

1 **Phosphonate-functionalized heteroleptic ruthenium(II) bis(2,2':6',2''-**
2 **terpyridine) complexes**

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13 *This paper is dedicated to our colleague Barry Lever whose contributions to*
14 *inorganic chemistry have extended over a long and distinguished career.*

15

16 **Abstract**

17 The heteroleptic complexes [Ru(**1**)(**4**)]PF₆]₂, [Ru(**2**)(**4**)]PF₆]₂,

18 [Ru(Phtpy)(**4**)]PF₆]₂ and [Ru(pytpy)(**4**)]PF₆]₂ (Phtpy = 4'-phenyl-

19 2,2':6',2''-terpyridine, pytpy = 4'-(4-pyridyl)-2,2':6',2''-terpyridine, **1** and **2** =

20 4-methyl ester-substituted derivatives of Phtpy and pytpy, **4** = ethyl

21 2,2':6',2''-terpyridine-4'-phosphonate) have been prepared. The single

22 crystal structure of ligand **1** (**1** = methyl 4-carboxy-4'-phenyl-2,2':6',2''-

23 terpyridine) is reported. The introduction of the 4-methyl ester group

24 causes a small red shift in the MLCT band of the ruthenium(II) complexes,

25 and small shift to more positive potential for the Ru²⁺/Ru³⁺ couple. The new

26 complexes should serve as a useful starting point for development of
27 ruthenium(II) dyes suited for sensitization of p-type semiconductors.

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30 **Introduction**

31 The {Ru(tpy)₂} chromophore (tpy = 2,2':6',2''-terpyridine) is one of the most
32 extensively studied domains¹ within metal oligopyridine coordination
33 chemistry. Tuning the photophysical and electrochemical properties of
34 {Ru(tpy)₂}-containing complexes is readily achieved through
35 functionalization of the ligand. In particular, the Kröhnke methodology² is a
36 facile means of introducing a wide variety of substituents into the 4'-
37 position of tpy. Although at room temperature in solution, [Ru(tpy)₂]²⁺ is
38 essentially non-emissive,³ judicious choice of electron-donating or accepting
39 substituents can lead to significant enhancement of emission properties.⁴

40 Among the many areas in which ruthenium(II) complexes containing
41 tpy-derived ligands have found a practical niche is that of the Grätzel solar
42 cell.⁵ Our own interests in the development of sensitizers for the
43 photoanode in dye-sensitized solar cells (DSCs) have moved in the direction
44 of earth-abundant metals, in particular copper.⁶ Although photon-to-power
45 conversion efficiencies reaching 3.77%⁷ have been achieved with a
46 copper(I) sensitizer anchored to the n-type semiconductor (TiO₂)
47 comprising the photoanode, this is significantly lower than those attained by
48 state-of-the-art ruthenium(II) dyes (>10%).⁸ One strategy for improving
49 performance is to harvest photons at both electrodes, but this requires
50 different dyes suited for interaction with either the photoanode (n-type

51 semiconductor) or photocathode (p-type) in a so-called tandem cell.⁹ In a
52 tandem DSC, the photocathode functions in an inverse mode with respect to
53 the photoanode, with excitation of the dye being followed by rapid hole
54 injection into the p-type semiconductor (e.g. NiO). Organic donor-acceptor
55 molecules are popular choices for photocathode sensitizers.¹⁰ Excitation of
56 the sensitizer leaves a hole in the original HOMO of the dye into which an
57 electron is transferred from the valence band of the p-type semiconductor.
58 Thus, the HOMO/LUMO requirements of a p-type sensitizer are the reverse
59 of those of an n-type dye. It has been demonstrated that $[\text{Ru}(\text{bpy})_2(\text{N}^{\wedge}\text{N})]^{2+}$
60 (bpy = 2,2'-bipyridine, $\text{N}^{\wedge}\text{N}$ = bipyridine-based anchoring ligand) complexes
61 sensitize NiO photocathodes and both CO_2H and $\text{PO}(\text{OH})_2$ anchors adsorb
62 onto NiO.¹¹ Ruthenium(II) complexes containing cyclometalated ligands,
63 and related to the archetypal $[\text{Ru}(\text{bpy})_2(\text{ppy})]^+$ ^{12,13} (Hppy = 2-
64 phenylpyridine) are also promising candidates for NiO sensitization.^{14,15}
65 Low level MO calculations indicate that the HOMO of $[\text{Ru}(\text{tpy})(4'-$
66 $(\text{HO})_2\text{OPtpy})]^{2+}$ type complexes (4'-($\text{HO})_2\text{OPtpy}$ = 2,2':6',2''-terpyridine-4'-
67 phosphonic acid) may be localized on the phosphonic acid anchoring unit.
68 We have therefore undertaken a preliminary investigation of several
69 complexes of this type with the aim of providing a starting point for the
70 development of dyes for p-type semiconductors. The ancillary ligands **1** and
71 **2** (Scheme 1) contain an ester functionality which provides a site for
72 variable functionalization, for example, through transesterification.

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75 **Experimental**

76 **General:** ^1H and ^{13}C NMR spectra were recorded at 295 K on Bruker Avance
77 III-400 or III-500 NMR spectrometers (chemical shifts with respect to
78 residual solvent peaks and $\delta(\text{TMS}) = 0$ ppm). Solution electronic absorption
79 and emission spectra were measured, respectively, using an Agilent 8453
80 spectrophotometer and Shimadzu 5301PC spectrofluorophotometer.
81 Solution quantum yields were measured using a Hamamatsu absolute PL
82 quantum yield spectrometer C11347 Quantaaurus_QY. A Shimadzu 8400S
83 spectrometer was used to record FT-IR spectra (all solid samples using a
84 Golden Gate accessory). Electrospray ionization (ESI) mass spectra and
85 high-resolution ESI mass spectra were recorded on Bruker esquire 3000^{plus}
86 and Bruker maXis 4G mass spectrometers. Electrochemical measurements
87 were carried out using cyclic voltammetry and were recorded using a CH
88 Instruments 900B potentiostat with glassy carbon working and platinum
89 auxiliary electrodes; a silver wire was used as a pseudo-reference electrode.
90 The solvent was HPLC grade MeCN and 0.05 M [$n\text{Bu}_4\text{N}$][PF_6] was used as
91 supporting electrolyte. All solutions were degassed with argon, and Cp_2Fe
92 was used as internal reference. A Biotage Initiator 8 reactor was used for
93 reactions under microwave conditions. Fluka silica 60 was used for column
94 chromatography.

95 The compounds (*E*)-1-(pyridin-2-yl)-3-(pyridin-4-yl)prop-2-en-1-
96 one,¹⁶ (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one,¹⁷ 1-(2-(4-
97 (methoxycarbonyl)pyridin-2-yl)-2-oxoethyl)pyridin-1-ium iodide,¹⁶ Phtpy¹⁷
98 pytpy¹⁸ and 4'-F₃CSO₃-2,2':6',2''-terpyridine¹⁹ were prepared according to
99 published methods (Phtpy = 4'-phenyl-2,2':6',2''-terpyridine, pytpy = 4'-(4-
100 pyridyl)-2,2':6',2''-terpyridine). $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from OXKEM.

101

102 **Compound 1**

103 Ammonium acetate (9.60 g, 124.68 mmol) was dissolved in MeOH (110 mL).
104 (*E*)-3-Phenyl-1-(pyridin-2-yl)prop-2-en-1-one (1.00 g, 4.76 mmol) and 1-(2-
105 (4-(methoxycarbonyl)pyridin-2-yl)-2-oxoethyl)pyridin-1-ium iodide (2.21
106 g, 5.71 mmol) were added and the brown solution was heated at reflux for
107 16 h, during which time a brown precipitate formed. The reaction mixture
108 was then cooled to room temperature and left to stand overnight in a
109 freezer. The brown precipitate was collected on a glass frit, washed with
110 cold MeOH and dried in air. Compound **1** was isolated as a pale brown
111 powder (0.56 g, 1.53 mmol, 33%). M.Pt. 197-198 °C. ¹H NMR (500 MHz,
112 CDCl₃) δ/ppm 9.16 (dd, *J* = 1.7, 0.9 Hz, 1H, H^{D3}), 8.86 (dd, *J* = 5.0, 0.9 Hz, 1H,
113 H^{D6}), 8.78 (d, *J* = 1.7 Hz, 1H, H^{B3}), 8.75 (d, *J* = 1.7 Hz, 1H, H^{B5}), 8.74 (ddd, *J* =
114 4.7, 1.9, 1.0 Hz, 1H, H^{A6}), 8.72 (dt, *J* = 7.9, 1.1 Hz, 1H, H^{A3}), 7.90 (m, 4H,
115 H^{A4+C2+D5}), 7.52 (m, 2H, H^{C3}), 7.47 (m, 1H, H^{C4}), 7.37 (ddd, *J* = 7.5, 4.8, 1.2 Hz,
116 1H, H^{A5}), 4.04 (s, 3H, H^{OMe}). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ / ppm 166.1
117 (C^{C=O}), 157.6 (C^{D2}), 156.2 (C^{A2}), 156.1 (C^{B2}), 155.3 (C^{B6}), 150.6 (C^{B4}), 150.0
118 (C^{D6}), 149.2 (C^{A6}), 138.5 (C^{C1}), 138.4 (C^{D4}), 137.2 (C^{A4}), 129.3 (C^{C4}), 129.1
119 (C^{C3}), 127.5 (C^{C2}), 124.1 (C^{A5}), 122.9 (C^{D5}), 121.7 (C^{A3}), 120.8 (C^{D3}), 119.5
120 (C^{B5}), 119.3 (C^{B3}), 52.9 (C^{OMe}). ESI-MS (MeOH/CHCl₃): *m/z* 390.0 [M+Na]⁺
121 (calc. 390.1), 368.0 [M+H]⁺ (base peak, calc. 368.1). IR (solid, ν/cm⁻¹) 3051
122 (w), 2969 (w), 1723 (s), 1583 (m), 1548 (m), 1467 (w), 1432 (m), 1378 (s),
123 1268 (s), 1218 (s), 1132 (w), 1099 (w), 989 (m), 887 (w), 800 (m), 775 (m),
124 764 (s), 754 (s), 731 (s), 707 (s), 694 (s), 681 (s), 662 (s), 620 (s), 517 (s).
125 UV/VIS λ/nm (CH₃CN, 4.44 × 10⁻⁵ mol dm⁻³) (ε / dm³ mol⁻¹ cm⁻¹) 253

126 (35000), 276 sh (27000), 310 sh (13000). Found C, 74.41; H, 4.67; N, 11.22;
127 $C_{23}H_{17}N_3O_2 \cdot 0.25H_2O$ requires C, 74.28; H, 4.74; N, 11.30%.

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130

131 **Compound 2**

132 Ammonium acetate (13 g, 160 mmol) was dissolved in MeOH (150 mL). (*E*)-
133 1-(Pyridin-2-yl)-3-(pyridin-4-yl)prop-2-en-1-one (0.92 g, 4.38 mmol) and 1-
134 (2-(4-(methoxycarbonyl)pyridin-2-yl)-2-oxoethyl)pyridin-1-ium iodide
135 (2.01 g, 5.25 mmol) were added and the brown suspension was heated at
136 reflux for 7 h; the solids slowly dissolved. The white precipitate which
137 formed was collected on a glass frit, washed with cold MeOH and Et₂O, and
138 dried in air. Compound **2** was isolated as a white powder (1.43 g, 3.88 mmol,
139 89%). M.Pt. 216-217 °C. ¹H NMR (500 MHz, CDCl₃) δ/ppm 9.15 (dd, *J* = 1.6,
140 0.9 Hz, 1H, H^{D3}), 8.86 (dd, *J* = 5.0, 0.9 Hz, 1H, H^{D6}), 8.78 (d, *J* = 1.7 Hz, 1H,
141 H^{B3}), 8.76 (m, 3H, H^{C2+B5}), 8.72 (m, 2H, H^{A6+A3}), 7.92 (m, 2H, H^{A4+D5}), 7.80 (dd,
142 *J* = 4.5, 1.7 Hz, 2H, H^{C3}), 7.39 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H, H^{A5}), 4.04 (s, 3H,
143 H^{OMe}). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ/ppm 165.9 (C^{C=O}), 156.9 (C^{D2}),
144 156.7 (C^{B2}), 155.6 (C^{B6}), 155.5 (C^{A2}), 150.6 (C^{C2}), 150.0 (C^{D6}), 149.3 (C^{A6}),
145 147.6 (C^{B4}), 145.9 (C^{C4}), 138.5 (C^{D4}), 137.2 (C^{A4}), 124.3 (C^{A5}), 123.2 (C^{D5}),
146 121.7 (C^{C3}), 121.6 (C^{A3}), 120.7 (C^{D3}), 119.1 (C^{B3}), 118.9 (C^{B5}), 53.0 (C^{OMe}). ESI
147 MS (MeOH/CHCl₃): *m/z* 391.1 [M+Na]⁺ (base peak, calc. 391.1), 369.2
148 [M+H]⁺ (calc. 369.1). IR (solid, ν/cm⁻¹) 3020 (w), 2961 (w), 1731 (s), 1583
149 (m), 1559 (m), 1538 (m), 1533 (m), 1475 (m), 1436 (m), 1378 (m), 1309

150 (w), 1292 (w), 1270 (m), 1263 (w), 1218 (m), 1211 (m), 1130 (w), 973 (w),
151 895 (w), 821 (m), 795 (s), 770 (s), 736 (w), 682 (m), 669 (m), 660 (m), 618
152 (m), 533 (m). UV/VIS λ /nm (ϵ / dm³ mol⁻¹ cm⁻¹) (CH₃CN, 4.22 × 10⁻⁵ mol
153 dm⁻³) 242 (33000), 281 (16000), 316 sh (10000). Found C, 70.96; H, 4.44; N,
154 15.19; C₂₂H₁₆N₄O₂·0.25H₂O requires C, 70.86; H, 4.46; N, 15.02%.

155

156 **Compound 3**

157 4'-F₃CSO₃-2,2':6',2''-Terpyridine (0.80 g, 2.10 mmol) and [Pd(PPh₃)₄] (0.24
158 g, 0.21 mmol) were suspended in MeCN (17 mL) in a microwave vial (20
159 mL), and then NEt₃ (0.38 g, 3.78 mmol) and diethyl phosphite (0.49 g, 3.57
160 mmol) were added. The brown suspension was heated in a microwave
161 reactor (140 °C, 30 min) and then allowed to cool to room temperature. The
162 reaction mixture was diluted with toluene and washed with aqueous NH₄OH
163 (32%) and H₂O. The organic layer was dried over MgSO₄, filtered and the
164 solvent removed in vacuo. The crude brown solid was purified by flash
165 column chromatography (SiO₂), first eluting with CH₂Cl₂ to remove Ph₃PO
166 and then with CH₂Cl₂/MeOH (98 : 2). Compound **3** was isolated as a pale
167 brown solid (0.65 g, 1.76 mmol, 84%). The NMR spectroscopic data matched
168 those published.²⁰

169

170 **[Ru(3)Cl₃]**

171 Compound **3** (0.60 g, 1.63 mmol) and RuCl₃·3H₂O (0.43 g, 1.63 mmol) were
172 suspended in EtOH (200 mL) and the reaction mixture was heated at reflux
173 for 3.5 h. The brown solid which formed was separated by filtration, washed
174 with cold EtOH and Et₂O and dried in air yielding a red-brown powder (0.83

175 g, 1.44 mmol, 88%). The product was used for the next step without further
176 purification and characterization.

177

178 **[Ru(Phtpy)(4)][PF₆]₂**

179 Phtpy (64 mg, 0.21 mmol) and [Ru(3)Cl₃] (119 mg, 0.21 mmol) were
180 suspended in dry EtOH (3.5 mL) in a microwave reactor vial. *N*-
181 Ethylmorpholine (3 drops) was added and the reaction mixture was heated
182 in a microwave reactor at 140 °C for 15 min. The dark red solution was
183 poured into aqueous NH₄PF₆ (250 mL) yielding a red precipitate which was
184 collected on Celite and washed with cold water (250 mL) and Et₂O (20 mL).
185 The residue was redissolved in CH₃CN and then solvent removed in vacuo to
186 give a dark red solid. This was purified by column chromatography (SiO₂,
187 eluted with CH₃CN/saturated aqueous KNO₃/H₂O 7 : 1 : 0.5 by vol.). The first
188 red band was collected, aqueous NH₄PF₆ added and solvent evaporated until
189 a red precipitate formed. This was collected on Celite and washed
190 thoroughly with cold H₂O (250 mL), cold EtOH (15 mL) and Et₂O (15 mL).
191 The residue was redissolved in CH₃CN and solvent removed in vacuo.

192 [Ru(Phtpy)(4)][PF₆]₂ was isolated as a red powder (200 mg, 0.192 mmol,
193 93%). ¹H NMR (400 MHz, CD₃CN) δ/ppm 9.06 (d, J_{PH} = 11 Hz, 2H, H^{F3}), 8.99
194 (s, 2H, H^{B3}), 8.68 (m, 4H, H^{A3+E3}), 8.20 (m, 2H, H^{C2}), 7.90 (m, 4H, H^{A4+E4}), 7.76
195 (m, 2H, H^{C3}), 7.68 (m, 1H, H^{C4}), 7.39 (m, 4H, H^{A6+E6}), 7.15 (m, 4H, H^{A5+E5}), 4.05
196 (m, 2H, H^{CH2(Et)}), 1.31 (t, J = 7.0 Hz, 3H, H^{CH3(Et)}). ¹³C {¹H} NMR (126 MHz,
197 CD₃CN) δ/ppm 159.3 (C^{E2}), 158.8 (C^{A2}), 156.2 (C^{B2}), 155.7 (d, J_{PC} = 12 Hz,
198 C^{F2}), 153.7 (C^{A6/E6}), 153.3 (C^{A6/E6}), 149.2 (C^{B4}), 139.0 (C^{A4+E4}), 137.9 (C^{C1}),
199 131.3 (C^{C4}), 130.6 (C^{C3}), 128.7 (C^{C2}), 128.5 (C^{A5/E5}), 128.2 (C^{A5/E5}), 126.4 (d,

200 $J_{PC} = 20$ Hz, C^{F3}), 125.6 ($C^{A3/E3}$), 125.4 ($C^{A3/E3}$), 122.5 (C^{B3}), 61.8 ($C^{CH2(Et)}$),
201 17.5 ($C^{CH3(Et)}$) (C^{F4} not resolved). IR (solid, ν/cm^{-1}) 3315 (br m), 1662 (w),
202 1605 (w), 1542 (w), 1473 (w), 1412 (m), 1392 (m), 1345 (m), 1289 (w),
203 1209 (m), 1162 (w), 1140 (m), 1078 (m), 1034 (m), 962 (w), 898 (w), 826
204 (s), 791 (s), 764 (s), 733 (m), 689 (s), 664 (m), 603 (m). ESI-MS (MeCN): m/z
205 751.4 [$M - H - 2PF_6$]⁺ (100%, calc. 751.1). HR ESI-MS m/z : 376.0621 [$M -$
206 $2PF_6$]²⁺ (base peak, calc. 376.0619), 751.1172 [$M - H - 2PF_6$]⁺ (calc.
207 751.1165). UV/VIS λ / nm (MeCN, 2.88×10^{-5} mol dm^{-3}) ($\epsilon / dm^3 mol^{-1} cm^{-}$
208 1) 274 (59000), 280 sh (54500), 310 (63000), 330 sh (34000), 485 (23000).
209 Emission (MeCN, 3×10^{-5} mol dm^{-3} , $\lambda_{ex} = 485$ nm): $\lambda_{em} = 647$ nm.
210 Satisfactory elemental analysis could not be obtained (see text).

211

212 **[Ru(pytpy)(4)][PF₆]₂**

213 The method was as for [Ru(Phtpy)(4)][PF₆]₂ starting with pytpy (160 mg,
214 0.52 mmol) and [Ru(3)Cl₃] (300 mg, 0.52 mmol). [Ru(pytpy)(4)][PF₆]₂ was
215 isolated as a red powder (130 mg, 0.125 mmol, 24%). ¹H NMR (500 MHz,
216 CD₃CN) δ/ppm 9.05 (d, $J_{PH} = 11$ Hz, 2H, H^{F3}), 9.03 (s, 1H, H^{B3}), 8.95 (m, 2H,
217 H^{C2}), 8.64 (d, $J = 7.9$ Hz, 2H, $H^{A3/E3}$), 8.61 (d, $J = 8.1$ Hz, 2H, $H^{A3/E3}$), 8.12 (m,
218 2H, H^{C3}), 7.94 (m, 2H, $H^{A4/E4}$), 7.88 (m, 2H, $H^{A4/E4}$), 7.42 (d, $J = 6.7$ Hz, 2H,
219 $H^{A6/E6}$), 7.35 (d, $J = 6.7$ Hz, 2H, H^{E6}), 7.18 (m, 2H, $H^{A5/E5}$), 7.15 (m, 2H, $H^{A5/E5}$),
220 4.05 (m, 2H, $H^{CH2(Et)}$), 1.32 (t, $J = 6.8$ Hz, 3H, $H^{CH3(Et)}$). ¹³C {¹H} NMR (126
221 MHz, CD₃CN) δ/ppm 158.7 (C^{E2}), 158.5 (C^{A2}), 158.0 (C^{F2}), 157.0 (C^{B2}), 153.8
222 ($C^{A6/E6}$), 153.7 ($C^{A6/E6}$), 151.5 (C^{C2}), 145.3 (C^{B4+C4}), 139.3 (C^{A4+E4}), 128.8
223 ($C^{A5/E5}$), 128.6 ($C^{A5/E5}$), 126.2 (d, $J_{PC} \approx 20$ Hz, C^{F3}), 126.1 ($C^{A3/E3}$), 126.0
224 ($C^{A3/E3}$), 123.2 (C^{B3}), 123.1 (C^{C3}), 63.2 ($C^{CH2(Et)}$), 17.2 ($C^{CH3(Et)}$) (C^{F4} not

225 resolved). IR (solid, ν/cm^{-1}) 3350 (br s), 1660 (w), 1599 (s), 1532 (w), 1475
226 (m), 1394 (m), 1352 (w), 1291 (w), 1202 (s), 1166 (w), 1075 (m), 1069 (m),
227 1038 (m), 1028 (s), 942 (m), 844 (s), 826 (s), 818 (s), 784 (m), 776 (m), 745
228 (m). ESI-MS (CH_3CN): m/z 376.5 $[\text{M} - 2\text{PF}_6]^{2+}$ (calc. 376.6). HR ESI-MS m/z :
229 376.5600 $[\text{M} - 2\text{PF}_6]^{2+}$ (base peak, calc. 376.5595), 752.1135 $[\text{M} - \text{H} - 2\text{PF}_6]^+$
230 (calc. 752.1117). UV/VIS λ / nm (CH_3CN , $1 \times 10^{-5} \text{ mol dm}^{-3}$) ($\epsilon / \text{dm}^3 \text{ mol}^{-1}$
231 cm^{-1}) 273 (54700), 282 sh (42000), 311 (50300), 331 sh (33000), 486
232 (21000). Emission (CH_3CN , $3.84 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda_{\text{ex}} = 486 \text{ nm}$): $\lambda_{\text{em}} = 704$
233 nm. Found: C, 42.94; H, 3.76; N, 10.33; $\text{C}_{37}\text{H}_{30}\text{F}_{12}\text{N}_7\text{O}_3\text{P}_3\text{Ru} \cdot \text{H}_2\text{O} \cdot 1.5\text{CH}_3\text{CN}$
234 (1122.60) requires C, 42.81; H, 3.28; N, 10.16%.

235

236 **[Ru(1)(4)][PF₆]₂**

237 The method was as for $[\text{Ru}(\text{Phtpy})(4)][\text{PF}_6]_2$ starting with **1** (71 mg, 0.19
238 mmol) and $[\text{Ru}(3)\text{Cl}_3]$ (112 mg, 0.19 mmol). $[\text{Ru}(1)(4)][\text{PF}_6]_2$ was isolated
239 as a red powder (177 mg, 0.161 mmol, 83%). ^1H NMR (400 MHz, CD_3CN)
240 δ/ppm 9.15 (d, $J = 1.4 \text{ Hz}$, 1H, $\text{H}^{\text{B}3/\text{B}5}$), 9.12 (d, $J_{\text{PH}} = 10. \text{ Hz}$, 2H, $\text{H}^{\text{F}3}$), 9.08 (d, J
241 $= 1.2 \text{ Hz}$, 1H, $\text{H}^{\text{D}3}$), 9.05 (d, $J = 1.4 \text{ Hz}$, 1H, $\text{H}^{\text{B}3/\text{B}5}$), 8.72 (d, $J = 8.2 \text{ Hz}$, 2H, $\text{H}^{\text{E}3}$),
242 8.66 (d, $J = 7.9 \text{ Hz}$, 1H, $\text{H}^{\text{A}3}$), 8.24 (m, 2H, $\text{H}^{\text{C}2}$), 7.94 (td, $J = 7.9, 1.5 \text{ Hz}$, 1H,
243 $\text{H}^{\text{A}4}$), 7.89 (td, $J = 7.9, 1.5 \text{ Hz}$, 2H, $\text{H}^{\text{E}4}$), 7.77 (m, 2H, $\text{H}^{\text{C}3}$), 7.69 (m, 1H, $\text{H}^{\text{C}4}$),
244 7.63 (d, $J = 5.8 \text{ Hz}$, 1H, $\text{H}^{\text{D}6}$), 7.56 (dd, $J = 5.8, 1.8 \text{ Hz}$, 1H, $\text{H}^{\text{D}5}$), 7.44 (d, $J = 5.5$
245 Hz, 1H, $\text{H}^{\text{A}6}$), 7.39 (dd, $J = 5.6, 1.4 \text{ Hz}$, 2H, $\text{H}^{\text{E}6}$), 7.18 (m, 1H, $\text{H}^{\text{A}5}$), 7.13 (ddd, J
246 $= 7.7, 5.6, 1.3 \text{ Hz}$, 2H, $\text{H}^{\text{E}5}$), 4.07 (m, 2H, $\text{H}^{\text{CH}2(\text{Et})}$), 3.90 (s, 3H, H^{OMe}), 1.29 (t, $J =$
247 7.0 Hz , 3H, $\text{H}^{\text{CH}3(\text{Et})}$). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CD_3CN) δ/ppm 165.0 ($\text{C}^{\text{C}=\text{O}}$),
248 160.6 ($\text{C}^{\text{D}2}$), 159.5 ($\text{C}^{\text{E}2}$), 159.0 ($\text{C}^{\text{A}2}$), 156.4 ($\text{C}^{\text{B}2}$), 156.0 ($\text{C}^{\text{B}6}$), 154.7 ($\text{C}^{\text{D}6}$),
249 155.6 (d, $J_{\text{PC}} = 14 \text{ Hz}$, $\text{C}^{\text{F}2}$), 153.7 ($\text{C}^{\text{A}6}$), 153.3 ($\text{C}^{\text{E}6}$), 149.4 ($\text{C}^{\text{B}4}$), 139.4 ($\text{C}^{\text{D}4}$),

250 139.2 (C^{A4+E4}), 137.6 (C^{C1}), 131.4 (C^{C4}), 130.6 (C^{C3}), 129.0 (C^{C2}), 128.6
251 (C^{A5+E5}), 128.2 (C^{D5}), 127.6 (d, J_{PC} = 10 Hz, C^{F3}), 126.8 (C^{E3}), 126.5 (C^{A3}),
252 125.1 (C^{D3}), 124.0 (C^{B3/B5}), 123.7 (C^{B3/B5}), 62.1 (C^{CH2(Et)}), 54.3 (C^{OMe}), 17.5
253 (C^{CH3(Et)}) (C^{F4} not resolved). IR (solid, ν/cm⁻¹) 3347 (br m), 1722 (w), 1605
254 (w), 1363 (m), 1268 (w), 1165 (w), 1137 (w), 1075 (w), 1032 (w), 945 (w),
255 825 (s), 787 (m), 767 (m), 700 (w), 607 (w). ESI-MS (CH₃CN): *m/z* 809.5 [M-
256 H-2PF₆]⁺ (base peak, calc. 809.1). HR ESI-MS *m/z*: 405.0654 [M - 2PF₆]²⁺
257 (base peak, calc. 405.0647), 809.1233 [M - H - 2PF₆]⁺ (calc. 809.1220).
258 UV/VIS λ / nm (CH₃CN, 3.6 × 10⁻⁵ mol dm⁻³) (ε / dm³ mol⁻¹ cm⁻¹) 274
259 (56000), 285 (51500), 309 (57000), 330 sh (41500), 491 (20000).
260 Satisfactory elemental analysis was not obtained (see text).

261

262 **[Ru(2)(4)][PF₆]₂**

263 The method was as for [Ru(Phtpy)(4)][PF₆]₂ starting with **2** (50 mg, 0.14
264 mmol) and [Ru(3)Cl₃] (78 mg, 0.14 mmol). [Ru(2)(4)][PF₆]₂ was isolated as
265 a red powder (35 mg, 0.032 mmol, 23%). ¹H NMR (500 MHz, CD₃CN) δ/ppm
266 9.23 (d, J_{PH} = 11.5 Hz, 2H, H^{F3}) overlapping with 9.14 (d, J = 1.5 Hz, 1H,
267 H^{B3/B5}), 9.12 (d, J = 1.3 Hz, 1H, H^{B3/B5}), 9.09 (d, J = 1.4 Hz, 1H, H^{D3}), 8.98 (m,
268 2H, H^{C2}), 8.77 (m, 3H, H^{A3+E3}), 8.19 (m, 2H, H^{C3}), 7.98 (td, J = 8.1, 1.4 Hz, 1H,
269 H^{A4}), 7.92 (td, J = 7.9, 1.5 Hz, 2H, H^{E4}), 7.61 (m, 2H, H^{D5+D6}), 7.46 (d, J = 5.6 Hz,
270 1H, H^{A6}), 7.38 (dd, J = 5.7, 1.3 Hz, 2H, H^{E6}), 7.21 (m, 1H, H^{A5}), 7.16 (ddd, J =
271 7.2, 5.6, 1.2 Hz, 2H, H^{E5}), 4.27 (m, 2H, H^{CH2(Et)}), 3.91 (s, 3H, H^{OMe}), 1.41 (t, J =
272 6.9 Hz, 3H, H^{CH3(Et)}). ¹³C {¹H} NMR (126 MHz, CD₃CN) δ/ppm 164.3 (C^{C=O}),
273 160.1 (C^{D2}), 159.5 (C^{F2}), 159.3 (C^{E2}), 158.8 (C^{A2}), 157.1 (C^{B2}), 156.5 (C^{B6}),
274 154.8 (C^{D6}), 153.7 (C^{A6}), 153.4 (C^{E6}), 151.7 (C^{C2}), 146.4 (C^{B4}), 145.2 (C^{C4}),

275 139.4 (C^{A4}), 139.3 (C^{E4}), 128.6 (C^{A5}), 128.5 (C^{E5}), 127.3 (C^{D5}), 126.4 (d, $J_{PC} \approx$
276 10 Hz, C^{F3}), 126.0 (C^{E3}), 125.7 (C^{A3}), 124.4 (C^{B3/B5}), 123.3 (C^{B3/B5}), 123.0
277 (C^{D3}), 123.1 (C^{C3}), 62.6 (C^{CH2(Et)}), 53.8 (C^{OMe}), 16.9 (C^{CH3(Et)}) (C^{F4} and C^{D4} not
278 resolved). IR (solid, ν/cm^{-1}) 3211 (br s), 1729 (m), 1635 (w), 1600 (w),
279 1475 (w), 1409 (m), 1344 (w), 1313 (m), 1268 (m), 1235 (m), 1165 (m),
280 1138 (m), 1076 (m), 1030 (m), 950 (m), 826 (s), 786 (s), 753 (m), 688 (m),
281 652 (m), 605 (m). ESI-MS (MeCN): m/z 405.6 [M - 2PF₆]²⁺ (calc. 405.6). HR
282 ESI-MS m/z : 405.5628 [M - 2PF₆]²⁺ (base peak, calc. 405.5623), 810.1187 [M
283 - H - 2PF₆]⁺ (calc. 810.1173). UV/VIS λ / nm (CH₃CN, 3.63×10^{-5} mol dm⁻³)
284 (ϵ / dm³ mol⁻¹ cm⁻¹) 274 (51000), 284 sh (43500), 308 (45000), 330 sh
285 (37000), 491 (18500). Satisfactory elemental analysis could not be obtained
286 (see text).

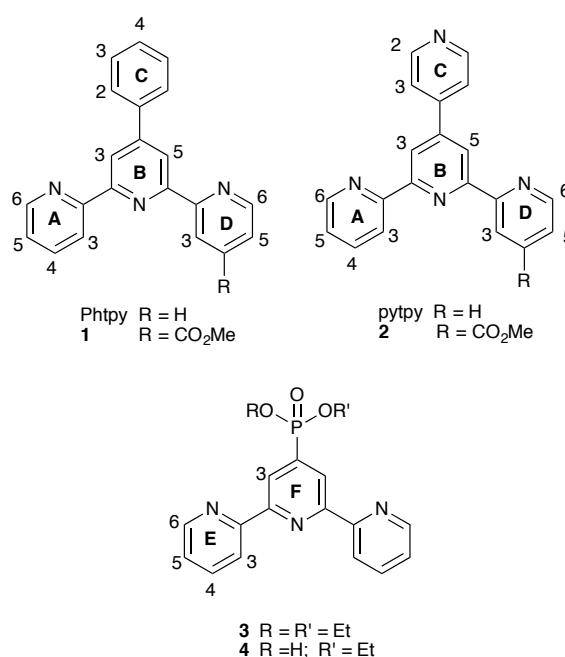
287

288 **Crystal structure determination of 1**

289 Data were collected on a Bruker-Nonius Kappa APEX diffractometer; data
290 reduction, solution and refinement used APEX2²¹ and SHELX13.²²
291 Absorption correction was made using the program 'sadabs', as part of the
292 'scale' package in AEPX2 software.²¹ The ORTEP plot was produced with
293 Mercury v. 3.0^{23,24} which was also used for structure analysis. C₂₃H₁₇N₃O₂, M
294 = 367.40, colorless plate, crystal dimensions 0.25 × 0.13 × 0.03 mm,
295 monoclinic, space group P2₁/c, $a = 9.9644(9)$, $b = 9.0359(8)$, $c =$
296 $20.0424(17)$ Å, $\beta = 96.975(6)^\circ$, $U = 1791.2(3)$ Å³, $Z = 4$, $D_c = 1.362$ Mg m⁻³,
297 $\mu(\text{Cu-K}\alpha) = 8.224$ mm⁻¹, $T = 123$ K. Total 18887 reflections, 3181 unique,
298 $R_{\text{int}} = 0.0428$. Refinement of 2763 reflections (254 parameters) with I
299 $> 2\sigma(I)$ converged at final $R1 = 0.0378$ ($R1$ all data = 0.0439), $wR2 = 0.1009$

300 ($wR2$ all data = 0.1048), gof = 1.064. CCDC 983369 contains the
 301 supplementary crystallographic data for this paper. These data can be
 302 obtained, free of charge, via
 303 <http://www.ccdc.cam.ac.uk/products/csd/request/> (or from the Cambridge
 304 Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax:
 305 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

306



307

308 Scheme 1. Structures of ligands **1–4** and of Phtpy and pytpy, with atom
 309 numbering used for NMR spectroscopic assignments; when $R = H$, ring A =
 310 ring D.

311

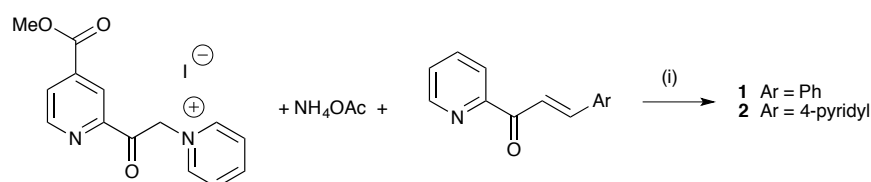
312 Results and discussion

313 Synthesis and characterization of ligands **1** and **2**

314 Compounds **1** and **2** (Scheme 1) are the 4'-phenyl and 4'-(4-pyridyl)
 315 analogues of 4'-tolyl-2,2':6,2''-terpyridine, the preparation and homoleptic
 316 ruthenium(II) complex of which were reported a decade ago by Potvin and

317 coworker.²⁵ Scheme 2 shows the Kröhnke synthesis of **1** and **2** which
318 yielded the compounds in 33 and 89%, respectively, as white solids. In the
319 electrospray mass spectrum of **1**, the base peak ($m/z = 338.0$) arises from
320 the $[M+H]^+$ ion, and a lower intensity peak at $m/z = 390.0$ was assigned to
321 $[M+Na]^+$. Corresponding peaks at $m/z 369.2$ and 391.1 in the mass spectrum
322 of **2** were also observed. The 1H and ^{13}C NMR spectra of **1** and **2** were fully
323 assigned with COSY, HMQC and HMBC techniques and were consistent with
324 the inequivalence of the outer pyridine rings of the tpy domain (Scheme 1)
325 and the presence of the ester group.

326



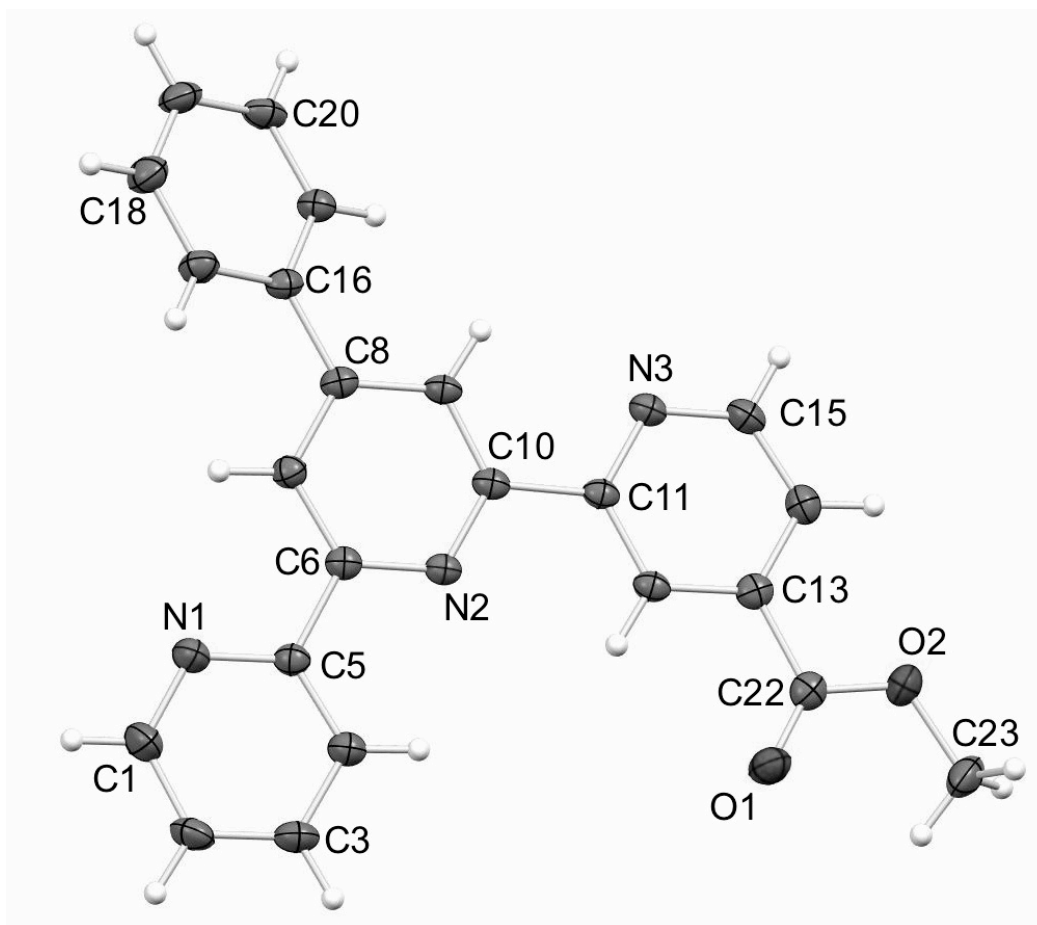
328

329 Scheme 2. Synthetic route to ligands **1** and **2**. Conditions: (i) MeOH, reflux.

330

331 Single crystals of **1** were grown by slow evaporation from a $CHCl_3$ solution of
332 the compound and the structure (Figure 1) was confirmed by X-ray
333 diffraction. Important bond parameters are given in the figure caption. The
334 tpy unit adopts a *trans,trans*-conformation, which is expected for a non-
335 protonated ligand. The tpy domain is essentially planar (the angles between
336 the least squares planes through the rings containing N1/N2 and N2/N3 =
337 5.5 and 4.5°); the phenyl ring is twisted 27.6° with respect to the pyridine
338 ring to which it is attached, consistent with minimizing H...H repulsions
339 between the two rings. The dominant packing interactions are (i) face-to-

340 face π -stacking of tpy domains across inversion centres, (ii) $H_{\text{methyl}} \dots N_{\text{pyridine}}$
 341 contacts ($H23A \dots N1^i = 2.98$, $H23B \dots N1^i = 2.81$ Å, symmetry code $i = 1+x, 1+y,$
 342 z), and (iii) $N_{\text{pyridine}} \dots HC$ contacts ($N3 \dots H3A^{ii} - C3^{ii} = 2.57$ Å, symmetry code ii
 343 $= x, 3/2 - y, 1/2 + z$).
 344



345
 346 Fig. 1. ORTEP representation of the structure of **1** (ellipsoids plotted at 50%
 347 probability level). Selected bond parameters: $N1-C1 = 1.342(2)$, $N1-C5 =$
 348 $1.3386(19)$, $N2-C6 = 1.3415(18)$, $N2-C10 = 1.3412(17)$, $N3-C11 =$
 349 $1.3463(17)$, $N3-C15 = 1.3295(19)$, $C13-C22 = 1.4993(19)$, $O1-C22 =$
 350 $1.2052(18)$, $C22-O2 = 1.3309(18)$, $O2-C23 = 1.4524(18)$ Å; $C5-N1-C1 =$
 351 $117.26(13)$, $C6-N2-C10 = 117.72(12)$, $C15-N3-C11 = 117.80(12)$, $O1-C22-$

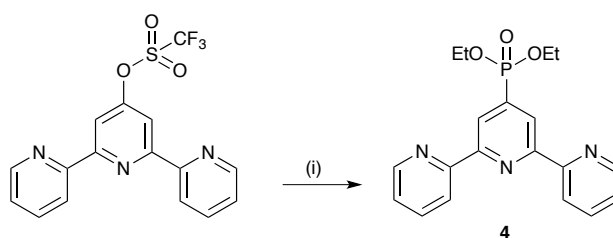
352 O2 = 124.63(13), O1-C22-C13 = 124.21(13), O2-C22-C13 = 111.15(12),
353 C22-O2-C23 = 117.15(12)°.

354

355

356 The diethylphosphonate-functionalized ligand **3** has previously been
357 reported by Grätzel and coworkers.²⁰ The literature synthesis (which gives
358 **3** in 72.3% yield) involves the [Pd(PPh₃)₄] catalysed reaction of 4'-bromo-
359 2,2':6',2''-terpyridine with diethyl phosphite in NEt₃ (95 °C for 3 h) followed
360 by dissolution of the mixture in MeOH and chromatographic workup. We
361 adopted the more convenient strategy shown in Scheme 2. The 4'-triflate-
362 functionalized tpy was readily prepared according to the route described by
363 Potts et al,¹⁹ and diethylphosphonate for triflate substitution occurs under
364 microwave conditions to give **4** in 84% yield. The NMR spectroscopic data
365 for **4** were consistent with those published.²⁰

366



368 Scheme 3. Synthesis of phosphonate **4**. Conditions: (i) [Pd(PPh₃)₄], NEt₃,

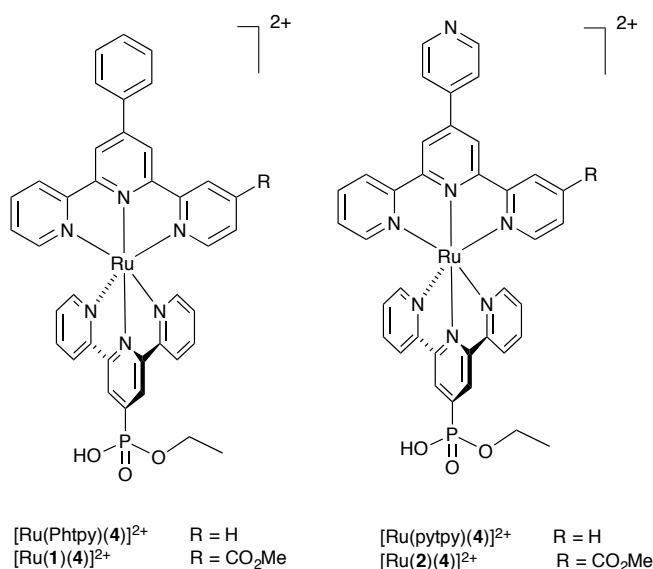
369 HP(O)(OEt)₂, MeCN, 140 °C, 30 min.

370

371 **Synthesis and characterization of heteroleptic ruthenium(II)**

372 **complexes**

373 The heteroleptic complexes discussed in this section are summarized in
 374 Scheme 4. Heteroleptic $[\text{Ru}(\text{Xtpy})(\text{Ytpy})]^{2+}$ complexes are typically prepared
 375 by first preparing an insoluble, paramagnetic ruthenium(III) complex
 376 $[\text{Ru}(\text{Xtpy})\text{Cl}_3]$, and treating this crude material with Ytpy in the presence of
 377 *N*-ethylmorpholine which acts as a reducing agent.²⁶ The precursor for the
 378 formation of the new ruthenium(II) complexes was $[\text{Ru}(\mathbf{3})\text{Cl}_3]$, prepared by
 379 reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with compound **3** in MeOH under reflux. $[\text{Ru}(\mathbf{3})\text{Cl}_3]$
 380 was isolated as a brown solid.



382 Scheme 4. Structures of the heteroleptic complex cations prepared as
 383 hexafluoridophosphate salts.

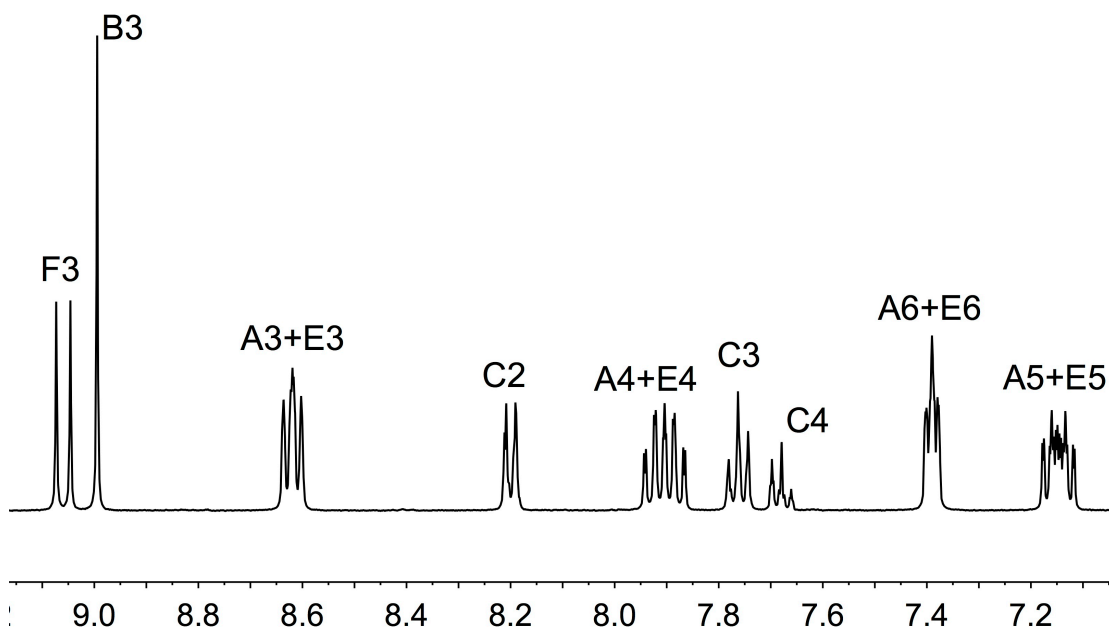
384

385 Model compounds containing Phtpy and pytpy (Scheme 1) were first
 386 prepared by reaction of $[\text{Ru}(\mathbf{3})\text{Cl}_3]$ with Phtpy and pytpy in the presence of
 387 *N*-ethylmorpholine. After anion exchange and chromatographic workup,
 388 followed by a second anion exchange (to remove $[\text{NO}_3]^-$ introduced from
 389 aqueous KNO_3 in the eluant), the ruthenium(II) salts were isolated as red
 390 solids. Electrospray mass spectrometric and NMR spectroscopic data were

391 consistent with the isolated products being complexes of the monoester **4**
392 (Scheme 2) rather than the diester **3**. Partial hydrolysis of **3** during
393 synthesis of ruthenium(II) complexes is known to occur under conditions of
394 high temperature reflux²⁰ or heating in DMF at 60 °C.²⁷ The second
395 hydrolysis step to the phosphonic acid needs acidic conditions or treatment
396 with Me₃SiBr. The ESI mass spectrum of [Ru(Phtpy)(**4**)]PF₆]₂ showed the
397 base-peak envelope at *m/z* 751.4 with an appropriate isotope pattern for
398 the ion [M – H – 2PF₆]⁺. The loss of H⁺ is consistent with the presence of the
399 acidic P–OH group. The high resolution ESI (HR-ESI) mass spectrum was
400 also recorded and peaks arising from [M – H – 2PF₆]⁺ and [M – 2PF₆]²⁺
401 confirmed the identity of [Ru(Phtpy)(**4**)]²⁺. The HR-ESI mass spectrum of
402 [Ru(pytpy)(**4**)]PF₆]₂ exhibited peak envelopes arising from the [M – H –
403 2PF₆]⁺ and [M – 2PF₆]²⁺ ions, and the latter was also observed in the ESI
404 mass spectrum.

405 The ¹H and ¹³C NMR spectra of CD₃CN solutions of
406 [Ru(Phtpy)(**4**)]PF₆]₂ and [Ru(pytpy)(**4**)]PF₆]₂ were consistent with the
407 presence of two tpy environments in each complex. A representative
408 spectrum is shown in Figure 2. Spectra were assigned using 2D methods
409 (COSY, HMQC and HMBC); 400 MHz ¹H spectra were routinely recorded for
410 better resolution of signals and 500 MHz ¹H for 2D measurements. The most
411 characteristic feature of the spectrum in Figure 2 is the appearance of a
412 singlet for protons H^{B3} (Phtpy ligand) and a doublet for the corresponding
413 protons H^{F3} (ligand **4**) arising from ³¹P-¹H coupling (11 Hz). For
414 [Ru(Phtpy)(**4**)]PF₆]₂, signals at δ 4.05 and 1.31 ppm in the ¹H NMR
415 spectrum and their relative integrals with respect to resonances in the

416 aromatic region were consistent with the monoester **4**; in the ^{13}C NMR
417 spectrum, corresponding signals at δ 61.8 and 17.5 ppm were observed.



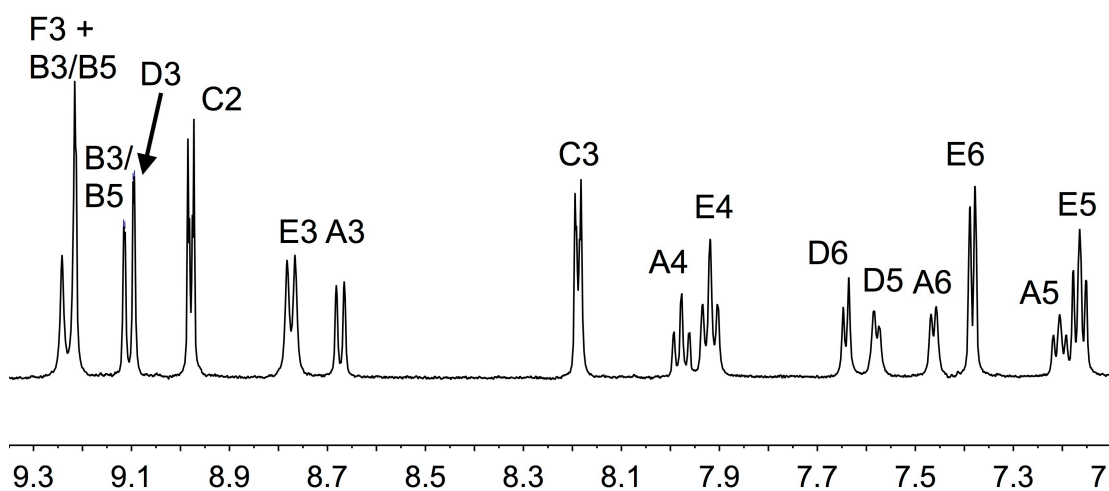
418
419 Fig. 2 Aromatic region of the 400 MHz ^1H NMR spectrum of
420 $[\text{Ru}(\text{Phtpy})(\mathbf{4})][\text{PF}_6]_2$. See Scheme 1 for ring labelling.

421

422 The preparations of $[\text{Ru}(\mathbf{1})(\mathbf{4})][\text{PF}_6]_2$ and $[\text{Ru}(\mathbf{2})(\mathbf{4})][\text{PF}_6]_2$ were
423 carried out in an analogous manner to those of $[\text{Ru}(\text{Phtpy})(\mathbf{4})][\text{PF}_6]_2$ and
424 $[\text{Ru}(\text{pytpy})(\mathbf{4})][\text{PF}_6]_2$. The base peak in the ESI mass spectrum of
425 $[\text{Ru}(\mathbf{1})(\mathbf{4})][\text{PF}_6]_2$ was assigned to $[\text{M} - \text{H} - 2\text{PF}_6]^+$; for $[\text{Ru}(\mathbf{2})(\mathbf{4})][\text{PF}_6]_2$, the
426 main peak envelope arose from $[\text{M} - 2\text{PF}_6]^{2+}$. High resolution ESI data
427 showed peaks arising from $[\text{M} - 2\text{PF}_6]^{2+}$ and $[\text{M} - \text{H} - 2\text{PF}_6]^+$ for both
428 complexes. The solution ^1H and ^{13}C NMR spectra (assigned by 2D methods)
429 of $[\text{Ru}(\mathbf{1})(\mathbf{4})][\text{PF}_6]_2$ and $[\text{Ru}(\mathbf{2})(\mathbf{4})][\text{PF}_6]_2$ were consistent with the presence
430 of the symmetrical ligand **4** and one asymmetrical ligand. Figure 3 shows
431 part of the ^1H NMR spectrum of $[\text{Ru}(\mathbf{2})(\mathbf{4})][\text{PF}_6]_2$. The doublet for H^{F3} ($J_{\text{PH}} =$
432 11.5 Hz) overlaps with one of the two doublets ($J_{\text{HH}} 1.3$ or 1.5 Hz) arising

433 from H^{B3} and H^{B5}. Pairs of signals for H^{E3}/H^{A3}, H^{E4}/H^{A4}, H^{E5}/H^{A5} and H^{E6}/H^{A6}
 434 with relative integrals 2 : 1 appear for the unsubstituted pyridine rings in
 435 ligand **4** and for ligands **1** or **2**, respectively The signal for H^{D3} ($J_{HH} = 1.4$ Hz)
 436 was distinguished from those of H^{B3} and H^{B5} by its COSY signature. The
 437 relative integrals for the signals for the ethyl groups in **4** in both complexes
 438 were consistent with the monoester.

439



440 Fig. 3 Aromatic region of the 500 MHz ¹H NMR spectrum of
 441

442 [Ru(**2**)(**4**)] [PF₆]₂. See Scheme 1 for ring labelling.

443

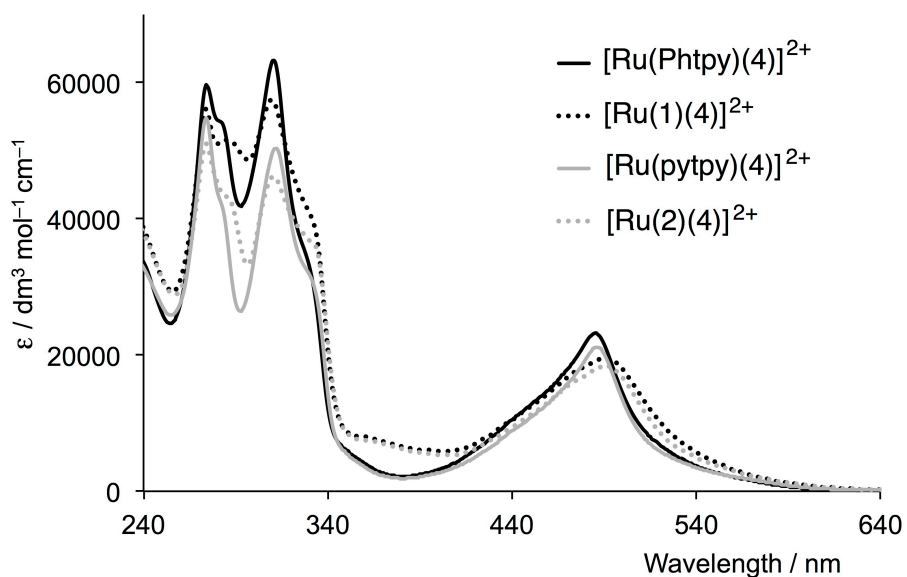
444 Yields of [Ru(Phtpy)(**4**)] [PF₆]₂ and [Ru(**1**)(**4**)] [PF₆]₂ were >80%
 445 yield, but for the complexes containing pytpy, lower yields of ca. 25% were
 446 observed, due, in part, to formation of some of the N-protonated species. We
 447 noted changes in the ¹H NMR spectra which were consistent with
 448 protonation of samples in solution. Satisfactory elemental analysis could not
 449 always be obtained for the hexafluoridophosphate salts, probably due to
 450 small amounts of residual NH₄PF₆. Traces of [NH₄]⁺ were seen in the ¹H NMR
 451 spectra (δ 6.02, $J(^{14}\text{N}^1\text{H}) = 53$ Hz) of some batches of the complexes. X-ray

452 quality crystals of solvated $[\text{Ru}(\text{pytpy})(\mathbf{4})][\text{PF}_6]_2$ were obtained, but only
453 preliminary structural data could be obtained because of persistent
454 twinning problems. However, these data were sufficient to confirm the
455 presence of the monoester ligand $\mathbf{4}$ and the octahedral coordination
456 environment of the ruthenium(II) centre bound by the bis(chelating) donor
457 sets of pytpy and ligand $\mathbf{4}$. Despite attempts, X-ray quality single crystals of
458 the other ruthenium(II) complexes were not obtained.

459

460 **Absorption and emission spectroscopic properties**

461 The absorption spectra of MeCN solutions of the complexes are shown in
462 Figure 4. Each exhibits a series of high-energy bands arising from ligand-
463 based, spin-allowed transitions, and a broad MLCT band in the visible
464 region. The values of λ_{max} for the MLCT absorptions (485–491 nm, see
465 experimental section) compare with 488 nm for both $[\text{Ru}(\text{Phtpy})_2][\text{PF}_6]_2$ ²⁶
466 and $[\text{Ru}(\text{pytpy})_2][\text{PF}_6]_2$.²⁸ The spectra for $[\text{Ru}(\text{Phtpy})(\mathbf{4})][\text{PF}_6]_2$ and
467 $[\text{Ru}(\text{pytpy})(\mathbf{4})][\text{PF}_6]_2$ are similar to one another and to those of the
468 homoleptic complexes $[\text{Ru}(\text{Phtpy})_2][\text{PF}_6]_2$ ²⁶ and $[\text{Ru}(\text{pytpy})_2][\text{PF}_6]_2$.²⁸ The
469 introduction of the methyl ester substituent leads to a change in the
470 appearance of the absorption maxima (Figure 4), the trend being the same
471 on going from $[\text{Ru}(\text{Phtpy})(\mathbf{4})][\text{PF}_6]_2$ to $[\text{Ru}(\mathbf{1})(\mathbf{4})][\text{PF}_6]_2$, and from
472 $[\text{Ru}(\text{pytpy})(\mathbf{4})][\text{PF}_6]_2$ to $[\text{Ru}(\mathbf{2})(\mathbf{4})][\text{PF}_6]_2$. The small red-shift in the MLCT
473 band upon introduction of the CO₂Me group is consistent with that observed
474 on going from $[\text{Ru}(\text{ttpy})_2]^{2+}$ to $[\text{Ru}(4\text{-MeO}_2\text{Cttpy})_2]^{2+}$ (ttpy = 4'-tolyl-
475 2,2':6',2''-terpyridine; 4-MeO₂Cttpy = 4-carboxymethyl-4'-tolyl-2,2':6',2''-
476 terpyridine).²⁵



478

479 Fig. 4. Absorption spectra of MeCN solutions of $[\text{Ru}(\text{Phtpy})(\mathbf{4})][\text{PF}_6]_2$,
 480 $[\text{Ru}(\text{pytpy})(\mathbf{4})][\text{PF}_6]_2$, $[\text{Ru}(\mathbf{1})(\mathbf{4})][\text{PF}_6]_2$ and $[\text{Ru}(\mathbf{2})(\mathbf{4})][\text{PF}_6]_2$. See
 481 experimental section for concentrations.

482

483 Excitation into the MLCT band of each of $[\text{Ru}(\text{Phtpy})(\mathbf{4})][\text{PF}_6]_2$ and
 484 $[\text{Ru}(\mathbf{1})(\mathbf{4})][\text{PF}_6]_2$ (in degassed MeCN at room temperature) gives rise to a
 485 weak emission at 647 and 665 nm, respectively, with a quantum yield below
 486 the detection limit of the instrument (QY <1%).

487

488 **Electrochemical properties**

489 The complexes are electrochemically active and cyclic voltammetric data are
 490 given in Table 1. The reversible oxidation observed for each complex arises
 491 from the $\text{Ru}^{2+}/\text{Ru}^{3+}$ couple. For the parent $[\text{Ru}(\text{tpy})_2]^{2+}$, this process occurs
 492 at +0.918 V,²⁶ and introducing electron-donating phenyl groups shifts it to
 493 lower potential (+0.895 V in $[\text{Ru}(\text{Phtpy})_2][\text{PF}_6]_2$).²⁶ Replacing one phenyl
 494 substituent by the electron-withdrawing phosphonic ester group shifts the

495 oxidation to +0.93 V (Table 1). A similar trend is seen on comparing the
 496 Ru²⁺/Ru³⁺ potential in [Ru(pytpy)₂][PF₆]₂ (+0.95 V)²⁸ with that in
 497 [Ru(pytpy)(**4**)]PF₆]₂ (+1.01 V). Introduction of the methyl ester unit results
 498 in a 0.03 V shift to more positive potential on going from
 499 [Ru(Phtpy)(**4**)]PF₆]₂ to [Ru(**1**)(**4**)]PF₆]₂, or from [Ru(pytpy)(**4**)]PF₆]₂ to
 500 [Ru(**2**)(**4**)]PF₆]₂. This is consistent with the trend observed from
 501 [Ru(tpy)₂]²⁺ to [Ru(4-MeO₂Cttpy)₂]²⁺.²⁵ A series of ligand-based reduction
 502 processes is observed for each complex (Table 1), consistent with
 503 expectations based on related compounds.

504

505

506 Table 1. Cyclic voltammetric data for the ruthenium(II) complexes with
 507 respect to Fc/Fc⁺ in MeCN solutions with [tBu₄N][PF₆] as supporting
 508 electrolyte, and a scan rate of 0.1 V s⁻¹ (ir = irreversible; qr = quasi-
 509 reversible).

Complex	$E_{1/2}^{\text{ox}} / \text{V}$	$E_{1/2}^{\text{red}} / \text{V}$
[Ru(Phtpy)(4)]PF ₆] ₂	+0.93	-1.68, -1.93 ^{qr}
[Ru(1)(4)]PF ₆] ₂	+0.96	-1.49, -1.90, -2.23 ^{ir}
[Ru(pytpy)(4)]PF ₆] ₂	+1.01	-1.57, -2.00 ^{ir}
[Ru(2)(4)]PF ₆] ₂	+1.04	-1.43, -1.85

510

511

512 Conclusions

513 We have prepared and characterized four new heteroleptic complexes
 514 containing {Ru(tpy)₂}-cores. One ligand contains a phosphonate ester group

515 designed to act as an anchoring group to metal oxide surfaces. The second
516 ligand is Phtpy or pytpy in the model systems and contains a methyl ester
517 functionality in the second of each pair of complexes. This provides a
518 suitable site for variable functionalization, for example, through
519 transesterification. We plan to use the heteroleptic complexes as a starting
520 point for development of ruthenium(II) dyes suited for sensitization of p-
521 type semiconductors.

522

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528 absorption spectroscopic measurements.

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