Electronic Supplementary Information for:

Novel ruthenium and iridium complexes of N-substituted carbazole as triplet photosensitisers

Junsí Wang¹, Yue Lu¹, William McCarthy¹, Robert Conway-Kenny¹, Brendan Twamley¹, Jianzhang Zhao⁵ and Sylvia M. Draper*¹

¹School of Chemistry, Trinity College Dublin, D2, Ireland
⁵State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, E-208 West Campus, 2 Ling-Gong Road, Dalian, 116024, P. R. China.

*smdraper@tcd.ie

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1.0 X-ray crystallography

**Experimental:** Data for RuC were collected on a Bruker APEX DUO using Cu Kα radiation (\( \lambda = 1.54184 \) Å). The sample was mounted on a Mitegen cryoloop and data collected at 100(2) K (Oxford Cobra cryosystem). Bruker APEX\(^1\) software was used to collect and reduce data, determine the space group, solve and refine the structures. Absorption corrections were applied using SADABS 2014.\(^2\) All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to calculated positions using a riding model with appropriately fixed isotropic thermal parameters. CCDC no. 1566335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

**Discussion:** The complex RuC displays a distorted octahedrally coordinated Ru centre (\( \Sigma = 72.9(6) ^\circ \))\(^3\) surrounded by two bipys and a carbazole ligand, with Ru-N bonds lengths of 2.054(4)-2.086(3) Å, see Figure S1. The ligand is not planar, with a significant twist of 48.46(9) \(^\circ\) between the bipy and the carbazole moieties. There is also an angle of 113.99(10) \(^\circ\) between the carbazole and the hexyl arm. The extended structure does not show the expected Ru bipy packing motifs as seen in the literature.\(^4\) In the structure of RuC, there are no strong intermolecular interactions or H-bonding. Weaker interactions are present and a Hirshfeld surface analysis\(^5\) shows the majority of these are CH...F and CH...π interactions (Figure S2 and S3).

**Figure S1.** Partially labelled atomic displacement (50% probability) image of RuC with both PF\(_6\) counter anions removed for clarity.

**Table 1** Crystal data and structure refinement for RuC

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<th>Parameter</th>
<th>Value</th>
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<tbody>
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<td>Identification code</td>
<td>TCD817</td>
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<tr>
<td>Empirical formula</td>
<td>( C_{50}H_{43}F_{12}N_{7}P_{2}Ru )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1132.92</td>
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<tr>
<td>Temperature/K</td>
<td>100(2)</td>
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<td>Crystal system</td>
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<td>( c/Å )</td>
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<td>( \alpha/° )</td>
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<tr>
<td>( \beta/° )</td>
<td>80.675(2)</td>
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<tr>
<td>( \gamma/° )</td>
<td>83.0251(18)</td>
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<td>Property</td>
<td>Value</td>
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<td>--------------------------------</td>
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<tr>
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<tr>
<td>( \rho_{\text{calc}} ) g/cm(^3)</td>
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<td>( \mu ) mm(^{-1})</td>
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<tr>
<td>F(000)</td>
<td>1148.0</td>
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<tr>
<td>Crystal size/mm(^3)</td>
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</tr>
<tr>
<td>Radiation</td>
<td>CuK( \alpha ) (( \lambda ) = 1.54178)</td>
</tr>
<tr>
<td>2( \theta ) range for data collection/°</td>
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</tr>
<tr>
<td>Index ranges</td>
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</tr>
<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
<td>8598 [R(<em>{\text{int}}) = 0.0686, R(</em>{\text{sigma}}) = 0.0548]</td>
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<tr>
<td>Data/restraints/parameters</td>
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<tr>
<td>Goodness-of-fit on F(^2)</td>
<td>0.994</td>
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<tr>
<td>Final R indexes [I&gt;=2( \sigma ) (I)]</td>
<td>R(_1) = 0.0494, wR(_2) = 0.1277</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R(_1) = 0.0640, wR(_2) = 0.1380</td>
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<tr>
<td>Largest diff. peak/hole / e Å(^3)</td>
<td>1.31/-0.35</td>
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</table>

**CCDC no.** 1566335

**Figure S2.** Hirschfeld surface mapped with \( d_{\text{norm}} \) for RuC over the range -0.29 to 1.37. PF\(_6\) anions and a neighbouring cation with close contacts are shown with some of the distances involved. The CH...π of C54...C4i is ca. 3.56Å.
Figure S3. Fingerprint plots of RuC broken down into contributions from specific pairs of atom types. The blue highlighted section of the plot is (A) internal H to external F (CH\(_2\)F interactions) and (B) internal C to external H contributions which includes the CH\(_\pi\) interactions. The corresponding highlighted Hirshfeld plot is on the right.

Table S2. Hydrogen bonds for RuC with d(D...A) maximum \(=\)3.5 Å [Å and °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
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<tbody>
<tr>
<td>C(8)-H(8)...F(2)#1</td>
<td>0.95</td>
<td>2.52</td>
<td>3.389(6)</td>
<td>151.5</td>
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<tr>
<td>C(9)-H(9)...F(5)#1</td>
<td>0.95</td>
<td>2.66</td>
<td>3.252(5)</td>
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<tr>
<td>C(9)-H(9)...F(6)#1</td>
<td>0.95</td>
<td>2.48</td>
<td>3.270(5)</td>
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<tr>
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<td>2.38</td>
<td>3.305(6)</td>
<td>164.0</td>
</tr>
<tr>
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<td>0.95</td>
<td>2.62</td>
<td>3.329(6)</td>
<td>131.7</td>
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<tr>
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<td>2.74</td>
<td>3.451(8)</td>
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<tr>
<td>C(37)-H(37)...F(4)</td>
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<td>2.57</td>
<td>3.197(6)</td>
<td>123.4</td>
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<td>C(42)-H(42)...F(3)#5</td>
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<td>2.52</td>
<td>3.423(5)</td>
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<td>C(44)-H(44)...F(1)#5</td>
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<td>2.27</td>
<td>3.051(6)</td>
<td>138.7</td>
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<td>C(48)-H(48)...F(7)#6</td>
<td>0.95</td>
<td>2.62</td>
<td>3.220(5)</td>
<td>121.8</td>
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<tr>
<td>C(49)-H(49)...F(11)#6</td>
<td>0.95</td>
<td>2.54</td>
<td>3.409(6)</td>
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<tr>
<td>C(50)-H(50)...F(11)#5</td>
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<td>2.49</td>
<td>3.300(5)</td>
<td>143.2</td>
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<tr>
<td>C(53)-H(53)...F(8)#5</td>
<td>0.95</td>
<td>2.59</td>
<td>3.469(7)</td>
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<tr>
<td>C(53)-H(53)...F(12)#5</td>
<td>0.95</td>
<td>2.58</td>
<td>3.452(6)</td>
<td>153.1</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

\#1 \(x,y-1,z\) \#2 \(-x+1,-y+1,-z+1\) \#3 \(x-1,y,z-1\)
\#4 \(-x+1,-y,z+1\) \#5 \(x-1,y,z\) \#6 \(-x+1,-y+1,-z+2\)
2.0 Synthesis and characterisation

L1: 3,6-dibromocarbazole (500.0 mg, 1.528 mmol), 1-bromohexane (380.1 mg, 2.322 mmol), KOH (171.1 mg, 3.056 mmol) were added to 30 mL THF. The mixture was heated to reflux for 2 h under stirring and then allowed to cool to room temperature, before added ice-cold water (30 mL) to the mixture. The product was extracted three times with dichloromethane (3 × 25 mL). The combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (CH₂Cl₂/hexane, 1:2, v/v). The product was obtained as a white solid. Yield: 445.0 mg, 70.3%. ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.17-8.17 (m, 2H), 7.59 (d, 1H, J = 1.4 Hz), 7.57 (d, 1H, J = 1.4 Hz), 7.31 -7.29 (m, 2H), 4.29 (t, 2H, J = 7.2 Hz), 1.87-1.81 (m, 2H), 1.35-1.27 (m, 6H), 0.90 (t, 3H, J = 6.8 Hz).

L2: L1 (300.0 mg, 0.733 mmol), [Pd(PPh₃)₂Cl₂] (25.6 mg, 0.036 mmol), PPh₃ (19.6 mg, 0.073 mmol) and CuI (13.7 mg, 0.073 mmol) were added to a round bottom flask under argon atmosphere. Degassed dry triethylamine (30 mL) was added to the mixture stirring gently and then trimethylsilylacetylene (287.0 mg, 2.933 mmol) was added via syringe. The mixture was heated to 80 °C overnight. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was subjected to column chromatography on silica gel (CH₂Cl₂/hexane, 1:5, v/v). The pale-yellow oil-like intermediate was obtained. Yield: 183.2 mg, 56.3%. ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.22 (s, 2H), 7.61-7.59 (m, 2H), 7.34 (s, 1H), 7.31 (s, 1H), 4.30 (t, 2H, J = 6.7 Hz), 1.90-1.86 (m, 2H), 1.37-1.26 (m, 6H), 0.89 (t, 3H, J = 6.5 Hz), 0.31 (s, 18H). The trimethylsilyl-protected intermediate (183.2 mg, 0.413 mmol) and KOH (95.0 mg, 1.667 mmol) were dissolved in methanol (20 mL) under a nitrogen atmosphere. After stirring for 2 h at room temperature, the mixture was washed with water (20 mL) and extracted into dichloromethane (3 × 25 mL). The combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel (CH₂Cl₂/hexane, 1:5, v/v). A pale-yellow oil-like product was obtained. Yield: 118 mg, 95.6%. ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.24 (s, 2H), 7.64 (d, 1H, J = 1.4 Hz), 7.62 (d, 1H, J = 1.4 Hz), 7.38 (s, 1H), 7.35 (s, 1H), 4.30 (t, 2H, J = 6.7 Hz), 3.11 (s, 2H), 1.89-1.85 (m, 2H), 1.38-1.28 (m, 6H), 0.90 (t, 3H, J = 6.9 Hz).

L3: 3-bromocarbazole (1.000 g, 4.065 mmol) 1-bromohexane (1.058 g, 6.412 mmol) and KOH (0.790 g, 14.107 mmol) were added to THF (30mL). The mixture was refluxed at 70°C for 2 h with stirring. After cooling to room temperature, the mixture was washed with ice-cold water and extracted into dichloromethane (3×25 mL). The combined organic layers were dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/hexane, 1:2, v/v). The colourless liquid product was isolated by removing the solvent under reduced pressure. Yield: 1.323 g, 98.6%. ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.24 (d, 1H, J = 1.9 Hz), 8.07 (d, 1H, J = 7.8 Hz), 7.58-7.50 (m, 2H), 7.44-7.42 (m, 1H), 7.31-7.27 (m, 2H), 4.38 (t, 2H, J = 7.3 Hz), 1.19-1.85 (m, 2H), 1.35-1.33 (m, 6H), 0.90 (t, 3H, J = 7.1 Hz)⁴ ESI-LC-MS: cal. for ([M+H]+) m/z = 330.0852, found m/z = 330.0848.
Under an argon atmosphere, \([\text{Pd(PPh}_3^3\text{)}_2\text{Cl}_2]\) (162.0 mg, 0.231 mmol), \(\text{PPh}_3\) (121.0 mg, 0.461 mmol) and \(\text{CuI}\) (88.0 mg, 0.461 mmol) were added to a three neck round bottom flask. \(\text{L3}\) (1.5233 g; 4.6123 mmol) as a degassed dry triethylamine (30 mL) solution was added to the mixture gently and then trimethylsilylthyn (0.453 g; 4.6123 mmol; 0.65 mL) was gently added via a springe. The mixture was refluxed at 90°C overnight with stirring. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (\(\text{CH}_2\text{Cl}_2/\text{Hexane}, 1:8, \text{v/v})\). The viscous, pale yellow liquid was isolated by removing the solvent system under reduced pressure. Yield: 0.942 g; 59%. This trimethylsilyl-protected intermediate (0.942 g; 2.711 mmol), \(\text{KF}\) (0.629 g, 108.45 mmol) and \(\text{KOH}\) (0.629 g; 108.45 mmol) were added to 50 mL methanol under an argon atmosphere. The mixture was stirring at room temperature for 3 h washed with water and extracted with dichloromethane three times (3 × 25 mL). The combined organic layers were dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the solvent was removed under reduced pressure to give an oil-like, pale-yellow liquid. The crude product was purified by column chromatography on silica gel (\(\text{CH}_2\text{Cl}_2/\text{Hexane}, 1:8, \text{v/v})\). Yield: 0.663 g, 89%.

\[\text{1}^1\text{H NMR (400 MHz, CDCl}_3, 298 \text{K)} \delta 8.26 \text{(d, 1H, } J = 1.2 \text{ Hz)}, 8.07 \text{(d, 1H, } J = 7.8 \text{ Hz)}, 7.59 \text{(dd, 1H, } J_1 = 8.5 \text{ Hz, } J_2 = 1.5 \text{ Hz)}, 7.51-7.46 \text{(m, 1H), 7.42-7.40 (m, 1H), 7.35-7.33 (m, 1H), 7.27-7.23 (m, 2H), 4.29 (t, 2H, } J = 7.1 \text{ Hz)}, 3.07 \text{(s, 1H), 1.90-1.82 (m, 2H), 1.31-1.28 (m, 6H), 0.86 (t, 3H, } J = 7.1 \text{ Hz).}\]

\(\text{RuCRu: Under an argon atmosphere, L2} (28.1 \text{ mg, 0.094 mmol}), \{\text{Ruthenium(II)(2,2’-dipyridine)}_2\text{[5-bromo-2,2’-bipyridine]}\} \text{(300.0 mg, 0.320 mmol)}, \{\text{Pd(PPh}_3^3\text{)}_2\text{Cl}_2\} \text{(3.5 mg, 0.005 mmol)}, \text{PPh}_3 \text{(2.7 mg, 0.010 mmol) and } \text{CuI} \text{(1.9 mg, 0.010 mmol)} \text{ were added in 20 mL of a dry mixture solvent (CH}_3\text{CN/(CH}_3\text{CH}_2\text{)}_3\text{N, 1:1, v/v). The mixture was stirred and heated at 60 °C overnight. The solvent was removed under reduced pressure, and the solid was dissolved in the minimum of acetonitrile. A saturated aqueous solution of potassium hexafluorophosphate was added dropwise to the solution to give a crude product as a dark-orange solid. After filtering, the crude product was purified by column chromatography on silica gel (CH}_3\text{CN/H}_2\text{O/sat. KNO}_3, 100: 9: 1, v/v/v) and then retreated with a saturated aqueous solution of potassium hexafluorophosphate. A red precipitate was collected by filtration, and washed with water and diethyl ether. Yield: 25.2 mg, 13.3%. \text{1}^1\text{H NMR (400 MHz, CD}_3\text{CN, 298 K)} \delta 8.31-8.23 \text{(m, 12H), 8.02 (s, 2H), 7.91 (dd, 2H, } J_1 =8.5 \text{ Hz, } J_2 =1.7 \text{ Hz), 7.87-7.78 (m, 10H), 7.61-7.60 (m, 4H), 7.52 (d, 2H, } J =5.4 \text{ Hz), 7.48-7.47 (m, 4H), 7.45 (d, 2H, } J =5.4 \text{ Hz), 7.36-7.31 (m, 4H), 7.20-7.13 (m, 1H), 4.12 (t, 2H, } J =7.1 \text{ Hz), 1.58-1.52 (m, 2H), 1.02-1.00 (m, 6H), 0.57 (t, 3H, } J =6.9 \text{ Hz).} \text{13}^1\text{C NMR (100 MHz, CD}_3\text{CN, 298 K)} \delta 157.92, 157.87, 157.83, 157.45, 156.36, 153.82, 152.90, 152.71, 152.68, 152.50, 142.23, 140.29, 138.83, 138.74, 130.98, 128.56, 128.52, 128.49, 125.48, 125.37, 125.33, 125.30, 125.20, 124.81, 123.06, 112.87, 111.26, 98.96, 83.87, 44.00, 32.06, 29.39, 27.23, 23.12, 14.12. \text{MALDI-TOF-MS: calc. for } \{\text{[C}_8\text{H}_{15}\text{N}_1\text{P}_3\text{Ru}_2]\} \text{ m/z } = 1870.2498, \text{ found } m/z = 1870.2555.\]
IrC\(\text{IrCl}^+\): Under an argon atmosphere, \(\text{L}_2\) (27.9 mg, 0.093 mmol), [Iridium(I)(2-phenylpyridine)\(_2\)(5-bromo-2,2'-bipyridine)][(PF\(_6\)]\(^8^-\) (287.4 mg, 0.326 mmol), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (3.5 mg, 0.005 mmol), PPh\(_3\) (2.7 mg, 0.010 mmol) and Cul (1.9 mg, 0.010 mmol) in 20 mL, were added to a dry mixture solvent (DMF/(CH\(_3\)CH\(_2\))\(_3\)N , 1:1, v/v). After stirring, the mixture was heated at 60 °C for 10 h. The solvent was removed under reduced pressure, and the solid was dissolved in the minimum volume of acetonitrile. A saturated aqueous solution of potassium hexafluorophosphate was added dropwise to the mixture to give the crude product as an orange solid. After it was filtered, the crude product was purified by column chromatography on silica gel (CH\(_3\)CN/H\(_2\)O/sat. KNO\(_3\), 200: 9: 1, v/v/v) and retreated with a saturated aqueous solution of potassium hexafluorophosphate. The orange precipitate was collected by filtration, and washed with water and diethyl ether. Yield: 81.7 mg, 46.3%. 

\(^1\)H NMR (600 MHz, CD\(_3\)CN, 298 K) \(\delta\) 8.31-8.29 (m, 4H), 8.02-8.00 (m, 4H), 7.91 (td, 2H, \(J = 7.9\) Hz, \(J = 1.3\) Hz), 7.87-7.84 (m, 4H), 7.52-7.51 (m, 2H), 7.40-7.34 (m, 6H), 7.29-7.27 (m, 2H), 6.89-6.87 (m, 2H), 6.84-6.81 (m, 6H), 6.76 (td, 2H, \(J = 7.4\) Hz, \(J = 1.1\) Hz), 6.70 (td, 2H, \(J = 7.4\) Hz, \(J = 1.2\) Hz), 6.13 (d, 2H, \(J = 7.5\) Hz), 6.05 (d, 2H, \(J = 7.6\) Hz), 4.15 (t, 2H, \(J = 7.0\) Hz), 1.62-1.57 (m, 2H), 1.09-1.01 (m, 6H), 0.60 (t, 3H, \(J = 7.1\) Hz).

\(^{13}\)C NMR (150 MHz, CD\(_3\)CN, 298 K) \(\delta\) 168.32, 168.27, 156.23, 155.21, 152.81, 151.71, 151.05, 150.70, 150.44, 145.13, 144.98, 142.33, 141.83, 141.31, 139.60, 139.58, 132.60, 132.40, 131.50, 131.37, 131.05, 129.42, 125.97, 125.90, 125.87, 125.53, 125.38, 124.57, 124.50, 123.74, 123.62, 123.13, 120.98, 120.87, 112.75, 111.31, 100.95, 99.23, 83.88, 44.08, 32.11, 29.46, 27.29, 23.17, 14.16. MALDI-TOF-MS: calc. for ([C\(_86\)H\(_65\)N\(_9\)Ir\(_2\)]\(^+\)) \(m/z\) = 1609.4622, found \(m/z\) = 1609.4680.

RuC: Under an argon atmosphere, [Ruthenium(II)(2,2'-bipyridine)\(_2\)(5-bromo-2,2'-bipyridine)][(PF\(_6\)]\(^2^-\) \(\approx\) (0.340 g, 0.426 mmol), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (15.0 mg; 0.021 mmol), PPh\(_3\) (11.0 mg; 0.0426 mmol) and CuI (8.0 mg, 0.0426 mmol) were added to a three neck round bottom flask. A solution of \(\text{L}^4\) (0.117g; 0.4262mmol) in 30mL mixture solvent ((CH\(_3\)CH\(_2\))\(_3\)N:CH\(_3\)CN, 1:1, v/v) was transferred into the round bottom flask via a long needle. The mixture was refluxed at 90°C overnight under stirring. After cooled to room temperature, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CH\(_3\)CN/H\(_2\)O/sat. KNO\(_3\), 200: 9: 1, v/v/v) and treated with a saturated aqueous solution of KPF\(_6\). The red precipitate was collected via filtration and washed with diethyl ether. Yield: 117 mg, 24%. Slow evaporation of a solution of RuC in acetone and hexane crystals suitable for single crystal X-ray diffraction studies. 

\(^1\)H NMR (400 MHz, CD\(_3\)CN, 298 K) \(\delta\) 8.58-8.52 (m, 6H), 8.28 (s, 1H), 8.19-8.07 (m, 7H), 7.79-7.88 (m, 2H), 7.80 (d, 1H, \(J = 5.6\) Hz), 7.76-7.72 (m, 3H), 7.60-7.55 (m, 4H), 7.49-7.41 (m, 5H), 7.30 (t, 1H, \(J = 7.9\) Hz), 4.36 (t, 2H, \(J = 7.2\) Hz), 1.85-1.78 (m, 2H), 1.28-1.25 (m, 6H), 0.82 (t, 3H, 6.9 Hz). 

\(^{13}\)C NMR (100 MHz, CD\(_3\)CN, 298 K) \(\delta\) 157.90, 157.87, 157.84, 157.78, 154.45, 156.11, 153.72, 152.87, 152.67, 152.62, 152.61, 152.46, 141.80, 141.71, 140.14, 138.82, 138.77, 138.67, 130.05, 128.56, 128.51, 128.50, 128.46, 128.41, 127.52, 125.47, 125.38, 125.30, 125.27, 125.15, 124.76, 123.58, 122.76, 121.36, 120.61, 111.73, 110.62, 110.54, 99.59, 83.52, 43.69, 32.07, 29.39, 27.27, 23.17, 14.16. MALDI-TOF-MS: calc. for ([C\(_50\)H\(_43\)N\(_7\)Ru]) \(m/z\) = 843.2623, found \(m/z\) = 843.2664.
Under an argon atmosphere, [Iridium(I)(2-phenylpyridine)$_2$(5-bromo-2,2'-bipyridine)](PF$_6$)$_8$ (0.340 g; 0.3861 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (13.5 mg, 0.019 mmol), PPh$_3$ (10.0 mg, 0.039 mmol) and CuI (7.5 mg; 0.039 mmol) were added to a three neck round bottom flask. A solution of $L^4$ (0.135 g, 0.490 mmol) in 30mL mixture solvent ((CH$_3$CH$_2$)$_3$N:CH$_3$CN, 1:1, v/v) was transferred into the reaction flask via a long needle. The resulting mixture was refluxed at 90°C overnight under stirring. After cooled to room temperature, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CH$_3$CN/H$_2$O/sat. KNO$_3$, 200:9:1, v/v/v) and treated with a saturated aqueous solution of KPF$_6$. The orange precipitate was collected via filtration and washed with diethyl ether. Yield: 215.0 mg, 52%.

$^1$H NMR (400 MHz, CD$_3$CN, 298 K) δ 8.52-8.49 (m, 2H), 8.23-8.20 (m, 2H), 8.12-8.06 (m, 4H), 8.03 (d, 1H, $J$=1.8 Hz), 7.98 (d, 1H, $J$=5.3 Hz), 7.88-7.80 (m, 4H), 7.74 (d, 1H, $J$=5.6 Hz), 7.62 (d, 1H, $J$=5.7 Hz), 7.57-7.47 (m, 5H), 7.29-7.25 (m, 1H), 7.11-7.04 (m, 4H), 6.99-6.91 (m, 2H), 6.33 (d, 1H, $J$=7.4 Hz), 6.27 (d, 1H, $J$=7.4 Hz), 4.36 (t, 2H, $J$=7.2 Hz), 1.84-1.80 (m, 2H), 1.31-1.25 (m, 6H), 0.83 (t, 3H, $J$=7.2 Hz).

$^{13}$C NMR (100 MHz, CD$_3$CN, 298 K) δ 168.28, 168.18, 156.20, 154.94, 152.69, 151.62, 150.98, 150.73, 150.41, 150.20, 145.04, 144.93, 141.84, 141.76, 141.69, 140.23, 139.54, 139.52, 132.51, 132.35, 131.44, 131.31, 130.11, 129.30, 127.55, 126.22, 125.93, 125.81, 125.79, 125.30, 125.23, 124.50, 124.48, 123.67, 123.64, 123.55, 122.81, 121.45, 120.93, 120.80, 120.64, 111.57, 110.64, 110.57, 99.82, 83.50, 43.73, 32.12, 29.45, 27.33, 23.16, 14.15. (peaks at 207.43 and 30.82 were assigned to acetone) MALDI-TOF-MS: calc. for [(C$_5$H$_3$N)$_3$Ir] $m/z$ = 930.3148, found $m/z$ = 930.3156.
3.0 NMR Spectra

RuCRu:

Figure S4. $^1$H NMR spectrum of RuCRu (400 MHz, CD$_3$CN), 20 °C.

Figure S5. $^{13}$C NMR spectrum of RuCRu (100 MHz, CD$_3$CN), 20 °C.
Figure S6. $^1$H NMR spectrum of IrCl (600 MHz, CD$_3$CN), 20 °C.

Figure S7. $^{13}$C NMR spectrum of IrCl (150 MHz, CD$_3$CN), 20 °C.
Figure S8. $^1$H NMR spectrum of RuC (400 MHz, CD$_3$CN), 20 °C.

Figure S9. $^{13}$C NMR spectrum of RuC (100 MHz, CD$_3$CN), 20 °C.
Figure S10. $^1$H NMR spectrum of IrC (400 MHz, CD$_3$CN), 20 °C.

Figure S11. $^{13}$C NMR spectrum of IrC (100 MHz, CD$_3$CN), 20 °C.
4.0 Emission spectra at room temperature and at low temperature (77K)

Figure S12. Emission spectra of a) RuCr, b) RuC, c) IrClr and d) IrC in CH₃CN at room temperature under a nitrogen atmosphere, and air. C = 1 × 10⁻⁵ M.

Figure S13. Normalised emission spectra of e) Ru, f) IrClr and g) IrC at room temperature and at low temperature (77 K) in CH₃CH₂OH/CH₃OH (4:1, v/v) under a nitrogen atmosphere. C = 1 × 10⁻⁵ M.

5.0 Cyclic Voltammetry Plots

Figure S14. Cyclic Voltammetry plots of a) RuCr, b) IrClr, c) RuC and d) IrC in CH₃CN under a nitrogen atmosphere at room temperature.

6.0 Nanosecond time-scaled transient different absorption spectra.
photosensitiser and triplet acceptor (DPA) was deaerated for at least 15 min with N\textsubscript{2} used for the upconversion measurements. For the upconversion experiment, the mixed solution of the was used as determined from the TTA-UC response.

Figure S15. Nanosecond time-scaled transient different absorption spectra of a) RuC, b) IrCl\textsubscript{r} and c) IrC in CH\textsubscript{3}CN under a nitrogen atmosphere at room temperature. The decay traces of d) RuC\textsubscript{r}, e) RuC, f) IrCl\textsubscript{r} and g) IrC at 400 nm. C = 1 × 10\textsuperscript{-5} M.

7.0 TTA upconversion and delayed fluorescence spectra

Figure S16. TTA- Upconversion generated using a) RuC, b) IrCl\textsubscript{r} or c) IrC as the triplet photosensitiser, and DPA as the triplet acceptor in deaerated CH\textsubscript{3}CN at room temperature. C[RuC] = 1.0 × 10\textsuperscript{-5} M with C[DPA] = 1.67 × 10\textsuperscript{-3} M; C[IrCl\textsubscript{r}] = 1.0 × 10\textsuperscript{-5} M with C[DPA] = 2.0 × 10\textsuperscript{-3} M; C[IrC] = 1.0 × 10\textsuperscript{-5} M with C[DPA] = 1.67 × 10\textsuperscript{-3} M.

Figure S17. Delayed fluorescence of DPA with a) RuC, b) IrCl\textsubscript{r} or c) IrC as the triplet photosensitiser for TTA upconversion. Each were selectively excited at 473 nm (nanosecond pulsed OPO laser synchronised with spectrofluorometer); (d) The prompt fluorescence decay of DPA was determined in a different experiment (excited with a picosecond 405 nm laser, with the decay of the emission at 428 nm monitored) in deaerated CH\textsubscript{3}CN at room temperature. C[Sensitisers] = 1.0 × 10\textsuperscript{-5} M. The optimised concentration of DPA was used as determined from the TTA-UC response.

**TTA Upconversion quantum yield:** Diode-pumped solid-state lasers (473 nm, continuous wave, CW) were used for the upconversion measurements. For the upconversion experiment, the mixed solution of the photosensitiser and triplet acceptor (DPA) was deaerated for at least 15 min with N\textsubscript{2} and the gas flow was
kept constant during the measurement. The solution was excited with the laser. Then the upconverted fluorescence was recorded with a spectrofluorimeter. The upconversion quantum yield was determined with the prompt fluorescence of the reference compound (BODIPY, \(\Phi_f = 71.2\%\) in CH\(_3\)CN) as the standard using the following equation:

\[
\Phi_{UC} = 2 \times \Phi_{std} \times \left(\frac{1 - 10^{-A_{std}}}{1 - 10^{-A_{sam}}}\right) \times \frac{I_{sam}}{I_{std}} \times \left(\frac{\eta_{sam}}{\eta_{std}}\right)^2
\]

The subscripts "sam" and "std" refer to the photosensitiser (sample) and the reference compound (standard), respectively. \(\Phi\), \(A\), \(I\), and \(\eta\) represent the quantum yield, absorbance, integrated photoluminescence intensity, and the refractive index of the solvents used for the standard and the samples, respectively. The equation is multiplied by a factor of 2, in order to make unity the maximum quantum yield possible.
### 8.0 Time-Dependent Density Theory calculation with Gaussian 09W

**Table S3.** Electronic Excitation Energies (eV) and corresponding Oscillator Strength (f), main configurations and CI coefficients of the Low-lying Electronic Excited States of the complex RuCRu calculated by TDDFT/B3LYP/GENECP/LANL2DZ, with CH₃CN as the solvent (PCM model) and based on the optimised Ground State Geometries.

<table>
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<th>TDDFT/B3LYP/GENECP/LANL2DZ</th>
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<td><strong>Energy</strong></td>
<td><strong>f</strong></td>
<td><strong>Composition</strong></td>
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<tr>
<td><strong>Singlet</strong></td>
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<td></td>
</tr>
<tr>
<td>S₀→S₁</td>
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<td>474.02 nm 2.5921 eV</td>
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<td><strong>Triplet</strong></td>
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<td>S₀→T₂</td>
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</tbody>
</table>

*a Only the selected low-lying excited states are presented. b Oscillator strengths. c Only the main configurations are presented. d The CI coefficients are in absolute values. e L stands for carboxyl localized ligand. f No spin-orbital coupling effect was considered, thus the f values are zero.*

**Figure S18.** Electron density maps of the frontier molecular orbitals of the complex RuCRu, based on its ground state optimised geometry as determined by the TDDFT calculations at the TDDFT/B3LYP/GENECP/LANL2DZ level with Gaussian 09W.
Table S4. Oscillator Strength \((f)\), main configurations and CI coefficients of the Low- Electronic Excitation Energies (eV) and corresponding lying Electronic Excited States of the complex RuC calculated by TDDFT/B3LYP/GENECPLANL2DZ, CH\(_3\)CN as the solvent (PCM model) and based on the optimised Ground State Geometries.

<table>
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<tr>
<th>Electronic transition</th>
<th>Energy (a) (\text{nm} \text{eV})</th>
<th>(f) (b)</th>
<th>Composition (c)</th>
<th>CI (d)</th>
<th>character</th>
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<td>(S_0 \rightarrow S_1)</td>
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<td></td>
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<td>H-2-L</td>
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<td>ILCT/MLCT</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-L</td>
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<td>Singlet</td>
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<td></td>
<td>H-3-L+1</td>
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<td>(S_0 \rightarrow S_{11})</td>
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<td>H-1-L</td>
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<td>ILCT/MLCT</td>
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<td>(S_0 \rightarrow T_1)</td>
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<td>ILCT</td>
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<td>0.2013</td>
<td>ILCT</td>
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<td>H-1-L</td>
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<td>H-2-L+1</td>
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<td>ML'CT/LL'CT</td>
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<td></td>
<td>H-1-L</td>
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<td>ILCT/MLCT</td>
</tr>
</tbody>
</table>

\(a\) Only the selected low-lying excited states are presented. \(b\) Oscillator strengths. \(c\) Only the main configurations are presented. \(d\) The CI coefficients are in absolute values. \(e\) L stands for carbazole localized ligand; \(L'\) stands for the other two bipyridine. \(f\) No spin-orbital coupling effect was considered, thus the \(f\) values are zero.

Figure S19 Electron density maps of the frontier molecular orbital of the complex RuC, based on the ground state optimised geometry generated by the TDDFT calculations at the TDDFT/B3LYP/GENECPLANL2DZ level with Gaussian 09W.
Table S5 Oscillator Strength (f), main configurations and CI coefficients of the Low-Electronic Excitation Energies (eV) and corresponding Electronic Excited States of the complex \textit{IrClr} calculated by TDDFT/B3LYP/GENECP/LANL2DZ, with CH$_3$CN as the solvent (PCM model) and based on the optimised Ground State Geometries.

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<th>Electronic Transition</th>
<th>Energy $^a$</th>
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<th>Composition $^c$</th>
<th>CI $^d$</th>
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<td></td>
<td>2.5290 eV</td>
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<td>Singlet</td>
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<td></td>
<td>2.7224 eV</td>
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<td>H-5-L+1</td>
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<td>0.3309</td>
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<td>$S_0\rightarrow S_{10}$</td>
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<td>3.1011 eV</td>
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<td>0.6095</td>
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<td>H-1-L</td>
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<tr>
<td>$S_0\rightarrow T_1$</td>
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<td>H-5-L</td>
<td>0.3189</td>
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</table>

$^a$ Only the selected low-lying excited states are presented. $^b$ Oscillator strengths. $^c$ Only the main configurations are presented. $^d$ The CI coefficients are in absolute values. $^e$ L stands for carbazole localized ligand; L’ stands for the other two 2-phenylpyridine. $^f$ No spin-orbital coupling effect was considered, thus the f values are zero.

Figure S20 Electron density maps of the frontier molecular orbitals of the complex \textit{IrClr}, based on ground state optimised geometry by the TDDFT calculations at the TDDFT/B3LYP/GENECP/LANL2DZ level with Gaussian 09W.
Table S6 Oscillator Strength (f), main configurations and CI coefficients of the Low- Electronic Excitation Energies (eV) and corresponding lying Electronic Excited States of the complex IrC calculated by TDDFT/B3LYP/GENECP/LANL2DZ, CH3CN as the solvent (PCM model) based on the optimised Ground State Geometries.

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<td>(S_0\rightarrow S_2)</td>
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<td>(S_0\rightarrow S_{15})</td>
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<td>MLCT/L'LCT</td>
</tr>
<tr>
<td>(S_0\rightarrow T_2)</td>
<td>516.52 nm 2.4004 eV</td>
<td>0.0000</td>
<td>H-1-L</td>
<td>0.6998</td>
<td>MLCT/L'LCT</td>
</tr>
</tbody>
</table>

\(a\) Only the selected low-lying excited states are presented. \(b\) Oscillator strengths. \(c\) Only the main configurations are presented. \(d\) The CI coefficients are in absolute values. \(e\) L stands for carbazole localized ligand; L' stands for the other two 2-phenylpyridine. \(f\) No spin-orbital coupling effect was considered, thus the f values are zero.

Figure S21 Electron density maps of the frontier molecular orbitals of the complex IrC, based on ground state optimised geometry by the TDDFT calculations at the TDDFT/B3LYP/GENECP/LANL2DZ level with Gaussian 09W.

References:
1 Bruker APEX v2012.12-0, Bruker AXS Inc., Madison, Wisconsin, USA.
2 SADABS (2014) Bruker AXS Inc., Madison, Wisconsin, USA; Sheldrick, G. M. University of Göttingen, Germany.