A small cationic donor–acceptor iridium complex with a long-lived charge-separated state†

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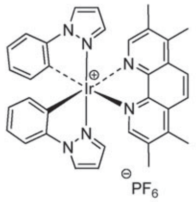
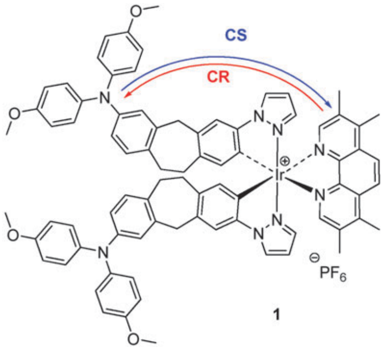
A cationic cyclometalated iridium complex with a triarylamine donor attached to the primary ligand sphere showed long-lived (0.04 and 1.7 μs) charge-separated states after photoexcitation which are due to a combined Marcus inverted region effect and spin-selection rules.

Redox cascades that display long-lived charge-separated (CS) states upon photoexcitation of a chromophore are model compounds for the initial steps in photosynthesis and may further be used in artificial photovoltaic devices.[1–4] Major traps that shorten the lifetime of the otherwise long-lived CS states are low-lying triplet states, obstacles that are inherent to all closed-shell organic chromophores as the triplet states are always lower in energy than the associated singlet states.[5] This circumstance usually limits the energy stored in the charge-separated state which therefore has to be lower than the lowest triplet state of the light absorbing chromophore. Consequently, this leads to energy loss because the lowest photon energy that can be absorbed by an organic chromophore is that of the lowest lying singlet state. Furthermore, in terms of energy conservation, it is generally advantageous if the energy of the lowest excitable state is as close as possible to the charge-separated state. In this communication we seek to circumvent the above mentioned problem by using a simple cyclometalated iridium complex as the chromophore which, owing to strong spin–orbit coupling, shows moderately strong singlet–triplet absorption and all other states may involve strong triplet components.[6] Thus, the lowest energy state directly accessible by photoexcitation is a triplet state whose energy can directly be used to induce charge separation. A further goal of this study is to keep the redox cascades as small as possible while still maintaining a long-lived CS state, an option that requires special design and is generally hard to achieve.[7,8]

While cationic mixed-ligand Ir complexes $[(C^\wedge N)_2Ir(N^\wedge N)]^+$ similar to **Ref** were recently used in organic light-emitting diodes (OLEDs),[9–12] we used this type of Ir complex chromophore directly linked to two equivalent donor components in order to construct a relatively small and simple (donor)$_2$–acceptor (D_2–A) molecule which may display a long-lived CS state. Triarylamine (TAA) was chosen as the donor (D) because of its high-lying triplet state (3.05 eV).[13] It was connected to the phenylpyrazole *via* a methylene- and an ethylene-bridge in order to minimise conformational flexibility. The Ir complex or, more precisely, the 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp) ligand serves as the acceptor (A).



Ref



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The TAA-substituted cyclometalating ligand **ppz$_{TAA}$** ($C^\wedge N$) for complex **1** was synthesised from 3,7-dibromo-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene: pyrazole was connected to this dibromo-compound *via* copper-catalysed coupling and the dianisylamine was attached by a palladium-catalysed Buchwald–Hartwig amination.

The target complexes were synthesised *via* the dichloro-bridged Ir(III) dimers $(C^\wedge N)_2Ir(\mu{-}Cl)_2Ir(C^\wedge N)_2$ which were synthesised following the classical method of Nonoyama by reacting the cyclometalating ligands with $IrCl_3$ in ethoxyethanol–water 3 : 1 at 110 °C for 12 h.[14] The mixed-ligand complexes were then prepared in dry dichlormethane by reaction of the corresponding dichloro-bridged iridium(III) dimer with the tmp ($N^\wedge N$) ligand, followed by metathesis with NH_4PF_6.[12,15]

The electrochemical properties of the bis-cyclometalated complex, its reference and the free ligand were examined by cyclic voltammetry, see Table 1.

The complexes show one reduction at about −2000 mV that is assigned to the reduction of the tmp ligand, an interpretation supported by electrochemical studies of related Ir(III) compounds. Furthermore, the complexes exhibit one oxidation wave at about 800–900 mV that is associated with

Table 1 Redox properties of the ligand, **Ref** and **1** *vs.* Fc/Fc$^+$ in MeCN (0.2 M tetrabutylammonium hexafluorophosphate at ν = 100 mV s^{-1})

	$E^{Ox}_{1/2}$ (Ir)/mV	$E^{Ox}_{1/2}$ (TAA)/mV	$E^{Red}_{1/2}$/mV	$\Delta E_{1/2} = E^{Ox} - E^{Red}$/mV
ppz$_{TAA}$	—	180_{rev}	—	—
Ref	890_{rev}[a]	—	-2010_{rev}	2900
1	800	180_{rev}	-2050_{rev}	2230

[a] rev = reversible process.

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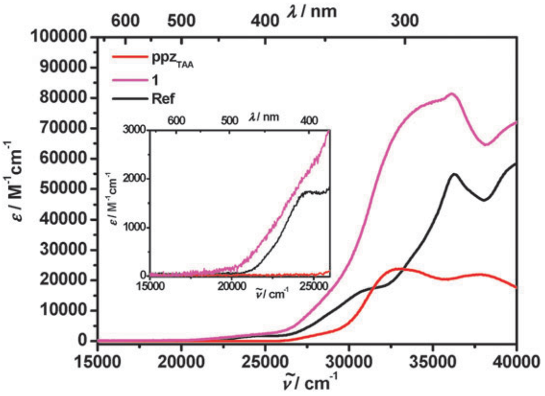

Fig. 1 Absorption spectra of **1**, **Ref** and $\mathbf{ppz_{TAA}}$ in MeCN solution at 298 K. The spectra in 2-MeTHF are virtually identical.

the bis-cyclometalated phenyl–Ir moiety.[12,16–18] Compound **1** shows one additional oxidation wave at 180 mV that we assign to the oxidation of the triarylamine by comparison with the free ligand.

The absorption spectra of the compounds in acetonitrile are given in Fig. 1. The complexes show the characteristic intense bands for the spin-allowed $^1\pi$–π^* ligand-centred (LC) transition in the C^N and N^N ligands between 35 000 and 40 000 cm^{-1}. The absorption bands between 17 000 and 26 000 cm^{-1} can be assigned to the spin-forbidden ^{3}MLCT absorption transitions caused by spin–orbit coupling associated with the iridium centre.[12,18] The moderately intense bands between 26 000 cm^{-1} and 35 000 cm^{-1} are a superposition of the characteristic localised transitions of the triarylamine subunit[5,19] and the typical spin-allowed metal-to-ligand charge-transfer (^{1}MLCT) dπ(Ir) → π* absorption shoulders.[12,18]

While **Ref** shows a strong and broad luminescence centred at 19 200 cm^{-1} in 2-MeTHF at RT the triarylamine-substituted complex **1** shows no emission at all. Obviously there is a very fast quenching process which inhibits luminescence from the Ir core. However, both complexes show intense luminescence with vibrational fine structure at 77 K with a lifetime in the μs regime which indicates the phosphorescent nature of the luminescence (see Table 2 and Fig. S3 in ESI†). Interestingly, unlike at RT, at 77 K complex **1** shows the same luminescence spectrum as **Ref** which proves that the quenching process at RT is a thermal reaction which is slowed down at 77 K. The structured blue-shifted emission spectra of **1** and **Ref** suggests a $^3\pi$–π^* LC transition.[9,17,18,20–22]

We assume that the missing luminescence from the Ir core in **1** at RT is due to charge-transfer quenching from the triarylamine to the tmp ligand yielding the CS state D^+(D)–A^-. This process has a quantum yield of about unity as was estimated by comparison of the luminescence quantum yield with that of **Ref**.[23] To prove this assumption transient absorption spectra were measured at RT in degassed 2-MeTHF (Fig. 2). **Ref** shows three absorption bands each with a lifetime of 3.5 μs, respectively. These bands can be assigned to the $^3[\text{Ir(C^N)}_2(\text{tmp})]^+$ states and are in good agreement with the luminescence lifetime at RT.

Table 2 Emission data

Compound	T/K	$\tilde{\nu}_{\text{em}}/\text{cm}^{-1}$	τ/μs	Φ_{em}
Ref	2-MeTHF (298)[a]	19 200	3.6	0.31
	2-MeTHF (77)[a]	19 600/21 100	18.3	—
1	2-MeTHF (298)[a]	—	—	—
	2-MeTHF (77)[a]	19 600/21 000	10.0	—
$\mathbf{ppz_{TAA}}$	CH_2Cl_2 (298)[b]	25 600	—	0.06

[a] Excitation at 28 200 cm^{-1} [355 nm]. [b] Excitation at 40 000 cm^{-1} [300 nm].

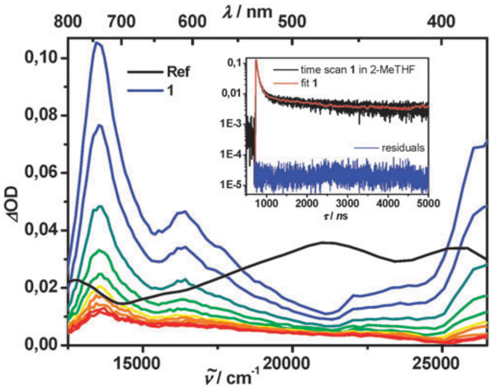

Fig. 2 Transient absorption spectra of **Ref** (excitation at 28 200 cm^{-1}) and **1** (excitation at 24 000 cm^{-1}) in 2-MeTHF at RT. Early spectra are shown in blue–green and late spectra are shown in orange–red colours (0–190 ns). Inset: time scan at 13 700 cm^{-1} for **1**.

For **1** the redox potential difference $\Delta E = E^{\text{Ox}} - E^{\text{Red}} =$ 2.23 V (see Table 1), which is an estimate for the energy of the CS state, is smaller than the lowest excited state energy of $^3[\text{Ir(C^N)}_2(\text{tmp})]^+$ as determined from the 00-transition of the luminescence spectrum at 77 K which yields 2.60 eV. Thus, charge separation is exothermic by *ca.* 0.4 eV after photoexcitation of the lowest excited triplet state. The transient absorption spectra of the CS state are expected to display characteristic features of the spectra of the isolated radical anion and the radical cation of **1**. Thus, for comparison, the spectra of the isolated radical ion species were generated by oxidation and reduction of **1** in acetonitrile by spectroelectrochemistry (Fig. 3).

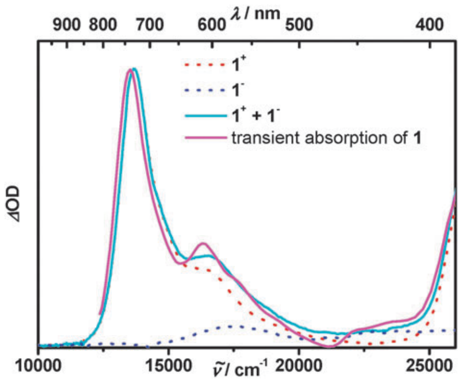

Fig. 3 Absorption spectra of radical cation $\mathbf{1}^+$ and radical anion $\mathbf{1}^-$. The cyan line shows the superimposed spectra of cation and anion. The pink line shows the transient absorption spectrum of **1** in 2-MeTHF with excitation at 24 000 cm^{-1} (416 nm).

In fact, pump probe spectroscopy at 24 000 cm^{-1} excitation yields transient signals as expected for the CS state, that is an intense band at 13 500 cm^{-1} which is typical of triarylamine cations,[19] and two less intense bands at 16 400 cm^{-1} and 22 600 cm^{-1} that can be assigned to the tmp radical anion.[24] Both signals decay biexponentially with the same time constants of 41 ns (95%) and 1.7 μs (5%).‡ Both components display the same spectral features and relative intensities. Thus, the two species from which these two processes originate must be very similar. Measurements in air equilibrated solutions reduce the time constants to 21 ns (95%) and 160 ns (5%). Obviously, triplet species play a major role in the deactivation pathway. However, we can exclude localised triplet species by comparison with the transient signals of **Ref** (Fig. 2) and with that of triphenylamine which shows a triplet–triplet absorption at *ca.* 19 000 cm^{-1}.[25] Thus, we suggest an almost degenerate equilibrium ^{3}CS ⇔ ^{1}CS which should indeed exhibit practically identical spectral features owing to the large distance between the radical centres. Furthermore, owing to the strong zero-field splitting in iridium complexes[26] the ^{3}CS state should split into three non-degenerate components even in the absence of an external magnetic field. Thus, we deal with an equilibrium of four states with similar energy (^{1}CS and 3 × ^{3}CS) whose rate of inter-conversion is of the same order or even slower than the deactivation processes to the ground state. Therefore, the above evaluated rate constants and amplitudes should be taken as apparent values and cannot directly be related to individual deactivation rates or to equilibrium concentrations.[27] A similar biphasic relaxation has indeed been observed for other transition metal complexes before.[28] Given the relatively small reorganisation energy of triarylamines *vs.* the free energy of −2.23 eV for charge recombination from either ^{3}CS or ^{1}CS state to S_0, both the spin-allowed $^1\text{CS} \rightarrow S_0$ and the spin-forbidden $^3\text{CS} \rightarrow S_0$ processes are likely to be in the Marcus inverted region.[29,30] This is in agreement with the observation that back electron transfer is much faster in the polar MeCN (τ_1 = 7 ns (94%); τ_2 = 218 ns (6%)) in which both the reorganisation energy is larger and the free energy of back electron transfer is smaller. Both terms should decrease the inverted region effect as observed. In addition, back electron transfer from ^{3}CS to the singlet ground state is spin-forbidden, which is the reason for the large time constant. Both lifetimes of these CS states even in MeCN are unusually long for such a small dyad and much longer than that of the recently published D–A dyad (70 ps) in which the iridium is coordinated by terpy ligands and where the donor also is a triarylamine. In this case, the energy of the CS state is only 1.50 eV which might be the reason for the shorter lifetime.[31]

In conclusion, our study demonstrates that relatively small D–A Ir complexes can show long-lived CS states due to a combination of inverted region effects and spin-selection rules. Quenching due to low-lying states is avoided because optical excitation already populates the lowest possible triplet states. Equally important, our study also demonstrates a severe quenching effect that might reduce the efficiency in triplet emitter based OLED devices if triarylamines are used as hole transporting components despite their high local triplet energies.

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Notes and references

‡ A somewhat better fit may be obtained by three time constants 26 ns (73%), 87 ns (22%) and 1.7 μs (5%).

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