Supporting Information

Stepwise Versus Pseudo-Concerted Two-Electron-Transfer in a
Triarylamine - Iridium Dipyrrin - Naphthalene Diimide Triade

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Synthesis.

Materials and Methods. All chemicals were of standard quality and were used without further purification. All experiments were carried out under inert-gas conditions (nitrogen, dried with Sicapent from Merck, oxygen was removed with a cupric oxide catalyst R3-11 from BASF) in flame-dried Schlenk tubes. If necessary, the solvents were purified and dried by standard procedures and kept under inert gas atmosphere. Flash column chromatography was carried out using silica gel “Silica 60 M” (40 – 63 μm) from Macherey-Nagel, Germany. Gel permeation chromatography (GPC) was performed with a Jasco recycling GPC/HPLC-system with two preparative GPC columns (styrol-divinylbenzene-copolymer network, 50 Å, 500 Å, 600 × 20.8 mm) from PSS (Mainz, Germany) a four channel UV/vis-detector (200 – 600 nm) and a fraction collector. The flow rate was 4 ml min⁻¹.

¹H and ¹³C NMR spectra were recorded with a Bruker AVANCE 400 FT spectrometer at 300 K and a Bruker AVANCE 600 DMX FT spectrometer at either 298.8 K for d₆-acetone or 303.6 K for CDCl₃. Multiplet signals or overlapping multiplet signals in the proton spectra that could not be assigned to first order couplings are given as (−). Mass spectra were recorded with a Bruker Daltonics autoflex ll (MALDI) with a DCTB (2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-
enylidene]malononitrile) matrix and with a Bruker Daltonic micrOTOF focus (ESI), respectively. Elemental analyses were performed with a vario Micro CHNS from elementar (Hanau, Germany).

Melting points are uncorrected and were determined by using a Reichert Thermovar Kofler melting point apparatus (Austria).

Starting with commercially available dibenzosuber-5-one (3) we synthesised the donor substituted phenylpyrazole ligands 9 and 10 and the phenylpyrazole ligand without triarylamine fragment, 11 (Scheme S1). Compound 4 was synthesised according to literature procedures and was further reduced with sodium borohydride to give compound 5 (see ref.2). After an Ullmann-type coupling with pyrazole we obtained compound 6 (see ref.3). Buchwald-Hartwig couplings of 6 with the diarylamines 7 and 8 (synthesis following ref.4) resulted in the donor substituted phenylpyrazoles 9 and 10. Compound 6 was dehalogenated by bromine lithium exchange at –78°C and quenched with HCl to yield 11.

Scheme S1. Synthesis of the donor substituted phenylpyrazoles 9 (X = OMe) and 10 (X = tBu) and the reference ligand 11 starting from dibenzosuber-5-one (3).
\textit{Bis(4,4'-di-tert-butyldiphenyl)amine (8).} The synthesis follows a slightly modified procedure according to ref.\textsuperscript{4}: 4-tert-Butylaniline (1.00 ml, 937 mg, 6.28 mmol), 1-tert-butyl-4-iodobenzene (1.12 ml, 1.63 g, 6.28 mmol), Pd\textsubscript{2}(dba)\textsubscript{3}•CHCl\textsubscript{3} (650 mg, 628 µmol), sodium-tert-butoxide (1.51 g, 15.7 mmol) und tri-tert-butylphosphane (942 µl, 942 µmol) were dissolved in dry toluene (20 ml) under nitrogen atmosphere and the reaction mixture was stirred at 115°C for 2 d. The solvent was removed under reduced pressure and the residue was treated with CH\textsubscript{2}Cl\textsubscript{2} (20 ml) and water (20 ml). The phases were separated and the aqueous phase was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 30 ml). The combined organic phase was washed with water (40 ml), dried with MgSO\textsubscript{4} and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: petrol ether : ethyl acetate = 50 : 1) to obtain the product as a brown solid.

Yield: 1.21 g (4.27 mmol, 68%) of a brown solid.

C\textsubscript{20}H\textsubscript{27}N [281.48]

\textit{\textsuperscript{1}H-NMR} (400.1 MHz, d\textsubscript{6}-acetone):

\[ \delta \text{ [ppm]} = 7.27 (\text{AA'}, 4\text{H}), 7.12 (\text{s}, 1\text{H}, \text{NH}), 7.04 (\text{BB'}, 4\text{H}), 1.29 (\text{s}, 18\text{H}, \text{CH}_3). \]

\textit{3-(4,4'-Di-tert-butyldiphenylamino)-7-pyrazolyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (10).} Compound 6 (595 mg, 1.75 mmol), bis(4-tert-butylphenyl)amine (542 mg, 1.93 mmol), Pd\textsubscript{2}(dba)\textsubscript{3}•CHCl\textsubscript{3} (145 mg, 140 µmol) and sodium-tert-butoxide (421 mg, 4.38 mmol) were dissolved in dry toluene (15 ml) under nitrogen atmosphere and degassed for 10 min. A 1.0 M solution of tert-butylphosphane in toluene (210 µl, 210 µmol) was added and the mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the residue was treated with CH\textsubscript{2}Cl\textsubscript{2} and water, the phases were separated and the aqueous phase was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 30 ml). The combined organic phase was washed with water, dried with MgSO\textsubscript{4} and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: petrol ether : ethyl acetate = 4 : 1) to obtain the product as an orange brown solid.

Yield: 730 mg (1.35 mmol, 77%) of an orange brown solid.

Melting point: 103-105°C

C\textsubscript{38}H\textsubscript{41}N\textsubscript{3} [539.75]
$^1$H-NMR (400.1 MHz, $d_6$-acetone):

$\delta$ [ppm] = 8.23 (dd, $^3J_{HH} = 2.5$ Hz, $^4J_{HH} = 0.6$ Hz, 1H), 7.69 (d, $^3J_{HH} = 2.4$ Hz, 1H), 7.63 (d, $^3J_{HH} = 1.7$ Hz, 1H), 7.59 (dd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 2.4$ Hz, 1H), 7.29 (AA', 4H), 7.24 (d, $^3J_{HH} = 8.2$ Hz, 1H), 7.05 (d, $^3J_{HH} = 8.2$ Hz, 1H), 6.98 (BB', 4H), 6.78 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 2.4$ Hz, 1H), 6.45 (dd, $^3J_{HH} = 2.5$ Hz, $^4J_{HH} = 1.77$ Hz, 1H), 4.10 (s, 2H), 3.13 – 3.22 (m, 4H), 1.30 (s, 18H, tBu).

$^{13}$C-NMR (100.6 MHz, $d_6$-acetone):

$\delta$ [ppm] = 146.93 (C$q$), 146.44 (C$q$), 145.93 (C$q$), 2 x 141.2 (CH, C$q$), 140.6 (C$q$), 139.3 (C$q$), 138.3 (C$q$), 134.5 (C$q$), 131.43 (CH), 131.38 (CH), 127.6 (CH), 126.9 (CH), 125.4 (CH), 124.2 (CH), 123.4 (CH), 120.0 (CH), 117.6 (CH), 108.0 (CH), 41.1 (CH$_2$), 34.8 (C$q$), 32.8 (CH$_2$), 32.5 (CH$_2$), 31.8 (CH$_3$).

MALDI-MS (pos.): m/z calc. for C$_{38}$H$_{41}$N$_3$ 539.330, found 539.321.
\(^1\)H-NMR of 10 (400.1 MHz, d\(_6\)-acetone)
$\textbf{13C-NMR of 10}$ (100.6 MHz, $d_6$-acetone)
3-Pyrazolyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (11). Compound 6 (200 mg, 384 µmol) was dissolved in dry THF and the solution was cooled to -78°C. A solution of tBuLi in pentane (652 µl, 1.24 mmol, 1.9 M) was added dropwise and the mixture was stirred at -40°C for 2 - 3 h. To the reddish solution 2 N HCl (340 µl, 284 µmol) was added during a period of 15 min. The reaction mixture was allowed to warm to rt and was then quenched with excess of 2 N HCl (10 ml). The organic solvent was removed under reduced pressure and the residue was taken up with CH₂Cl₂ and water, the phases were separated and the aqueous phase was extracted with CH₂Cl₂ (3 × 40 ml). The combined organic phase was washed with water, dried with MgSO₄ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petrol ether : CH₂Cl₂ = 1 : 1 → 1 : 2) to obtain the product as a colourless solid.

Yield: 100 mg (384 µmol, 62%) of a colourless solid.

C₁₈H₁₆N₂ [260.33]

¹H-NMR (400.1 MHz, CDCl₃):
δ [ppm] = 7.88 (dd, ³J_HH = 2.4 Hz, ⁴J_HH = 0.6 Hz, 1H), 7.71 (dd, ³J_HH = 1.7 Hz, ⁴J_HH = 0.5 Hz, 1H), 7.58 (d, ⁴J_HH = 2.4 Hz, 1H), 7.40 (dd, ³J_HH = 8.2 Hz, ⁴J_HH = 2.4 Hz, 1H), 7.10 - 7.20 (-, 5H), 6.44 (dd, ³J_HH = 2.4 Hz, ⁴J_HH = 1.8 Hz, 1H), 4.17 (s, 2H), 3.20 (s, 4H).

¹³C-NMR (100.6 MHz, CDCl₃):
δ [ppm] = 140.9 (CH), 140.4 (C_q), 139.2 (C_q), 138.6 (C_q), 138.4 (C_q), 137.7 (C_q), 130.7 (CH), 129.7 (CH), 129.2 (CH), 127.0 (CH), 126.8 (CH), 126.3 (CH), 120.1 (CH), 117.3 (CH), 107.4 (CH), 41.1 (CH₂), 32.5 (CH₂), 32.2 (CH₂).

MALDI-MS (pos.): m/z calc. for C₁₈H₁₆N₂ 216.131, found 216.136.
$^1$H-NMR of 11 (400.1 MHz, CDCl$_3$)
$^{13}$C-NMR of 11 (100.6 MHz, CDCl$_3$)
Naphthalene diimides (13 and 14) were synthesised by a microwave mediated condensation (Scheme S2) of naphthalene-1,4,5,8-tetracarboxylic dianhydride with 2,5-di-tert-butylaniline and a second amine (aniline or 17). Compound 17 could be obtained by reaction of 4-nitrobenzaldehyde (15) with pyrrole in the presence of catalytic amounts of iodine\(^5\) and subsequent reduction of the nitro-group with 10\% Pd/C and hydrogen gas in THF.\(^6\)

Scheme S2. Synthesis of the NDI substituted dipyrromethane 14 and the reference compound 13 (without dipyrromethane).

**N-(2,5-Di-tert-butylphenyl)-N′-phenyl-naphthalene-1,4,5,8-tetracarboxylic diimide (13).**

Naphthalene-1,4,5,8-tetracarboxylic dianhydride (12) (500 mg, 1.86 mmol) and 2,5-di-tert-butylaniline (459 mg, 2.24 mmol) and aniline (174 mg, 1.86 mmol) were dissolved in DMF (18 ml) and heated in a microwave oven (300 W, 140°C) 1 h. The solvent was removed under reduced pressure and the resulting solid was purified by flash column chromatography on silica gel (eluent: petrol ether : ethyl acetate = 10 : 1 → 1 : 1) to obtain the product as a grey solid.

Yield: 145 mg (270 µmol, 15\%) of a grey solid.
Melting point: >350°C

C_{34}H_{30}N_{2}O_{4} [530.61].

^1H-NMR (400.1 MHz, CDCl₃):

δ [ppm] = 8.86 (s, 4H), 7.58 – 7.62 (t, 3H), 7.54 (t, 1H), 7.49 (dd, ^3J_{HH} = 8.6 Hz, ^4J_{HH} = 2.2 Hz, 1H), 7.34 (t, 2H), 7.02 (d, ^4J_{HH} = 2.2 Hz, 1H), 1.34 (s, 9H, tBu), 1.28 (s, 9H, tBu).

^13C-NMR (100.6 MHz, CDCl₃):

δ [ppm] = 164.0 (Cₐ), 163.2 (Cₐ), 150.6 (Cₐ), 143.9 (Cₐ), 134.8 (Cₐ), 132.2 (Cₐ), 131.62 (CH), 131.60 (CH), 129.8 (CH), 129.4 (CH), 129.2 (CH), 128.6 (CH), 127.7 (CH), 127.51 (Cₐ), 127.46 (Cₐ), 127.4 (Cₐ), 127.2 (Cₐ), 126.8 (CH), 35.7 (Cₐ), 34.4 (Cₐ), 31.9 (CH₃), 31.4 (CH₃).

MALDI-MS (pos.): m/z calc. for C_{34}H_{30}N_{2}O_{4} 530.220, found 530.120.
$^1$H-NMR of 13 (400.1 MHz, CDCl$_3$)
$^{13}$C-NMR of 13 (100.6 MHz, CDCl$_3$)
N-(2,5-Di-tert-butylphenyl)-N’-(4-(di(1H-pyrrol-2-yl)methyl)phenyl)-naphthalene-1,4,5,8-tetracarboxylic diimide (14). Naphthalene-1,4,5,8-tetracarboxylic dianhydride (12) (1.12 g, 4.16 mmol) and 2,5-di-tert-butylaniline (855 mg, 4.16 mmol) were dissolved in DMF (26 ml) and heated in a microwave oven (300 W, 140°C) for 30 min. 5-(4-Aminophenyl)dipyromethane (17) (988 mg, 4.16 mmol) was added and the mixture was again heated for 30 min. in the microwave oven (300 W, 140°C). The solvent was removed under reduced pressure and the resulting solid was purified by flash column chromatography on silica gel (eluent: petrol ether : ethyl acetate = 4:1 → 3:1 → 2:1 → 1:1 → 1:2) to obtain the product as a brown solid.

Yield: 484 mg (720 µmol, 17%) of a brown solid.

Melting point: 175°C (dec.)

C_{43}H_{38}N_{4}O_{4} [674.78].

¹H-NMR (400.1 MHz, CDCl₃):
δ [ppm] =  8.81 – 8.87 (m, 4H), 8.11 (br d, ³J_{HH} = 1.7 Hz, 2H, NH), 7.63 (d, ³J_{HH} = 8.6 Hz, 1H), 7.51 (dd, ³J_{HH} = 8.6 Hz, ⁴J_{HH} = 2.2 Hz, 1H), 7.37 (AA’, 2H), 7.23 (BB’, 2H), 7.04 (d, ⁴J_{HH} = 2.2 Hz, 1H), 6.67 (ddd, ³J_{HH} = 4.2 Hz, ³J_{HH} = 2.6 Hz, ⁴J_{HH} = 1.6 Hz, 2H), 6.17 (dd, ³J_{HH} = 5.9 Hz, ³J_{HH} = 2.7 Hz, 2H), 5.98 (dddd, ³J_{HH} = 3.3 Hz, ³J_{HH} = 2.4 Hz, ⁴J_{HH} = 1.5 Hz, ⁴J_{HH} = 0.8 Hz, 2H), 5.57 (s, 1H), 1.34 (s, 9H, tBu), 1.29 (s, 9H, tBu).

¹³C-NMR (100.6 MHz, CDCl₃):
δ [ppm] = 163.9 (Cₘ), 163.2 (Cₘ), 150.6 (Cₘ), 143.8 (Cₘ), 143.4 (Cₘ), 133.4 (Cₘ), 132.1 (Cₘ), 132.0 (Cₘ), 131.6 (4 x CH), 129.7 (CH), 129.2 (CH), 128.8 (CH), 127.7 (CH), 127.5 (Cₘ), 127.44 (Cₘ), 127.40 (Cₘ), 127.1 (Cₘ), 126.9 (CH), 117.7 (CH), 108.7 (CH), 107.8 (CH), 43.9 (Cₘ), 35.7 (Cₘ), 34.4 (Cₘ), 31.9 (CH₃), 31.4 (CH₃).

MALDI-MS (pos.): m/z calc. for C_{43}H_{38}N_{4}O_{4} 674.289, found 674.311.
$^1$H-NMR of 14 (400.1 MHz, CDCl$_3$)
$^{13}$C-NMR of 14 (100.6 MHz, CDCl$_3$)
Scheme S3. Synthesis of the dinuclear cyclometalated \( \mu \)-chloro bridged iridium(III) complexes (18 – 20) and the target complexes 1, 2 and 1’.

General procedure for the synthesis of the dinuclear cyclometalated \( \mu \)-chloro bridged iridium(III) complexes (18 – 20) according to ref.\(^7-9\) (GP I). \( \text{Ir(III)}\text{Cl}_3 \cdot n\text{H}_2\text{O} \) (Hereaus, Hanau, Germany) (1 eq.) and a 1-phenylpyrazole derivative (2.25 eq.) were suspended in a mixture of 2-ethoxyethanol and deionized water (3 : 1) under nitrogen atmosphere. The suspension was stirred at 100°C for 24 h. Precipitation was completed by pouring the reaction mixture into water. The grey solid was filtered off, washed with water (3 \( \times \) 10 ml) and hexane (20 ml) and dried. The dinuclear complexes were used for the next reaction step without further purification.

Tetrakis(3-pyrazolyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene)(\( \mu \)-dichloro) diiridium(III) (18) following GP I. \( \text{Ir(III)}\text{Cl}_3 \cdot n\text{H}_2\text{O} \) (139 mg, 393 \( \mu \)mol), 3-pyrazolyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (11) (215 mg, 826 \( \mu \)mol) in a 3 : 1 2-ethoxyethanol-water mixture (20 ml), 100°C, 12 h.

Yield: 280 mg (197 \( \mu \)mol, 95%) of a grey solid.

\( \text{C}_{72}\text{H}_{60}\text{Cl}_2\text{Ir}_2\text{N}_8 \) [1492.64]
MALDI-TOF (pos.): $m/z$ calc. for $C_{72}H_{60}Cl_2Ir_2N_8$ 1488.352, found 1488.313 (100%)

$m/z$ calc. for $C_{36}H_{30}ClIrN_4$ 744.176, found 744.162 (50%).

Tetrakis(3-N,4',4''-dimethoxydiphenylamino)-7-pyrazolyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene($\mu$-dichloro)diiridium(III) (19) following GP I. Ir(III)Cl$_3$$\cdot$$n$H$_2$O (100 mg, 284 $\mu$mol), 3-N-(4,4'-dimethoxydiphenylamino)-7-pyrazolyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (9) (311 mg, 638 $\mu$mol) in a 3 : 1 2-ethoxyethanol-water mixture (15 ml), 100°C, 12 h.

Yield: 337 mg (281 $\mu$mol, 99%) of a grey solid.

$C_{128}H_{112}Cl_2Ir_2N_{12}O_8$ [2401.67]

MALDI-TOF (pos.): $m/z$ calc. for $C_{64}H_{56}ClIrN_6O_4$ 1198.365, found 1198.327,

$m/z$ calc. for $C_{64}H_{56}IrN_6O_4$ 1163.396, found 1163.319.

Tetrakis(3-N,4,4'-di-tert-butyldiphenylamino)-7-pyrazolyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene($\mu$-dichloro)diiridium(III) (20) following GP I. Ir(III)Cl$_3$$\cdot$$n$H$_2$O (131 mg, 371 $\mu$mol), 3-N-(4,4'-di-tert-butyldiphenylamino)-7-pyrazolyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (10) (400 mg, 741 $\mu$mol) in a 3 : 1 2-ethoxyethanol-water mixture (15 ml), 100°C, 12 h.

Yield: 414 mg (159 $\mu$mol, 86%) of a grey solid.

$C_{152}H_{160}Cl_2IrN_{12}$ [2610.31]

MALDI-TOF (pos.): $m/z$ calc. for $C_{76}H_{80}ClIrN_6$ 1304.576, found 1304.592,

$m/z$ calc. for $C_{76}H_{80}IrN_6$ 1269.608, found 1269.630.
General procedure for the synthesis of neutral cyclometalated iridium(III) dipyrrinato complexes according to ref.\textsuperscript{10} (GP II). The dipyrrormethane ligand (14) (1 eq.) was dissolved in dry THF and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.1 eq.) was added under nitrogen atmosphere and the mixture was stirred at rt for 2-3 h. Potassium carbonate (20 eq.) was added and after stirring for 15 min. followed by the addition of the dinuclear iridium(III) complex (18, 19 or 20) (0.5 eq.). The mixture was stirred at 80°C for 12 h. The solvent was removed under reduced pressure and the residue was treated with CH\textsubscript{2}Cl\textsubscript{2} and the solids were filtered off and washed with excess of CH\textsubscript{2}Cl\textsubscript{2}. The crude product was purified by flash column chromatography on silica gel and preparative recycling GPC (CHCl\textsubscript{3}, 4 ml min\textsuperscript{-1}). Finally, the product was precipitated by dropping a CH\textsubscript{2}Cl\textsubscript{2} solution in to hexane.

Synthesis of 1 following GP II. Compound 9 (150 mg, 222 \(\mu\)mol), DDQ (56.0 mg, 250 \(\mu\)mol), potassium carbonate (614 mg, 4.45 mmol), dinuclear iridium(III) complex 19 (294 mg, 120 \(\mu\)mol) in THF (20 ml), 80°C, 12 h. Eluent: CH\textsubscript{2}Cl\textsubscript{2}: MeOH = 99.5 : 0.5) and GPC. Yield: 52.0 mg (30.0 \(\mu\)mol, 13%) of a red solid.

Melting point: >275°C (dec.)

C\textsubscript{107}H\textsubscript{91}IrN\textsubscript{10}O\textsubscript{8} [1837.15]

\(\textsuperscript{1}H\)-NMR (600.1 MHz, \textit{d}\textsubscript{6}-acetone):

\(\delta\) (ppm) = 8.86 (d, \(\textsuperscript{3}J_{HH} = 3.3\) Hz, 4H), 8.47 (d, \(\textsuperscript{3}J_{HH} = 2.5\) Hz, 2H), 7.62 – 7.65 (--, 3H), 7.59 (BB', 2H), 7.51 (dd, \(\textsuperscript{3}J_{HH} = 8.6\) Hz, \(\textsuperscript{4}J_{HH} = 2.3\) Hz, 1H), 7.39 (d, \(\textsuperscript{4}J_{HH} = 2.3\) Hz, 1H), 7.32 (s, 2H), 7.09 (dd, \(\textsuperscript{3}J_{HH} = 1.3\) Hz, \(\textsuperscript{4}J_{HH} = 1.3\) Hz, 2H), 7.03 (dd, \(\textsuperscript{3}J_{HH} = 2.2\) Hz, \(\textsuperscript{4}J_{HH} = 0.5\) Hz, 2H), 6.95 (AA", 8H), 6.88 (d, \(\textsuperscript{3}J_{HH} = 8.3\) Hz, 2H), 6.85 (BB", 8H), 6.70 (d, \(\textsuperscript{3}J_{HH} = 8.2\) Hz, 2H), 6.61 (dd, \(\textsuperscript{3}J_{HH} = 2.4\) Hz, \(\textsuperscript{4}J_{HH} = 2.4\) Hz, 2H), 6.59 (dd, \(\textsuperscript{3}J_{HH} = 2.7\) Hz, \(\textsuperscript{4}J_{HH} = 2.3\) Hz, 2H), 6.57 (dd, \(\textsuperscript{3}J_{HH} = 4.3\) Hz, \(\textsuperscript{4}J_{HH} = 1.3\) Hz, 2H), 6.27 (dd, \(\textsuperscript{3}J_{HH} = 4.3\) Hz, \(\textsuperscript{4}J_{HH} = 1.3\) Hz, 2H), 6.13 (s, 2H), 3.84 (--, 4H), 3.76 (s, 12H, OMe), 2.78 – 3.00 (m, 8H), 1.32 (s, 9H, \textsuperscript{1}Bu), 1.28 (s, 9H, \textsuperscript{1}Bu).
\(^{13}\text{C-NMR}\) (150.9 MHz, d\(_6\)-acetone):

\[\delta [\text{ppm}] = 164.8 \text{ (C}_q\text{)}, 163.8 \text{ (C}_q\text{)}, 156.6 \text{ (C}_q\text{)}, 152.9 \text{ (CH)}, 150.6 \text{ (C}_q\text{)}, 148.3 \text{ (C}_q\text{)}, 147.6 \text{ (C}_q\text{)}, 144.6 \text{ (C}_q\text{)}, 143.4 \text{ (C}_q\text{)}, 142.1 \text{ (C}_q\text{)}, 140.9 \text{ (C}_q\text{)}, 140.7 \text{ (C}_q\text{)}, 138.1 \text{ (CH)}, 137.4 \text{ (C}_q\text{)}, 136.6 \text{ (C}_q\text{)}, 135.8 \text{ (C}_q\text{)}, 135.7 \text{ (CH)}, 135.6 \text{ (C}_q\text{)}, 134.1 \text{ (C}_q\text{)}, 132.9 \text{ (C}_q\text{)}, 132.8 \text{ (C}_q\text{)}, 131.7 \text{ (CH)}, 131.6 \text{ (CH)}, 131.5 \text{ (CH)}, 131.0 \text{ (CH)}, 129.4 \text{ (CH)}, 129.1 \text{ (CH)}, 128.8 \text{ (CH)}, 128.5 \text{ (CH)}, 128.3 \text{ (C}_q\text{)}, 128.2 \text{ (C}_q\text{)}, 128.1 \text{ (C}_q\text{)}, 127.0 \text{ (C}_q\text{)}, 126.8 \text{ (CH)}, 126.7 \text{ (CH)}, 122.2 \text{ (CH)}, 120.0 \text{ (CH)}, 117.5 \text{ (CH)}, 115.4 \text{ (CH)}, 112.4 \text{ (CH)}, 108.0 \text{ (CH)}, 55.6 \text{ (CH}_2\text{)}, 41.3 \text{ (C}_q\text{)}, 36.0 \text{ (C}_q\text{)}, 34.8 \text{ (Cq)}, 33.3 \text{ (CH}_2\text{)}, 32.7 \text{ (CH}_2\text{)}, 32.0 \text{ (CH}_3\text{)}, 31.5 \text{ (CH}_3\text{)}.

**ESI pos. (high resolution):** m/z calc. for C\(_{107}\)H\(_{91}\)IrN\(_{10}\)O\(_8\)\(^+\) 1834.66218, found 1834.6597

\[\Delta = -1.30 \text{ ppm (6%)}\]

m/z calc. for C\(_{107}\)H\(_{91}\)IrN\(_{10}\)O\(_8\)\(^{2+}\) 917.33109, found 917.33235

\[\Delta = 1.37 \text{ ppm (100%).}\]

**CHN-analysis:** calc. for C\(_{107}\)H\(_{91}\)IrN\(_{10}\)O\(_8\) C-%: 69.95, H-%: 4.99, N-%: 7.62,

found for C\(_{107}\)H\(_{91}\)IrN\(_{10}\)O\(_8\) C-%: 69.42, H-%: 4.89, N-%: 7.64.
$^1$H-NMR of 1 (600.1 MHz, d$_6$-acetone)
$^{13}$C-NMR of 1 (150.9 MHz, $d_6$-acetone)
Synthesis of 2 following GP II. 11 (77.0 mg, 114 µmol), DDQ (28.0 mg, 124 µmol), potassium carbonate (286 mg, 2.07 mmol), dinuclear iridium(III) complex 18 (80.0 mg, 52.0 µmol) in THF (15 ml), 80°C, 12 h. Eluent: CH₂Cl₂ : MeOH = 99.5 : 0.5) and GPC.

Yield: 40 mg (28.0 µmol, 27%) of a red solid.

Melting point: >260°C (dec.)

C₈₁H₆₆Ir₈N₄O₄ [1410.68].

¹H-NMR (600.1 MHz, CDCl₃):
δ [ppm] = 8.84 (s, 4H), 7.97 (d, ³Jₜₜ = 2.3 Hz, 2H), 7.67 (AA’, 2H), 7.62 (d, ³Jₜₜ = 8.6 Hz, 1H), 7.50 (dd, ³Jₜₜ = 8.6 Hz, ²Jₗₗ = 2.2 Hz, 1H), 7.37 (BB’, 2H), 7.15 (dd, ³Jₜₜ = 6.2 Hz, ²Jₗₗ = 2.6 Hz, 2H), 7.02 – 7.09 (-, 9H), 7.00 (dd, ³Jₜₜ = 1.3 Hz, ²Jₗₗ = 1.2 Hz, 2H), 6.97 (dd, ³Jₜₜ = 2.2 Hz, ²Jₗₗ = 0.5 Hz, 2H), 6.62 (dd, ³Jₜₜ = 4.3 Hz, ²Jₗₗ = 1.3 Hz, 2H), 6.43 (dd, ³Jₜₜ = 2.7 Hz, ²Jₗₗ = 2.3 Hz, 2H), 6.25 (dd, ³Jₜₜ = 4.3 Hz, ²Jₗₗ = 1.3 Hz, 2H), 6.09 (s, 2H), 4.02 (s, 4H), 2.88 – 3.10 (m, 8H), 1.34 (s, 9H), 1.29 (s, 9H).

¹³C-NMR (150.9 MHz, CDCl₃):
δ [ppm] = 164.0 (C₉), 163.1 (C₉), 152.6 (CH), 150.6 (C₁), 146.9 (C₉), 143.8 (C₉), 142.3 (C₉), 140.8 (C₉), 140.0 (C₉), 139.4 (C₉), 137.4 (CH), 137.0 (C₉), 135.3 (CH), 135.0 (C₉), 134.9 (C₉), 134.3 (C₉), 132.2 (C₉), 131.80 (C₉), 131.78 (CH), 131.7 (CH), 131.6 (CH), 131.1 (CH), 129.7 (CH), 129.2 (CH), 129.0 (CH), 127.7 (CH), 127.5 (C₉), 127.4 (C₉), 127.33 (C₉), 127.30 (CH), 127.1 (C₉), 126.9 (CH), 126.5 (CH), 126.0 (CH), 124.9 (CH), 116.9 (CH), 111.3 (CH), 106.8 (CH), 41.0 (CH₂), 35.7 (C₉), 34.5 (C₉), 33.1 (CH₂), 32.5 (CH₂), 31.9 (CH₃), 31.4 (CH₃).

ESI pos. (high resolution): m/z calc. for C₇₉H₆₆Ir₈N₄O₄ 1380.472920, found 1380.47390, δ = 0.71 ppm.

CHN-analysis: calc. for C₇₉H₆₆Ir₈N₄O₄ C-%: 68.63, H-%: 4.74, N-%: 8.10, found for C₇₉H₆₆Ir₈N₄O₄ C-%: 68.44, H-%: 5.05, N-%: 7.80.
$^1$H-NMR of 2 (600.1 MHz, CDCl$_3$)
$^{13}$C-NMR of 2 (150.9 MHz, CDCl$_3$)
Synthesis of 1’ following GP II. Compound 10 (109 mg, 161 µmol), DDQ (40.0 mg, 177 µmol), potassium carbonate (445 mg, 3.22 mmol), dinuclear iridium(III) complex 20 (210 mg, 80.0 µmol) in THF (15 ml), 80°C, 12 h. Eluent: CH₂Cl₂ : petrol ether = 3 : 2) and GPC.

Yield: 79 mg (44.2 µmol, 28%) of a red solid.

Melting point: >270°C (dec.)

C₁₁₉H₁₁₅IrN₁₀O₄ [1941.47]

¹H-NMR (600.1 MHz, d₆-acetone):
δ [ppm] = 8.86 (s, 4H), 8.40 (d, ³J₃H₁ = 2.7 Hz, 2H), 7.62 – 7.64 (-, 3H), 7.58 (BB', 2H), 7.51 (dd, ³J₃H₁ = 8.6 Hz, ⁴J₃H₁ = 2.3 Hz, 1H), 7.38 (d, ³J₃H₁ = 2.2 Hz, 1H), 7.29 (s, 2H), 7.27 (AA', 8H), 7.09 (dd, ³J₃H₁ = 1.3 Hz, ³J₉H₁ = 1.3 Hz, 2H), 7.02 (dd, ³J₉H₁ = 2.1 Hz, ⁴J₉H₁ = 0.5 Hz, 2H), 6.94 (d, ³J₃H₁ = 8.24 Hz, 2H), 6.90 (BB', 8H), 6.87 (d, ³J₃H₁ = 2.3 Hz, 2H), 6.73 (dd, ³J₉H₁ = 8.1 Hz, ⁴J₉H₁ = 2.4 Hz, 2H), 6.56 – 6.57 (-, 2H), 6.24 (dd, ³J₉H₁ = 4.3 Hz, ⁴J₉H₁ = 1.3 Hz, 2H), 6.16 (s, 2H), 3.87 (d, ³J₃H₁ = 9.6 Hz, 4H), 2.81 – 3.00 (m, 8H), 1.33 (s, 9H, tBu), 1.29 (s, 36H, tBu), 1.28 (s, 9H, tBu).

¹³C-NMR (150.9 MHz, d₆-acetone):
δ [ppm] = 164.8 (Cq), 163.8 (Cq), 152.9 (CH), 150.6 (Cq), 148.2 (Cq), 146.6 (Cq), 146.3 (Cq), 145.7 (Cq), 144.6 (Cq), 143.4 (Cq), 141.1 (Cq), 140.8 (Cq), 138.1 (CH), 137.5 (Cq), 136.5 (Cq), 135.9 (CH), 135.6 (Cq), 135.6 (CH), 134.7 (Cq), 134.1 (Cq), 132.9 (Cq), 131.8 (CH), 131.7 (CH), 131.5 (CH), 131.3 (CH), 129.4 (Cq), 129.1 (CH), 128.8 (CH), 128.5 (CH), 128.3 (Cq), 128.2 (Cq), 128.1 (Cq), 126.8 (CH), 126.74 (CH), 126.69 (CH), 125.1 (CH), 124.2 (CH), 122.9 (CH), 117.6 (CH), 112.4 (CH), 108.0 (CH), 41.2 (CH₂), 36.1 (Cq), 34.8 (Cq), 34.7 (Cq), 33.1 (CH₂), 32.9 (CH₂), 32.0 (CH₃), 31.7 (CH₃), 31.5 (CH₃).

ESI pos. (high resolution): m/z calc. for C₁₁₉H₁₁₅IrN₁₀O₄ 1938.870320, found 1938.87120, Δ = 0.45 ppm.

CHN Analyse: calc. for C₁₁₉H₁₁₅IrN₁₀O₄ C-%: 73.62, H-%: 5.97, N-%: 7.21,
found for C₁₁₉H₁₁₅IrN₁₀O₄ C-%: 73.35, H-%: 6.03, N-%: 7.37
$^1$H-NMR of 1' (600.1 MHz, d$_6$-acetone)
$^{13}$C-NMR of 1 (150.9 MHz, d$_6$-acetone)
**Cyclic Voltammetry.** Cyclic voltammograms were measured with a computer controlled GAMRY instruments (Reference 600) potentiostat (Warminster, PA, USA) under an argon atmosphere in dry and oxygen-free MeCN solutions with tetrabutylammonium hexafluorophosphate (TBAH) (0.2 M) as the supporting electrolyte. The concentration of the solute was lower than 0.5 mM in MeCN due to weak solubility. A conventional three electrode set-up consisting of a platinum disc working electrode (Ø = 1 mm), a Ag/AgCl LEAK FREE reference electrode (Warner Instruments, Hamden, CT, USA) and a platinum wire counter electrode was used. The reference electrode was first referenced against the ferrocene/ferrocenium redox couple. The measurements were performed at a scan rate of 250 mV s\(^{-1}\). Chemical and electrochemical reversability of the redox processes were checked by multi thin layer experiments and measurements at different scan rates (from 10 – 1000 mV s\(^{-1}\)), respectively.

**Table S1.** Cyclic voltammetry of 1, 1\(^\prime\) and 2 (1 – 5 mM) in 0.2 M TBAH/MeCN, at \(v = 250 \text{ mV s}\(^{-1}\) vs. Fc/Fc\(^+\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E(1/2)) Red3 (Ir(dipy)) / mV</th>
<th>(E(1/2)) Red1(2) (NDI) / mV</th>
<th>(E(1/2)) Ox1 (TAA) / mV</th>
<th>(E(pa)) Ox2 (Ir(dipy)) / mV</th>
<th>(\Delta E(1/2)) / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1945(^{i}) (-1425(^{i}))</td>
<td>-960(^{f}) (-1405(^{f}))</td>
<td>225(^{f})</td>
<td>565(^{i})</td>
<td>1185</td>
</tr>
<tr>
<td>2</td>
<td>-1945(^{i}) (-1405(^{i}))</td>
<td>-950(^{f}) (-1410(^{f}))</td>
<td>-</td>
<td>510(^{i})</td>
<td>1460</td>
</tr>
<tr>
<td>1(^\prime)</td>
<td>-1910(^{i}) (-1410(^{i}))</td>
<td>-940(^{f}) (-1410(^{f}))</td>
<td>410(^{f})</td>
<td>575(^{i})</td>
<td>1350</td>
</tr>
</tbody>
</table>

\(^{i}\) irreversible, \(^{f}\) reversible

**UV/vis spectroscopy.** All solvents were spectroscopic grade and were used without further purification. Absorption spectra were recorded with a JASCO V-670 UV/vis/NIR spectrometer in 1 cm quartz cuvettes from Starna (Pfungstadt, Germany) at 23°C.
Spectroelectrochemistry (SEC). The set-up consists of a cylindrical quartz cell with an optically transparent and polished bottom, a platinum disc working electrode (6 mm diameter), a gold-coated metal plate as counter electrode and an Ag/AgCl pseudo-reference electrode. The cell was charged with dry and oxygen-free MeCN solution with tetrabutylammonium hexafluorophosphate (TBAH) (0.2 M) as the supporting electrolyte. Using an EG & G Princeton Applied Research Model 283 potentiostat potentials between 50 or 100 mV steps were applied to the working electrode. UV/vis spectra (JASCO V-670 UV/vis/NIR spectrometer) were recorded in reflection at the polished working electrode, with 100 µm distance between the cell bottom and the surface of the working electrode (adjusted with a micrometer screw). The concentration of 1 was 2.4×10⁻⁶ mol l⁻¹. The spectra of “pure” radical anion (NDI⁻) and cation (TAA⁺) were obtained by subtracting the spectra of neutral 1 from the spectra measured at most negative and most positive potentials. For the cation (TAA⁺) spectra a factor of 0.5 was taken into account. The resulting spectra for NDI⁻, TAA⁺ and the sum of both radical ions are shown in Figure S1 and are in excellent agreement with the transient signal for the lowest excited state (CS₂) (see fs- and ns-transient absorption).

Figure S1. SEC of 1 in MeCN at 298 K: spectra of both first reduction (blue) and first oxidation (green) and sum of the NDI⁻ and TAA⁺ spectra (red).
**Femtosecond transient absorption pump-probe** set-up consists of a Helios transient spectrometer from Ultrafast Systems and is driven by Solstice CPA femtosecond laser from Newport Spectra Physics which has a pulse duration of 100 fs. The pump wavelengths of 378 nm and 480 nm are generated by a TOPAS-C with a pulse duration of about 140 fs. For probing the excited sample the fundamental wavelength of 800 nm is used to generate a white light continuum from 400 – 800 nm. For the detailed setup see ref.\textsuperscript{12} All experiments were performed in quartz cuvettes from spectrocell (Oreland, PA) with an optical path length of 2 mm equipped with a micro-stirrer. All samples were dissolved in MeCN and filtered. Before the measurement the solution was purged with pure argon for at least 30 min. The concentration of the samples were $2.6 \times 10^{-5} – 6.3 \times 10^{-5}$ mol l\textsuperscript{-1} and the attenuated energy of the pump-probe experiments was 100 – 245 nJ at both excitation wavelengths. The time-resolved spectra were analysed by global fitting with GLOTARAN\textsuperscript{13} employing a target model (i.e. branched model) modelling the IRF (ca. 150 fs), the white light dispersion (chirp), and the coherent artifact (the model used has the time characteristics of the IRF) at time zero to yield the species associated difference spectra (SADS) and their corresponding time constants. The number of components $n$ was first estimated by singular value decomposition. Then, the transient map is deconvoluted into the $n$ SADS under the assumption of a kinetic scheme which is represented by a $K$ matrix in which the off-diagonal elements contain the rate constants between different states while the diagonal elements contain the total rate constants for each state. Solving a set of differential equations $d/dt(c(t)) = Kc(t)$ yields the time dependent concentrations $c(t)$ for all species. The experimentally observed transient map (time x wavelength) $\Psi$ can then be put as $\Psi = C(\theta)E^T$ in which matrix $C$ contains the concentration profiles of all components and matrix $E$ the species associated spectra. Details about this procedure can be found in ref.\textsuperscript{14,15}
Figure S2. fs-Transient absorption data corrected for chirp and scattered light (excitation at 26500 cm\(^{-1}\) (378 nm) and 20800 cm\(^{-1}\) (480 nm)) of 1 in MeCN.

Figure S3. Species associated difference spectra (SADS) of 1 from a global target analysis of a transient map obtained by 378 nm excitation in MeCN. The colors of spectra refer to the states in Figure 5. In this fit, the CS\(_1\) species was explicitly included as the green SADS. However, because of the very small contribution to the overall transient map, we consider the spectral features of the green CS\(_1\) spectrum to be quite unreliable.
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**Figure S4.** fs-Transient absorption data corrected for chirp and scattered light (excitation at 26500 cm\(^{-1}\) (378 nm) and 20800 cm\(^{-1}\) (480 nm)) of 2 in MeCN.

**Figure S5.** Species associated difference spectra (SADS) of 1´ from a global target analysis of a transient map obtained by a 378 nm excitation and b 480 nm excitation in MeCN. The colour of spectra refer to the states in Figure 3. The red spectrum refers to the CS\(_2\) state where tert-Bu groups are attached at the TAAs.
Figure S6. fs-Transient absorption data corrected for chirp and scattered light (excitation at 26500 cm\(^{-1}\) (378 nm) and 20800 cm\(^{-1}\) (480 nm)) of 1´ in MeCN.

Table S2. Rate constants for singlet-triplet ISC (\(^{1,3}\)NDI), charge transfer (hot-CT and CT), charge separation (CS\(_1\) and CS\(_2\)), phosphorescence (\(^3\)Ir) and charge recombination (S\(_0\)) of 1, 2 and 1´ at different excitation wavelength (\(\lambda_{\text{ex}}\)) in MeCN.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{ex}}) / nm</th>
<th>(k(^{1,3}\text{NDI} \rightarrow ^3\text{NDI}) / 10^{11} \text{s}^{-1})</th>
<th>(k(^{1,3}\text{NDI} \rightarrow \text{hot-CT}) / 10^{12} \text{s}^{-1})</th>
<th>(k(\text{hot-CT} \rightarrow \text{CT}) / 10^{12} \text{s}^{-1})</th>
<th>(k(\text{CT} \rightarrow CS_1) / 10^{10} \text{s}^{-1})</th>
<th>(k(CS_1 \rightarrow CS_2) / 10^9 \text{s}^{-1})</th>
<th>(k(CS_1 \rightarrow S_0) / 10^8 \text{s}^{-1})</th>
<th>(k(CS_2 \rightarrow S_0) / 10^8 \text{s}^{-1})</th>
<th>(k(\text{CT} \rightarrow S_0) / 10^9 \text{s}^{-1})</th>
<th>(k(^{3}\text{Ir} \rightarrow CS_1) / 10^7 \text{s}^{-1})</th>
<th>(k(^{3}\text{Ir} \rightarrow S_0) / 10^7 \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>378 480</td>
<td>9.1 - 1.6</td>
<td>4.6 &gt; 2.0</td>
<td>- 1.7</td>
<td>3.1 1.2</td>
<td>1.2 1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>378 480</td>
<td>8.3 7.5 1.4</td>
<td>3.8 - 5.9</td>
<td>- 1.7</td>
<td>- 1.1 1.1</td>
<td>1.4 1.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1´</td>
<td>378 480</td>
<td>12 4.0 3.6</td>
<td>17 7.3 31 5.5</td>
<td>8.0 3.4 31 -</td>
<td>1.1 1.2</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>
Nanosecond transient absorption spectra were measured with an Edinburgh LP 920 Laser Flash spectrometer. All solvents were spectroscopic grade and used without further purification. Measurements were carried out in a 1 cm quartz cell (Starna, Pfungstadt, Germany). The samples were degassed by bubbling argon through the solution for at least 30 min. The samples were excited with 5 ns laser pulses at 18800 cm\(^{-1}\) (532 nm), 24000 cm\(^{-1}\) (416 nm) or 28200 cm\(^{-1}\) (355 nm). The excitation pulse was produced by a Continuum Minilite II Nd:YAG laser operating at 10 Hz and the probe pulse was provided by a pulsed Xe flash lamp. For experiments at 24000 cm\(^{-1}\) the THG of the fundamental of 9400 cm\(^{-1}\) (1064 nm) was shifted to lower energy by means of a 50 cm Raman shifter which was charged with hydrogen (45 bar). The corresponding energy was selected by a Pellin-Broca prism. The 24000 cm\(^{-1}\) pump energy was used in order to avoid ionisation of the triarylamine moieties.\(^2\) The instrument response (ca. 8 ns) of the setup was determined by measuring the scattered light using a LUDOX AS-30 colloidal silica suspension in water. Decay curves with a lifetime shorter than 100 ns were deconvoluted with the IRF using the corresponding spectrometer software. Longer decays were fitted with the Tail-Fit function of the spectrometer software. Residuals and autocorrelation function (without any significant structure) served as the main criteria in the evaluation of the fit.

![Figure S7. ns-Transient absorption spectra of 1 in MeCN (left) and corresponding time scan and fit at 16500 cm\(^{-1}\) (606 nm) (right). Early spectra are shown in blue / green and late spectra in yellow / orange / red colours (1: 0 – 3345 ns).](image)
Figure S8. ns-Transient absorption spectra of 1\(^{\ddagger}\) in MeCN (left) and corresponding time scan and fit at \(16500\) cm\(^{-1}\) (606 nm) (right). Early spectra are shown in blue / green and late spectra in yellow / orange / red colours (1\(^{\ddagger}\): 0 – 135 ns).

Measurements were performed at different concentrations (1.4 – 5.2\(\times\)10\(^{-5}\) mol l\(^{-1}\)) and pulse energy (0.2 mJ – 1.2 mJ). Within these ranges there is no significant variation of lifetimes or amplitudes which excludes the presence of bimolecular deactivation processes. Measurements in air-saturated solvents showed no significant changes of lifetimes. The quantum yield of CS state formation was estimated by actinometry at 28200 cm\(^{-1}\) (355 nm) vs. benzophenone\(^{16}\) (in benzene) and at 18800 cm\(^{-1}\) (532 nm) and 24000 cm\(^{-1}\) (416 nm) vs. Ru(bpy)\(_2\)Cl\(_2\)\(^{17}\) (in H\(_2\)O) with the following equation:  
\[
\Phi_{CS} = \Phi_{ref} \times \left( \frac{\Delta OD_{CS} \times \varepsilon_{ref}}{\Delta OD_{ref} \times \varepsilon_{CS}} \right)^{12,18}.
\]

We used 7220 l mol\(^{-1}\) cm\(^{-1}\) for the \(\varepsilon_{ref}\) value of the benzophenone transient absorption signal at 18900 cm\(^{-1}\) (530 nm) and 11300 l mol\(^{-1}\) cm\(^{-1}\) for the Ru(bpy)\(_2\)Cl\(_2\) transient signal at 23300 cm\(^{-1}\) (430 nm). The triplet state quantum yield for both references are according to literature\(^{19-21}\) close to unity, therefore we set \(\Phi_{ref} = 1\). Actinometric measurements for complex 1 (\(\varepsilon_{CS} = 39210\) l mol\(^{-1}\) cm\(^{-1}\) at 21100 cm\(^{-1}\) (473 nm)) in MeCN at 28200 cm\(^{-1}\) (355 nm) pump energy result in a quantum yield of about 47% and for the other two pump wavelengths at 18800 cm\(^{-1}\) (532 nm) and 24000 cm\(^{-1}\) (416 nm) we determined a quantum yield close to unity\(^{22}\). For the \(\varepsilon_{CS}\) values see Spectroelectrochemistry section.
**Emission Spectroscopy.** Steady state emission spectra at room temperature were recorded on a PTI (Photon Technology International) fluorescence spectrometer QM-2000-4 with a cooled photomultiplier (R928 P) and a 75 W xenon short arc lamp in 1 cm quartz cells from Starna (Pfungstadt, Germany). All solvents were spectroscopic grade and were used without further purification. The concentration was ca. $10^{-5} - 10^{-6}$ M and oxygen was removed by bubbling inert gas through the solutions for at least 30 min before each measurement. The luminescence quantum yields were determined by a calibrated integrating sphere (labsphere, North Sutton, NH, USA).

**Reorganisation energies.** Reorganisation energies for the self-exchange ($\lambda_v$) of the NDI anion, TAA cation and Ir(dipy) cation were either extracted from literature for NDI (0.39 eV)$^{23}$ and TAA (0.12 eV)$^{24}$ or calculated via the NICG (neutral in cation geometry) method for the Ir(ppz)$_2$(dipy) cation (0.25 eV). With the NICG method the inner reorganisation energy $\lambda_v$ in the gas phase is determined by the following equation: $\lambda_v = (n^+ + c^0) - (n^0 + c^+)$ using DFT calculations, where $n^+$ is the energy of the unsubstituted Ir(ppz)$_2$(dipy) complex with a positive charge (+) and doublet multiplicity at the geometry of the neutral complex. $c^0$ is the energy of the neutral Ir(ppz)$_2$(dipy) fragment and singlet multiplicity at the cationic geometry. For $n^0$ and $c^+$ the energies were calculated with singlet multiplicity (neutral complex) and with doublet multiplicity (cation), respectively, at the neutral and positive complex geometry. All calculations were performed using Gaussian09 with PBE1PBE functional and a 6-31G* basis set for C, H and N and pseudo potentials (SDD) for the Ir atom.$^{28}$ The inner reorganisation energy for a specific process was calculated as the average of the self-exchange reorganisation energy of the involved molecular units. The solvent reorganisation ($\lambda_o$) energies were estimated by the Born equation$^{25,29,30}$ (eq. S1):

$$\lambda_o = \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{2r_D} + \frac{1}{2r_A} + \frac{1}{d_{DA}} \right) \left( \frac{1}{n^2} + \frac{1}{D} \right)$$  \hspace{1cm} (S1)

In this equation $e$ represents the elementary charge, $n$ is the refractive index and $D$ the static dielectric constant of the solvent. Radii of the donor and acceptor ($r_D$, $r_A$) chromophores were determined by calculating the geometries of the redox units with MM2 and extracting the radii of the Connolly Molecular Surface with ChemBio3D Ultra 12.0. The centre to centre distance ($d_{DA}$) of the redox units were computed using Gaussian09$^{28}$ (see above). With equation S2 und S3$^{25}$
\[ \lambda = \lambda_o + \lambda_v \] and 
\[ \Delta G^* = \left( \frac{\lambda + \Delta G_{00}}{4\lambda} \right)^2 \]
we determined the free energy of activation \( \Delta G^* \) for the corresponding ET processes (see Table S3).

**Table S3.** Reorganisation energies (\( \lambda_o \)) calculated by the Born equation (eq. S1) for the CS (\(^3\)Ir → CS\(_1\), CS\(_1\) → CS\(_2\), \(^3\)Ir → CS\(_2\)) and CR processes (CS\(_2\) → S\(_0\), CS\(_1\) → S\(_0\)) of complex 1, 2 and 1\(^{'}\) and their corresponding \( \lambda_v \) and \( \Delta G^* \) values.

<table>
<thead>
<tr>
<th></th>
<th>( r_D )</th>
<th>( r_A )</th>
<th>( d_{DA} )</th>
<th>( \lambda_o, \lambda_v (\Delta G^*) ) (CS(_1) → CS(_2))</th>
<th>( \lambda_o, \lambda_v (\Delta G^*) ) ((^3)Ir → CS(_1))</th>
<th>( \lambda_o, \lambda_v (\Delta G^*) ) ((^3)Ir → CS(_2))</th>
<th>( \lambda_o, \lambda_v (\Delta G^*) ) (CS(_2) → S(_0))</th>
<th>( \lambda_o, \lambda_v (\Delta G^*) ) (CS(_1) → S(_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.81</td>
<td>3.97</td>
<td>2.01(^a)</td>
<td>0.88</td>
<td>0.91</td>
<td>1.36</td>
<td>1.36</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.23(^b)</td>
<td>(0.13)</td>
<td>(0.13)</td>
<td>(0.12)</td>
<td>(0.03)</td>
<td>(0.01)</td>
</tr>
<tr>
<td>2</td>
<td>5.32</td>
<td>3.97</td>
<td>1.00(^c)</td>
<td>-</td>
<td>0.32</td>
<td>-</td>
<td>-</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td>(0.13)</td>
<td></td>
<td></td>
<td></td>
<td>(0.01)</td>
</tr>
<tr>
<td>1(^{'})</td>
<td>4.81</td>
<td>3.97</td>
<td>2.01(^a)</td>
<td>0.88</td>
<td>0.91</td>
<td>1.28</td>
<td>1.28</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.23(^b)</td>
<td>(0.19)</td>
<td>(0.13)</td>
<td>(0.15)</td>
<td>(0.01)</td>
<td>(0.01)</td>
</tr>
</tbody>
</table>

\(^a\) centre to centre distance (\(d_{DA}\)) between TAA and NDI, \(^b\) between TAA and Ir(dipy) or \(^c\) between NDI and Ir(dipy).

**State energies.** State energies of CS\(_1\) and CS\(_2\) (see Table S4) were estimated by the redox potentials in MeCN of TAA, Ir(ppz\(_2\))(dipy) and NDI, respectively, corrected for Coulomb attraction of the charges using Rehm-Wellner equation (eq. S4\(^{31}\)).

\[ \Delta G_{00}^{00} = \frac{N_A}{1000} ze\left[ E_{ox}(D/D^+) - E_{red}(A/A^-) \right] - \frac{N_A e^2}{1000 \cdot 4 \pi \varepsilon_0} \left[ \frac{1}{2 r_D} + \frac{1}{2 r_A} \left( \frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_s} \right) + \frac{1}{\varepsilon_s d_{DA}} \right] \]  

(S4)

In this equation \(N_A\) is the Avogadro constant and \( \left[ E_{ox}(D/D^+) - E_{red}(A/A^-) \right] \) reflects the redox-difference between oxidation of the donor (TAA or Ir(ppz\(_2\))(dipy)) and reduction of the acceptor (NDI). The redox-differences were taken from the cyclic voltammetry experiments (see Table S1). \( \varepsilon_s \) is the dielectric constant of the solvent used in the CV and in the transient absorption (\(\varepsilon_s\)) measurements. \( r_D \) and \( r_A \) are the radii of the donor and the acceptor, respectively. \( d_{AD} \) is the centre to centre distance of donor and acceptor (see reorganisation energies).

**Table S4.** Rehm-Wellner data for the CS\(_2\) states of 1 and 1\(^{'}\) and of the CS\(_1\) state of 2.
By fitting a tangent on the rising edge of the high energy side of the emission band we determined the state energy of the $^3\text{Ir(ppz)}_2(\text{dipy})$ state for 1, 2 and 1’ and for the CT state of 13, respectively. The $^1\text{NDI}$ state energy was estimated by fitting a tangent to the rising edge of the low energy side of the absorption spectra. These data are given in Fig. 1 in the main text of the paper. $^3\text{NDI}$ state energy was extracted from ref$^{32,33}$.

Dexter-type concerted TET.

**Figure S9.** HOMO-LUMO diagram of triade 1 with a hypothetical concerted TET.
Orbital plots of 1. LUMO and LUMO-1 of 1 were calculated at DFT level of theory (see section Reorganisation energies)

Figure S10. Orbital pictures of the LUMOs involved in the ET process $^3\text{Ir} \rightarrow \text{CS}_1$. LUMO (b symmetry) (left) and LUMO (a symmetry) (right) of complex 1 calculated at DFT level of theory.

References


