Orotate containing anionic luminescent Iridium(III) complexes and their use in soft salts

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Electronic Supplementary Information

Materials and methods.

All commercially available starting materials were used as received without further purification. All synthetic procedures involving $IrCl_3 \cdot H_2O$ and other Ir(III) species were carried out in inert gas atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance AC-300 spectrometer in $CDCl_3$, using tetramethylsilane (TMS) as internal standard. Elemental analyses (CHN) were performed with a Perkin Elmer 2400 microanalyzer by the Microanalytical Laboratory at the University of Calabria. Infrared spectra (KBr) in the range 4000-400 cm^{-1} were recorded on a Spectrum 100 FT-IR Perkin Elmer spectrometer.

Conductivity measurements were performed in acetonitrile and water solutions with an InoLab Cond Level 1–720 conductometer equipped with a LR 325/001 immersion cell.

Electrochemical studies

All potentials were measured with IR compensation using an Epsilon electrochemical analyser. Voltammetry experiments were performed in a 3 mL cell of dry, and degassed (N_2) acetonitrile solution using tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte, a Pt disk working electrode, a Pt wire counter-electrode and an Ag wire as a pseudo-reference electrode. Voltammograms were recorded at a 100 $mV.s^{-1}$ scan rate from ca. 10^{-3} M complex solution. Redox potentials are given relative to a ferrocene/ ferrocenium (Fc/Fc^+) redox couple used as an internal reference.

Estimation of HOMO/LUMO energy values was performed taking into account -4.8 eV for Fc/Fc^+

Photophysics.

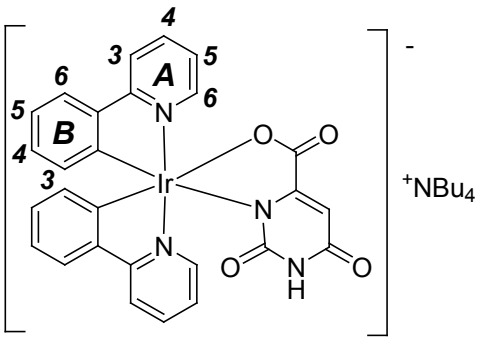
Spectrofluorimetric grade solvents (Acros Organics) were used for the photophysical investigations in solution. Absorption spectra were recorded with an UV-Vis Perkin-Elmer Lambda 900 spectrophotometer. Steady-state emission spectra were recorded on a Horiba Jobin Yvon Fluorolog 3 spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube.

Emission quantum yields of samples were determined using the optically dilute method on deaerated solutions whose absorbance at excitation wavelengths was <0.2; $Ru(bpy)_3Cl_2$ (bpy = 2-2' -bipyridine) in H_2O was used as the standard (ϕ = 0.028).[1] The experimental uncertainty on the emission quantum yields is 10% .

Time-resolved measurements were carried out using the time correlated single-photon counting (TCSPC) option on the Fluorolog3. A NanoLED at 379 nm, fwhm < 200 ps, was used to excite the sample. Excitation sources were mounted directly on the sample chamber at 90° to a single-grating emission monochromator (2.1 nm mm^{-1} dispersion; 1200 grooves per mm) and collected with a TBX-04-D single-photon-counting detector. The photons collected at the detector were correlated with the excitation pulse using a time-to-amplitude converter (TAC). Signals were collected using an IBH Data Station Hub photon counting module and data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). Goodness of fit was assessed by minimizing the reduced Chi squared function (χ^2) and visual inspection of the weighted residuals.

[1] (1) (a) Demas N.; Crosby, G. A. *J. Phys. Chem*., **1971**, *75*, 991–1024; (b) Nakamaru, K. *Bull. Chem. Soc. Jpn*., **1982**, *55*, 2697 - 2705.

Synthesis of the Ir(III) anionic complexes A1 and A2.

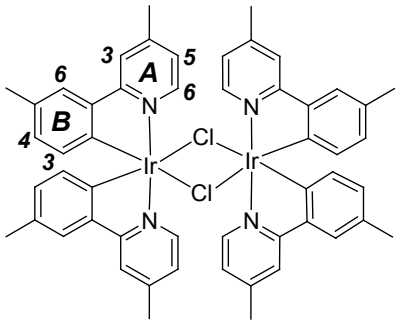


Complex A1, [(*ppy*)$_2$Ir(*or*)]TBA: To a mixture of dichloro bridged precursor [(*ppy*)$_2$Ir(μ-Cl)]$_2$[1] (100 mg, 0.093 mmol) and a small excess of orotic acid monohydrate (36 mg, 0.205 mmol) in 15 mL CH_2Cl_2/MeOH (4:1 v/v), tetrabutylammonium hydroxide (1M in MeOH, 0.41 mL) was added dropwise, under purging N_2. The colour changed to orange. The reaction mixture was stirred under N_2 for 3 days. Then the solvents were evaporated, and the pure product was obtained after filtration on celite in $CHCl_3$ and recrystallization from $CHCl_3$/Hexane as a yellow solid (124 mg, yield 73%). M. p. = 200°C Dec.

^{1}H NMR (DMSO-d$_6$, 300 MHz): δ 9.59 (s, 1H, *or*-NH), 8.45 (d, ^{3}J = 6.1 Hz, 1H, H^{A6}), 8.34 (d, ^{3}J = 5.7 Hz, 1H, H$^{A6'}$), 8.10 (d, ^{3}J = 8.4 Hz, 1H, H^{A3}), 8.03 (d, ^{3}J = 8.0 Hz, 1H, H$^{A3'}$), 7.88 (t, ^{3}J = 7.7 Hz, 1H, H^{A5}), 7.81 (t, ^{3}J = 8.0 Hz, 1H, H$^{A5'}$), 7.67 (d, ^{3}J = 7.8 Hz, 1H, H^{B6}), 7.56 (d, ^{3}J = 7.0, 1H, H$^{B6'}$), 6.31 (overlapped peaks, 2H, H$^{A4,A4'}$), 6.75 (t, ^{3}J = 7.8 Hz, 1H, H^{B5}), 6.58 (overlapped peaks, 2H, H$^{B5',B4}$), 6.43 (d, ^{3}J = 7.4 Hz, 1H, H$^{B4'}$), 6.05 (d, ^{3}J = 7.6 Hz, 1H, H^{B3}), 5.94 (d, ^{3}J = 7.5 Hz, 1H, H$^{B3'}$), 5.67 (d, ^{4}J = 1.9 Hz, C*H*-or), 3.13 (m, 8 H, NCH_2), 1.53 (m, 8H, NCH$_2$CH_2), 1.28 (m, 8H, NCH$_2$CH$_2$CH_2), 0.91 (t, ^{3}J = 7.3 Hz, 12H, -CH_3).

Elemental analysis: $C_{43}H_{54}IrN_5O_4$ (897.38 g/mol) calc.: C, 57.57; H, 6.07; N, 7.81; found: C, 57.37; H, 6.23; N, 7.53.

IR (KBr): ν = 2962, 2874 cm^{-1} (NBu_4^+); ν_{asym} = 1646, 1634, 1607 cm^{-1} (C=O acid, C=O or); ν_{sym} = 1359 cm^{-1} (C=O acid).

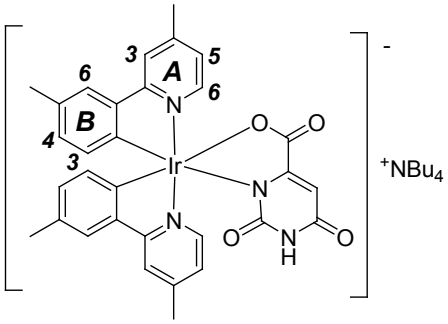


Precursor complex [(*ppy-CH₃*)₂Ir(μ-*Cl*)]₂: $IrCl_3 \cdot 3H_2O$ (340 mg, 1.14 mmol) was solubilized in 5 mL of degassed distilled water under inert atmosphere (N_2). 4,5'-dimethyl,2-phenylpyridine (385 mg, 2.27 mmol)[2] was solubilized in 15 mL of degassed 2-ethoxyethanol and added to the reaction mixture. The resulting solution was stirred at reflux under N_2. After 24 hrs., a precipitate was filtered off, washed with acetone and water and dried under vacuum to yield a green solid (539 mg, yield 80%). M. p. >250°C Dec.

^{1}H NMR ($CHCl_3$-d_1, 300 MHz): δ 9.04 (d, ^{3}J=5.88 Hz, 4H, H^{A6}), 7.64 (s, 4H, H^{A3}), 7.27 (s, 4H, H^{B6}), 6.51 (d, ^{3}J=4.8 Hz, 4H, H^{A5}), 6.38 (d, ^{3}J=4.8 Hz, 4H, H^{B4}), 5.82 (d, ^{3}J=7.83 Hz, 4H, H^{B3}), 2.61 (s, 12H, $-CH_3{}^A$), 2.09 (s, 12H, $-CH_3{}^B$).

Elemental analysis: $C_{52}H_{48}Cl_2Ir_2N_4$ (1184.25 g/mol) calc.: C, 52.74; H, 4.09; N, 4.73; found: C, 52.64; H, 4.18; N, 4.50.

IR (KBr): ν = 3039, 2916, 2863 cm^{-1} ($-CH_3$); ν = 1619, 1540, 1477, 1446, 1268, 1032, 810 cm^{-1}.

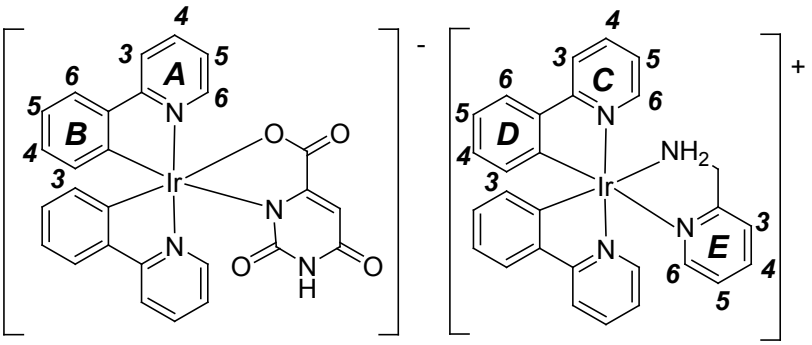


Complex A2, [(*ppy-CH₃*)₂Ir(*or*)]TBA: To a mixture of dichloro bridged precursor [(*ppy-CH₃*)₂Ir(*μ*-Cl)]₂ (100 mg, 0.084 mmol) and a small excess of orotic acid monohydrate (32 mg, 0.185 mmol) in 15 mL CH_2Cl_2/MeOH (4:1 v/v), tetrabutylammonium hydroxide (1M in MeOH, 0.37 mL) was added dropwise, under purging N_2. The colour changed to orange. The reaction mixture was stirred under N_2 for 3 days. Then the solvents were evaporated, and the pure product was obtained after filtration on celite in CH_2Cl_2 and recrystallization from CH_2Cl_2/Et_2O as a yellow solid (117 mg, yield 71%). M. p. = >250°C Dec.

^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.49 (s, 1H, *or*-NH), 8.21 (d, ^{3}J = 5.7, 1H, H^{A6}), 8.13 (d, ^{3}J = 5.9, 1H, $H^{A6'}$), 7.87 (s, 1H, H^{A3}), 7.78 (s, 1H, $H^{A3'}$), 7.43 (s, 1H, H^{B6}), 7.30 (s, 1H, $H^{B6'}$), 7.08 (overlapped peaks, 2H, $H^{A5,A5'}$), 6.39 (d, ^{3}J = 7.4, 1H, H^{B4}), 6.24 (d, ^{3}J = 8.0 Hz, 1H, $H^{B4'}$), 5.90 (d, ^{3}J = 7.9 Hz, 1H, H^{B3}), 5.79 (d, ^{3}J = 7.6 Hz, 1H, $H^{B3'}$), 5.63 (d, ^{4}J = 1.0 Hz, C*H*-or), 3.13 (m, 8 H, NCH_2), 2.08 (d, 6H, ^{3}J = 9.3 Hz, *ppy*-CH_3), 1.53 (m, 8H, NCH_2CH_2), 1.28 (m, 8H, $NCH_2CH_2CH_2$), 0.91 (t, ^{3}J = 7.3 Hz, 12H, $-CH_3$).

Elemental analysis: $C_{47}H_{62}IrN_5O_4$ (953.44 g/mol) calc.: C, 59.22; H, 6.56; N, 7.35; found: C, 58.94; H, 6.88; N, 7.15.

IR (KBr): ν = 2962, 2874 cm^{-1} (NBu_4^+); ν_{asym} = 1660, 1645, 1620 cm^{-1} (C=O acid, C=O or); ν_{sym} = 1361 cm^{-1} (C=O acid).

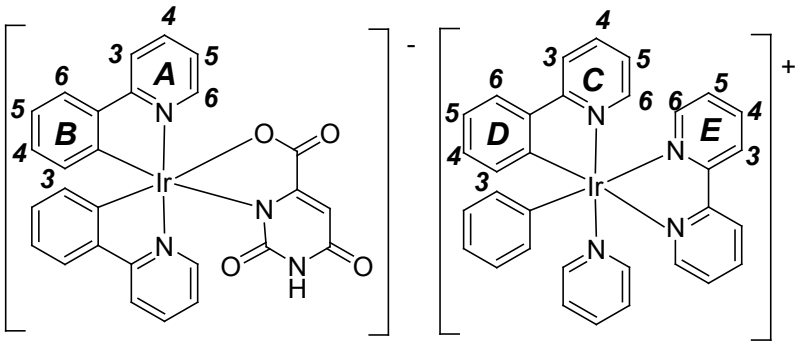


Complex C_1A_1, [(*ppy-CH*$_3$)$_2$Ir(*or*)][(*ppy*)$_2$Ir(*pam*)]: Complexes **A1** (50 mg, 0.0546 mmol) and **C1** (**[(*ppy*)Ir$_2$(*pam*)]Cl**), (35 mg, 0.0546 mmol) were dissolved in a mixture of methanol/water (50 mL, 4:1 v/v) at room temperature, and the resulting mixture was stirred in an open vessel to allow a slow evaporation of methanol to 1/3 of its initial volume. The product, precipitated as crystalline yellowish solid, was filtered out and washed several times with large amounts of water. (59 mg, yield 81%). M. p. = 240°C Dec.

^{1}H NMR (DMSO-d$_6$, 300 MHz): δ 9.60 (s, 1H, *or*-NH), 8.98 (d, ^{3}J = 5.7 Hz, 1H, H^{E6}), 8.44 (d, ^{3}J = 5.7 Hz, 1H, H^{A6}), 8.35 (d, ^{3}J = 5.6 Hz, 1H, H$^{A6'}$), 8.27 (d, ^{3}J = 8.0 Hz, 1H, H^{C6}), 8.22 (d, ^{3}J = 8.0 Hz, 1H, H^{E3}), 8.10 (d, ^{3}J = 8.2 Hz, 1H, H^{3A}), 8.04-7.64 (overlapped peaks, 11H, H$^{A3',E4,E5,C3,A5,C3',C4,C4',A5',B6,E3}$), 7.54 (d, ^{3}J = 6.7 Hz, 1H, H^{C5}), 7.32 (overlapped peaks, 6H, H$^{B6',C5',D6,D6',A4,A4'}$), 7.96-6.71 (overlapped peaks, 5H, H$^{D4,D4',D5,B5,D5'}$), 6.58 (overlapped peaks, 2H, H$^{B5',B4}$), 6.43 (t, ^{3}J = 7.4 Hz, 1H, H$^{B4'}$), 6.18 (d, ^{3}J = 7.7 Hz, 1H, H^{D3}), 6.11 (d, ^{3}J = 7.5 Hz, 1H, H$^{D3'}$), 6.05 (d, ^{3}J = 7.7 Hz, 1H, H^{B3}), 5.94 (d, ^{3}J = 7.6 Hz, 1H, H$^{B3'}$), 5.67 (d, ^{4}J = 1.1 Hz, C*H*-or), 5.50 (m, 1H, NH_2), 5.02 (m, 1H, NH_2), 4.55 (m, 1H, CH_2), 4.30 (m, 1H, CH_2).

Elemental analysis: $C_{55}H_{42}Ir_2N_8O_4$ (1264.26 g/mol) calc.: C, 52.69; H, 3.35; N, 8.87; found: C, 52.67; H, 3.66; N, 8.32.

IR (KBr): ν = 1619, 1640, 1610 cm^{-1} (C=O acid, C=O *or*); ν_{sym} = 1364 cm^{-1} (C=O acid).

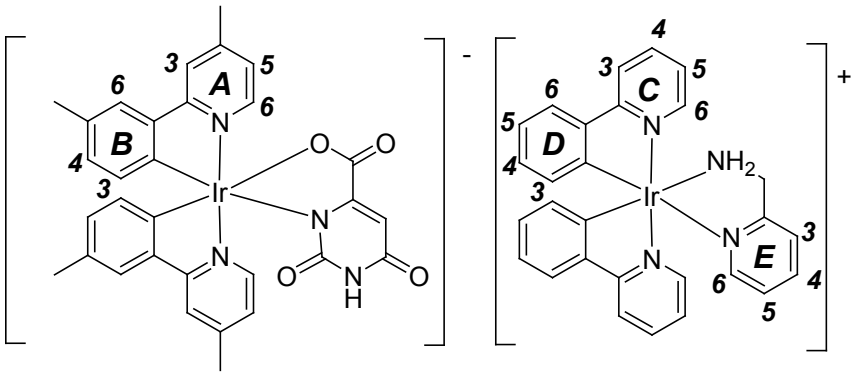


Complex C2A1, [(*ppy*)$_2$Ir(*or*)][(*ppy*)$_2$Ir(*bpy*)]: Complexes **A1** (50 mg, 0.0546 mmol) and **C2** (**[(*ppy*)Ir$_2$(*bpy*)]OOCCH$_3$·2H$_2$O**), (41 mg, 0.0546 mmol) were dissolved in a mixture of methanol/water (50 mL, 4:1 v/v) at room temperature, and the resulting mixture was stirred in an open vessel to allow a slow evaporation of methanol to 1/3 of its initial volume. The product, precipitated as crystalline yellowish solid, was filtered out and washed with abundant water. (56 mg, yield 75%). M. p. = 250°C Dec.

^{1}H NMR (DMSO-d$_6$, 300 MHz): δ 9.56 (s, 1H, *or*-NH), 8.86 (d, ^{3}J = 8.3 Hz, 2H, H^{E6}), 8.42 (d, ^{3}J = 5.1 Hz, 1H, H^{A6}), 8.33 (d, ^{3}J = 5.8 Hz, 1H, H$^{A6'}$), 8.23 (overlapped peaks, 4H, H^{C6,E3}), 8.07 (d, ^{3}J = 5.9 Hz, 1H, H^{3A}), 8.01 (d, ^{3}J = 8.6 Hz, 1H, H$^{A3'}$), 7.88 (overlapped peaks, 8H, H$^{E4,E5,A5,A5',C3}$), 7.67 (overlapped peaks, 3H, H^{B6,C5}), 7.60 (d, ^{3}J = 5.2 Hz, 2H, H^{D6}), 7.52 (d, ^{3}J = 7.2 Hz, 1H, H$^{B6'}$), 7.30 (overlapped peaks, 2H, H$^{A4,A4'}$), 7.14 (t, ^{3}J = 6.2 Hz, 2H, H^{C4}), 7.00 (t, ^{3}J = 7.1 Hz, 2H, H^{D5}), 6.88 (t, ^{3}J = 7.5 Hz, 2H, H^{D4}), 6.72 (d, ^{3}J = 7.3 Hz, 1H, H^{B5}), 6.56 (overlapped peaks, 2H, H$^{B5',B4}$), 6.41 (d, ^{3}J = 6.9 Hz, 1H, H$^{B4'}$), 6.17 (d, ^{3}J = 7.1 Hz, 2H, H^{D3}), 6.03 (d, ^{3}J = 8.0 Hz, 1H, H^{B3}), 5.92 (d, ^{3}J = 7.0 Hz, 1H, H$^{B3'}$), 5.65 (d, ^{4}J = 1.1 Hz, C*H*-or).

Elemental analysis: $C_{59}H_{44}Ir_2N_8O_4$ (1314.27 g/mol) calc.: C, 53.95; H, 3.38; N, 8.53; found: C, 53.56; H, 3.37; N, 8.30.

IR (KBr): ν_{asym} = 1660, 1632, 1606 cm^{-1} (C=O acid, C=O *or*); ν_{sym} = 1362 cm^{-1} (C=O acid).

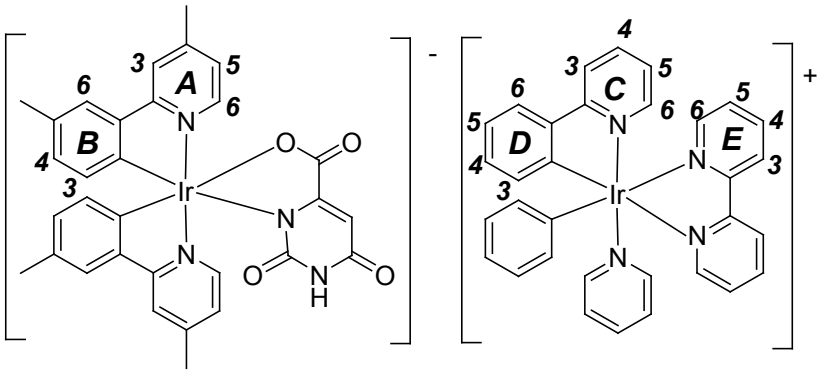


Complex C1A2, [(*ppy*-CH_3)$_2$Ir(*or*)][(*ppy*)Ir$_2$(*pam*)]: Complexes **A2** (50 mg, 0.0514 mmol) and **C$_1$** (**[(*ppy*)Ir$_2$(*pam*)]Cl**), (33 mg, 0.0514 mmol) were dissolved in a mixture of methanol/water (50 mL, 4:1 v/v) at room temperature, and the resulting mixture was stirred in an open vessel to allow a slow evaporation of methanol to 1/3 of its initial volume. The product, precipitated as crystalline yellowish solid, was filtered out and washed with abundant water. (55 mg, yield 78%). M. p. = >250°C.

^{1}H NMR (DMSO-d$_6$, 300 MHz): δ 9.51 (s, 1H, *or*-NH), 8.96 (d, ^{3}J = 5.9, 1H, H^{E6}), 8.22 (overlapped peaks, 3H, H$^{C6,C6',A6}$), 8.13 (d, ^{3}J = 5.9 Hz, 1H, H$^{6A'}$), 7.89 (overlapped peaks, 8H, H$^{E4,E5,C3,A3,C3',C4,C4'A3'}$), 7.62 (d, ^{3}J = 5.8 Hz, 1H, H^{E3}), 7.52 (d, ^{3}J = 5.3 Hz, 1H, H^{C5}), 7.43 (s, 1H, H^{B6}), 7.30 (overlapped peaks, 4H, H$^{C5',D6,D6',6B}$), 7.08 (overlapped peaks, 2H, H$^{A5,A5'}$), 6.91 (t, ^{3}J = 7.4 Hz, 1H, H^{D4}), 6.84 (t, ^{3}J = 7.5 Hz, 1H, H$^{D4'}$), 6.78 (t, ^{3}J = 7.4 Hz, 1H, H^{D5}), 6.71 (t, ^{3}J = 7.6 Hz, 1H, H$^{D5'}$), 6.39 (d, ^{3}J = 7.4 Hz, 1H, H^{A4}), 6.24 (d, ^{3}J = 8.0 Hz, 1H, H$^{A4'}$), 6.16 (d, ^{3}J = 7.5 Hz, 1H, H^{D3}), 6.09 (d, ^{3}J = 7.4 Hz, 1H, H$^{D3'}$), 5.90 (d, ^{3}J = 7.7 Hz, 1H, H^{A3}), 5.78 (d, ^{3}J = 7.6 Hz, 1H, H$^{A3'}$), 5.63 (d, ^{4}J = 2.0 Hz, 1H, C*H*-or), 5.50 (m, 1H, NH_2), 4.99 (m, 1H, NH_2), 4.54 (m, 1H, CH_2), 4.30 (m, 1H, CH_2), 2.07 (d, 6H, ^{3}J = 9.5 Hz, ppy-CH_3).

Elemental analysis: $C_{59}H_{50}Ir_2N_8O_4$ (1320.32 g/mol) calc.: C, 53.70; H, 3.82; N, 8.49; found: C, 53.33; H, 3.88; N, 8.28.

IR (KBr): ν = 2916, 2858 cm^{-1} (CH_3);ν_{asym} = 1660, 1632, 1607 cm^{-1} (C=O acid, C=O *or*); ν_{sym} = 1370 cm^{-1} (C=O acid).



Complex C2A2, [(*ppy*)$_2$Ir(*or-CH$_3$*)][(*ppy*)$_2$Ir(*bpy*)]: Complexes **A2** (50 mg, 0.0514 mmol) and **C2** (**[(*ppy*)Ir$_2$(*bpy*)]OOCCH$_3$·2H$_2$O**), (39 mg, 0.0514 mmol) were dissolved in a mixture of methanol/water (50 mL, 4:1 v/v) at room temperature, and the resulting mixture was stirred in an open vessel to allow a slow evaporation of methanol to 1/3 of its initial volume. The product, precipitated as crystalline yellowish solid, was filtered out and washed with abundant water. (60 mg, yield 80%). M. p. = 200°C Dec.

^{1}H NMR (DMSO-d$_6$, 300 MHz): δ 9.49 (s, 1H, *or*-NH), 8.86 (d, ^{3}J = 8.0, 2H, H^{E6}), 8.23 (overlapped peaks, 5H, H^{C6,E3,A6}), 8.12 (d, ^{3}J = 6.0 Hz, 1H, H$^{6A'}$), 7.88 (overlapped peaks, 7H, H^{E4,E5,C3,A3}), 7.78 (s, 1H, H$^{A3'}$), 7.67 (t, ^{3}J = 6.4 Hz, 2H, H^{C5}), 7.60 (d, ^{3}J = 5.6 Hz, 2H, H^{D6}), 7.53 (s, 1H, H^{B6}), 7.29 (s, 1H, H$^{B6'}$), 7.12 (overlapped peaks, 4H, H$^{C4,A5,A5'}$), 7.00 (t, ^{3}J = 7.2 Hz, 2H, H^{D5}), 6.88 (t, ^{3}J = 7.4 Hz, 2H, H^{D4}), 6.39 (d, ^{3}J = 7.6 Hz, 1H, H^{A4}), 6.24 (d, ^{3}J = 7.6 Hz, 1H, H$^{A4'}$), 6.17 (d, ^{3}J = 7.4 Hz, 2H, H^{D3}), 5.90 (d, ^{3}J = 7.7 Hz, 1H, H^{A3}), 5.79 (d, ^{3}J = 7.6 Hz, 1H, H$^{A3'}$), 5.62 (d, ^{4}J = 2.2 Hz, C*H*-or), 2.08 (d, 6H, ^{3}J = 9.4 Hz, ppy-C*H$_3$*).

Elemental analysis: $C_{63}H_{52}Ir_2N_8O_4$ (1370.34 g/mol) calc.: C, 55.25; H, 3.83; N, 8.18; found: C, 54.95; H, 3.90 ; N, 7.82.

IR (KBr): ν = 2916, 2847 cm^{-1} (CH$_3$);ν_{asym} = 1660, 1622, 1609 cm^{-1} (C=O acid, C=O *or*); ν_{sym} = 1369 cm^{-1} (C=O acid).

[1] A.M. Talarico, E.I. Szerb, T.F. Mastropietro, I. Aiello, A. Crispini and M. Ghedini, *Dalton Trans.*, 2012, **41**, 4919;
[2] S. Jung, Y. Kang, H.-S. Kim, Y.-H. Kim, C.-L. Lee, J.-J. Kim, S.-K. Lee, and S.-K. Kwon , *Eur. J. Inorg. Chem.* 2004, 3415

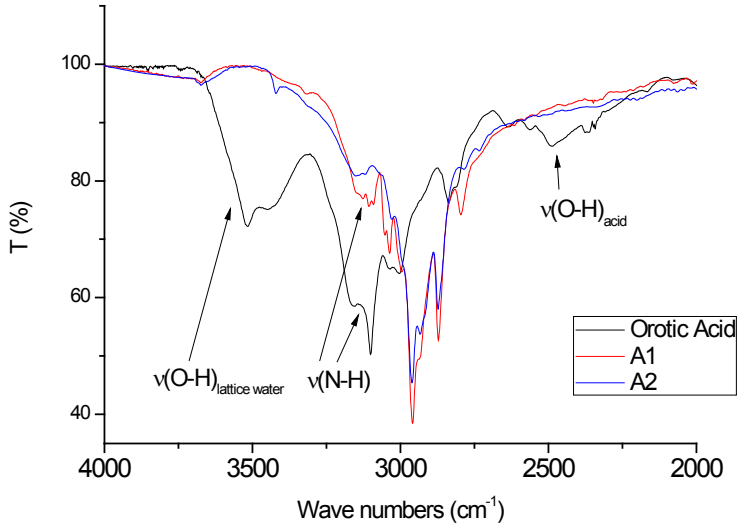


Figure S1. IR spectra of orotic acid and complexes $\mathbf{A_1}$ and $\mathbf{A_2}$.

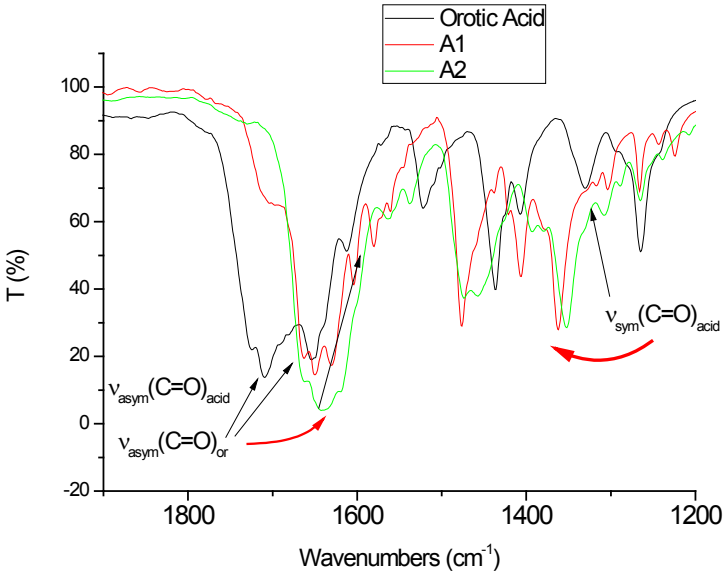


Figure S2. IR spectra of orotic acid and complexes $\mathbf{A_1}$ and $\mathbf{A_2}$.

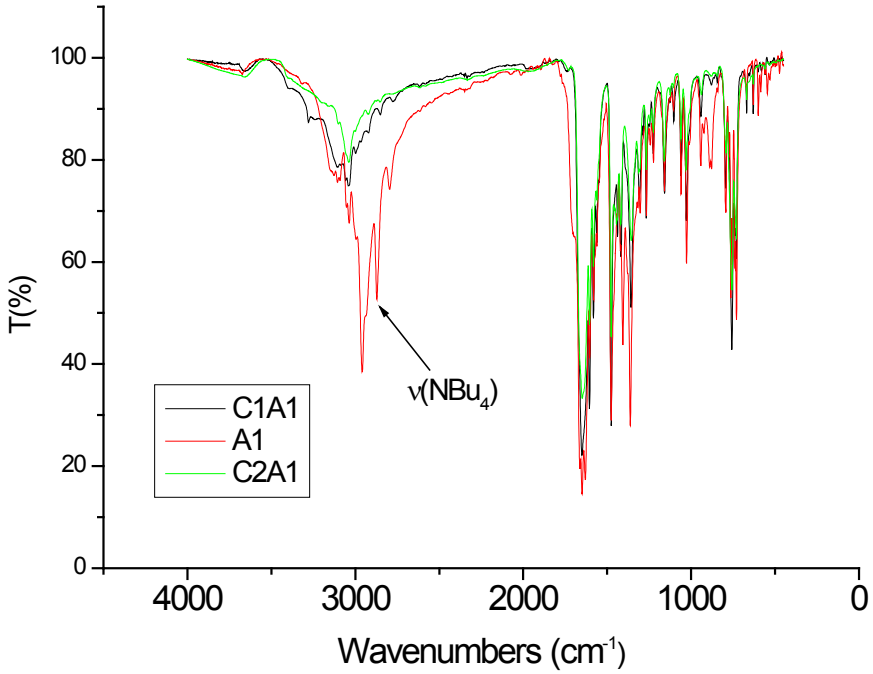


Figure S3. IR spectra complexes $\mathbf{A_1}$ and corresponding soft salts **C1A1** and **C2A1**.

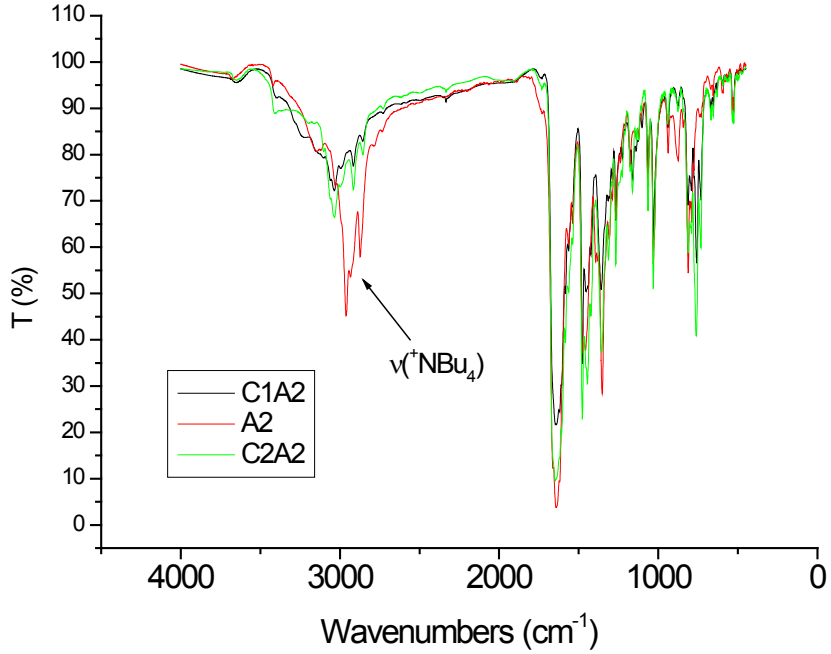


Figure S4. IR spectra complexes **A2** and corresponding soft salts **C1A2** and **C2A2**.

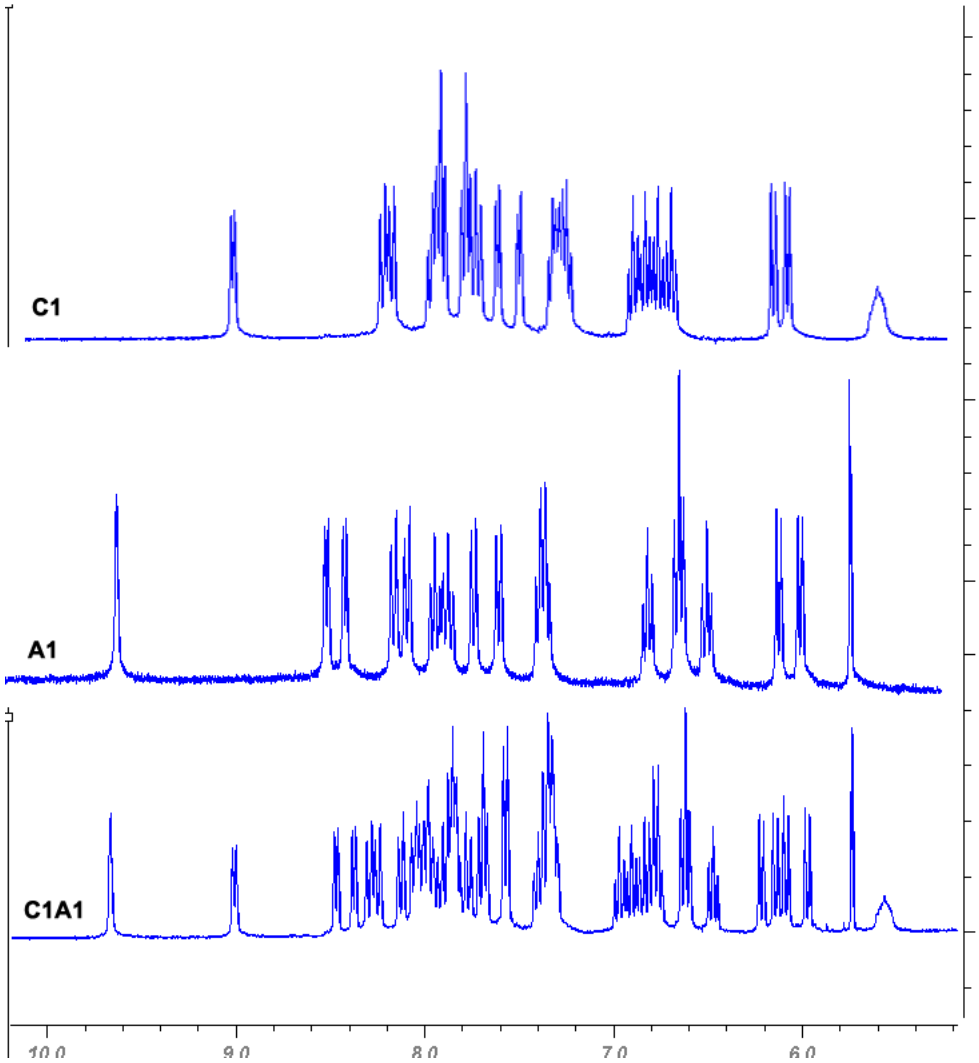


Figure S5. ^{1}H NMR spectra in dmso-d_6 of complexes **C1** and **A1** and their corresponding soft salt **C1A1**.

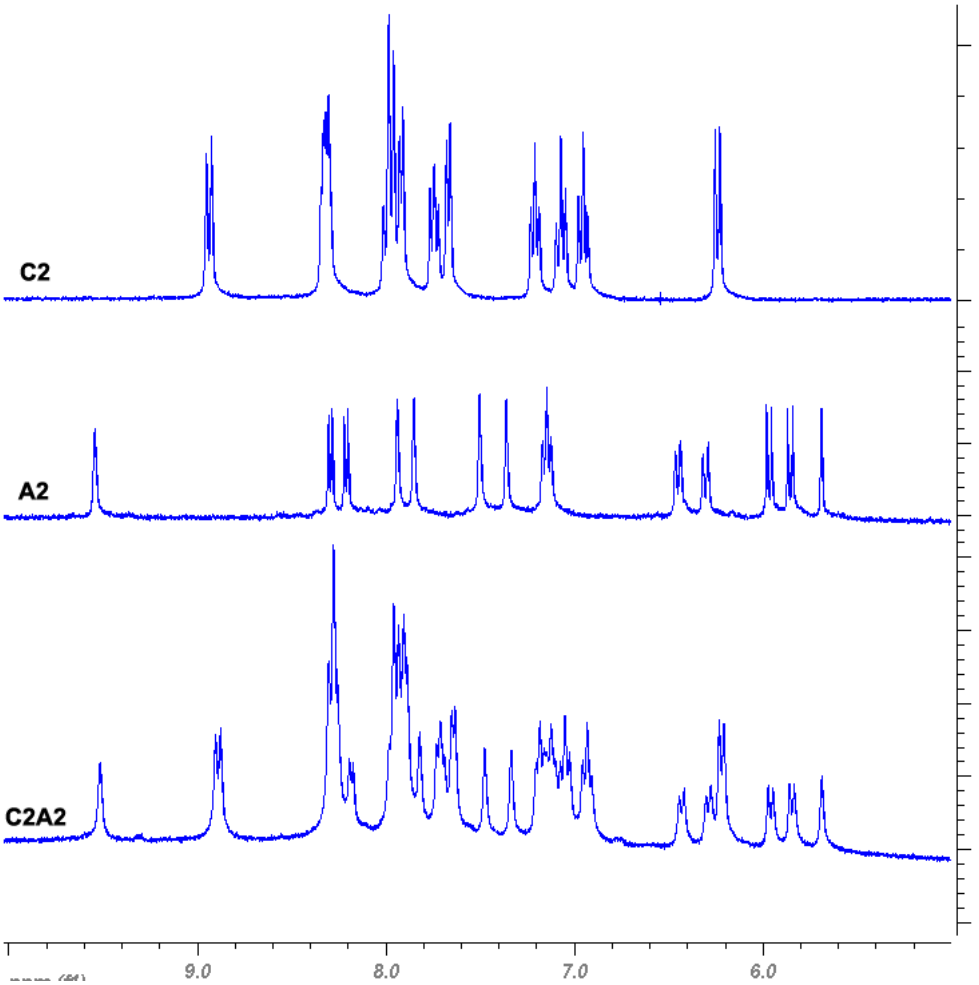


Figure S6. ^{1}H NMR spectra in dmso-d_6 of complexes **C2** and **A2** and their corresponding soft salt **C2A2**.

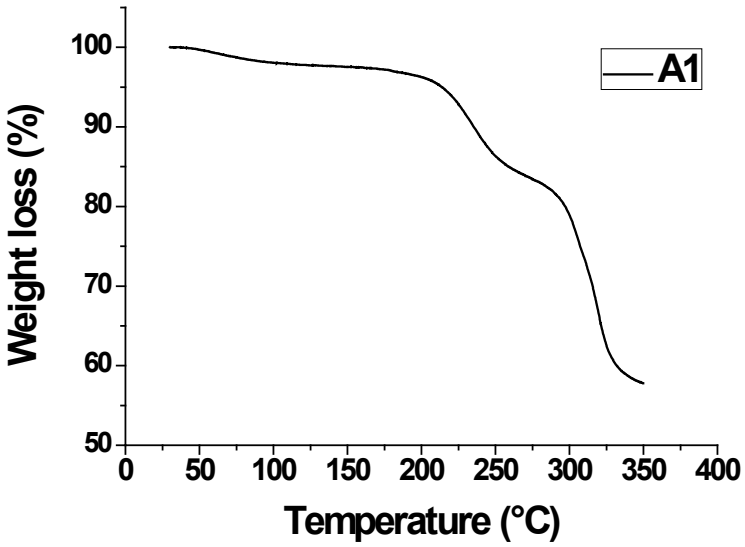


Figure S7. TGA measurements obtained for **A1** (scan rate: 10°C/min, under N_2)

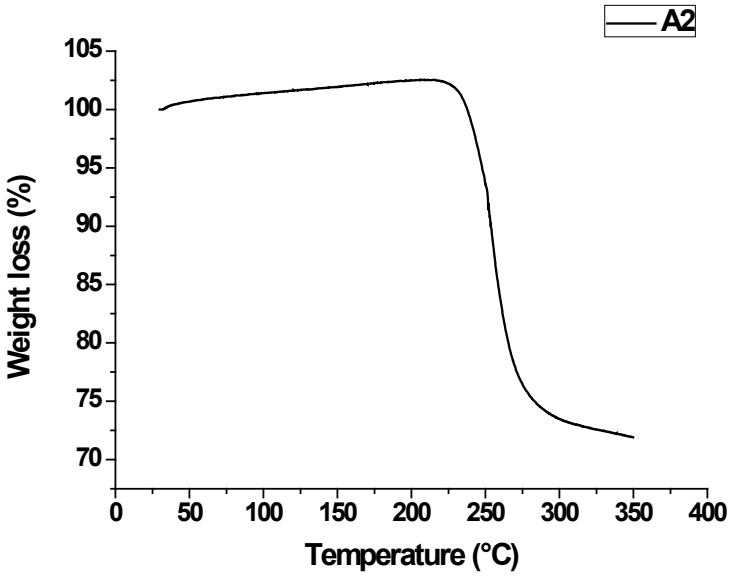


Figure S8. TGA measurements obtained for **A2** (scan rate: 10°C/min, under N_2)

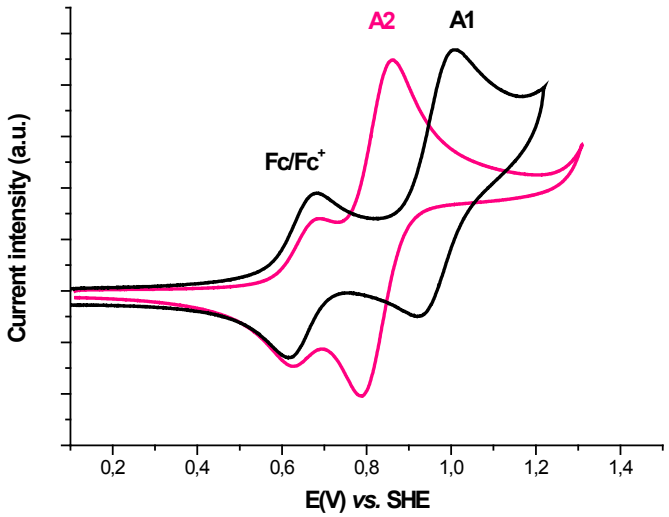


Figure S9. CV traces of **A1** and **A2** in presence of Ferrocene. Scan rate 100 $mV.s^{-1}$ in dry acetonitrile.

Table S1. Spectroscopic data of the samples in acetonitrile solutions.

samples	λ_{abs} (nm)	ε / M^{-1} cm^{-1}
C1.ClO$_4$	420	3733
	384	4874
	343	7539
	258	42842
C2.Cl	467	1331
	381	5068
	309	17290
	257	39133
A1NBu$_4$	465	1927
	405	3904
	341	10988
	258	29865
A2NBu$_4$	470	3660
	415	5486
	342	14801
	266	37180
C1A1	465	2896
	389	10249
	345	20093
	258	73199
C1A2	470	3461
	416	8192
	342	21159
	263	75366
C2A1	467	2599
	408	6704
	340	17413
	309	28474
	258	68405
C2A2	470	4129
	415	8145
	342	21285
	309	32581
	263	75198

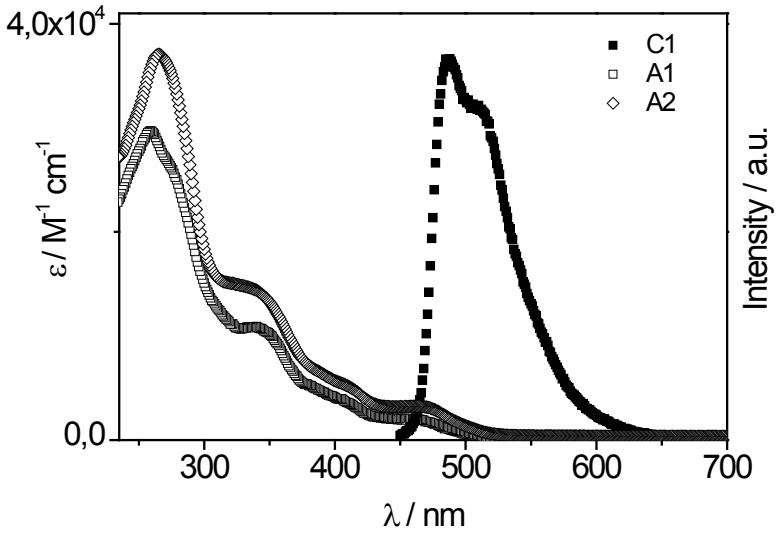


Figure S10. Superimposition of the emission spectrum of **C1** energy donor with the absorption spectra of both **A1** and **A2** energy acceptors relative to the soft salts **C1A1**, **C1A2**.

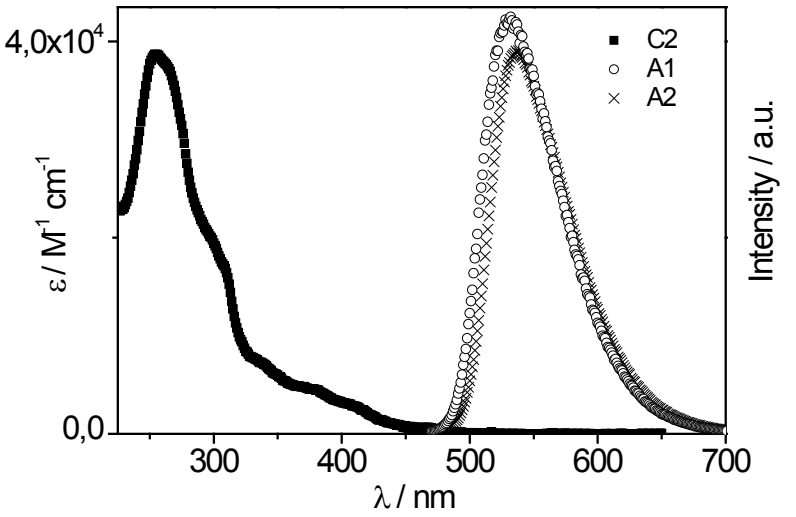


Figure S11. Superimposition of the emission spectrum of **A1** and **A2** energy donors with the absorption spectra of **C2** energy acceptor relative to the soft salts **C2A1**, **C2A2**