09, (C\(_{5,5'}\)); 123.79, (C\(_{5''}\)); 121.44, (C\(_{3,3'}\)); 118.85, (C\(_{3',5'}\))
2.3.14 \(4'-(9-\text{Anthryl})-2,2':6',2''-\text{terpyridine (9-atpy)} (L^{13})\)

**Yield:** 2.08 g, 51%

**Melting point:** 133–135 °C

**Molecular formula (mol. wt.):** \(C_{29}H_{19}N_3\) (409.48 g/mol)

**Microanalysis data:**

- **Calc. (%):** C, 85.06; H, 4.68; N, 10.26
- **Found (%):** C, 85.34; H, 4.81; N, 10.39

**IR (KBr, 4000–600 cm\(^{-1}\):** 3127, \(\nu(C-H)\); 1595, 1577, \(\nu(C=\text{C})\); 1531, \(\nu(C=\text{N})\); 1373, 1333, (pyridine skeleton band); 776, \(\delta(C-H)\)

**\(^1\text{H NMR (CDCl}_3, 400 \text{ MHz)} \delta/\text{ppm:}** 8.955, (s, 1H, \(H_{A10}\)); 8.756, (d, 2H, \(H_{3,3'}\)); 8.495, (s, 2H, \(H_{3,3'}\)); 8.400, (d, 2H, \(H_{6,6'}\)); 8.053, (d, 4H, \(H_{A1,A4,A5,A8}\)); 7.974, (dd, 2H, \(H_{4,4'}\)); 7.573–7.503, (complex, 6H, \(H_{A2,A3,A6,A7,H_{5,5'}}\))
$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$/ppm: 154.20, (C$_{2,2',6',2''}$); 148.99, (C$_{6,6''}$); 141.71, (C$_4$); 137.05, (C$_{4,4''}$); 131.33, (C$_{A9}$); 128.90, (C$_{A11,12}$); 128.57, (C$_{A10}$); 127.43, (C$_{5,5''}$); 126.95, (C$_{A4,5}$); 126.41, (C$_{A1,8,13,14}$); 125.40, (C$_{A2,3,6,7}$); 125.38, (C$_{3,3''}$); 123.10, (C$_{3',5'}$)

2.3.15 4'-(3-Benzylxyphenyl)-2,2':6',2''-terpyridine(3-boptpy) (L$^{14}$)

Yield: 1.23 g, 30%
Melting point: 146–148 °C
Molecular formula (mol. wt.): C$_{28}$H$_{21}$N$_3$O (415.49 g/mol)
Microanalysis data:
Calc. (%): C, 80.94; H, 5.09; N, 10.11
Found (%): C, 80.76; H, 5.28; N, 10.35

IR (KBr, 4000–500 cm$^{-1}$): 3054, $\nu$(C–H)$_{A'}$; 2971, $\nu$(C–H)$_{A''}$; 1515, 1464, $\nu$(C=C); 1395, $\nu$(C=N); 1395, 1320, (pyridine skeleton band); 1220, $\nu$(C-O-C)$_{\text{sym}}$; 1084, $\nu$(C-O-C)$_{\text{asym}}$; 1068, (monosubstituted benzene); 1119, 796, (m–substituted benzene)
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$/ppm: 8.76, (d, 2H, H$_{3,3'}$); 8.72, (s, 2H, H$_{3',5'}$); 8.67, (d, 2H, H$_{6,6'}$); 7.49–7.34, (complex, 11H); 7.28, (d, 1H, H$_{Ph6}$); 7.16, (d, 1H, H$_{Ph4}$); 5.17, (s, 2H, CH$_2$)

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$/ppm: 157.63, (C$_{Ph3}$); 156.13, (C$_{2',6'}$); 155.27, (C$_{2,2'}$); 151.7, (C$_4$); 149.1, (C$_{6,6'}$); 148.28, (C$_{Ph1}$); 136.86, (C$_{4,4'}$); 136.75, (C$_{Bz1}$); 130.26, (C$_{Ph5}$); 129.03, (C$_{Bz3,5}$); 127.56, (C$_{Bz4}$); 127.08, (C$_{Bz2,6}$); 123.7, (C$_{5,5'}$); 121.34, (C$_{3,3'}$); 119.6, (C$_{Ph6}$); 118.06, (C$_{3',5'}$); 114.76, (C$_{Ph2}$); 113.17, (C$_{Ph4}$); 70.75, (CH$_2$)
2.4 References