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Synthesis and photoinduced electron transfer in platinum(II) bis(*N*-(4-ethynylphenyl)carbazole)-bipyridine fullerene complexes†

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Platinum(II) bis(*N*-(4-ethynylphenyl)carbazole)bipyridine fullerene complexes, (**Cbz**)₂–**Pt(bpy)**–**C**₆₀ and ([†]**BuCbz**)₂–**Pt(bpy)**–**C**₆₀, were synthesized. Their photophysical properties were studied by electronic absorption and emission spectroscopy and the origin of the transitions was supported by computational studies. The electrochemical properties were also studied and the free energies for charge-separation and charge-recombination processes were evaluated. The photoinduced electron transfer reactions in the triads were investigated by femtosecond and nanosecond transient absorption spectroscopy. In dichloromethane, both triads undergo ultrafast charge separated (CS) states, namely (Cbz)₂⁺⁺–Pt(bpy)–C₆₀⁻⁻ and (^tBuCbz)₂⁺⁺–Pt(bpy)–C₆₀⁻⁻, and the CS states would undergo charge recombination to give the ${}^{3}C_{60}*$ state, which subsequently decays to the ground state in 22–28 µs.

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Introduction

The study of photoinduced electron transfer reactions in donor-acceptor systems has been an active area of research owing to their potential applications in artificial photosynthesis and photovoltaic devices.¹ Donor-acceptor systems, particularly those utilizing fullerene as an electron acceptor, have attracted considerable attention in recent years.² Fullerene is known to be an excellent electron acceptor due to its symmetrical shape, large size, and π -electron delocalization over the three-dimensional surface.^{2b,3} With small reorganization energy, efficient charge separation and slow charge recombination were accomplished by utilizing C₆₀ as an electron acceptor. On the other hand, carbazole (Cbz), an aromatic amine, and its derivatives are known to be good electron donors⁴ and have been employed to develop a number of Cbz-C₆₀ donoracceptor systems with their photoinduced intramolecular electron transfer reactions well investigated.⁵ It has been demonstrated that the lifetime of the triplet charge-separated (CS) state in a Cbz- C_{60} dyad generated via ${}^{3}C_{60}^{*}$ is significantly longer than that of the singlet CS state generated *via* ${}^{1}C_{60}^{*}$,^{5b} as charge recombination (CR) from the triplet CS state to the singlet ground state is a spin-forbidden process. One effective approach to develop Cbz–C₆₀ systems that are capable of generating the triplet CS state would be to utilize transition metal-based chromophores for the development of donor–chromophore–acceptor triads. Transition metal-based chromophores which have low lying metal-to-ligand charge-transfer (MLCT) excited states, such as Ru(Π),⁶ Re(Π),⁷ Os(Π),⁸ Ir(Π),^{1b,6a,b,8g,9} Cu(Π)¹⁰ and Pt(Π),¹¹ have been extensively studied. Owing to the ultrafast intersystem crossing (ISC) through the strong spin–orbit coupling imparted by the heavy metal centres, charge transfer processes generally occur at the ³MLCT excited state, and hence the spin-multiplicity of the CS state can be controlled.

Unlike Ru(π),⁶ Re(π),⁷ Os(π),⁸ Ir(π),^{1b,6a,b,8g,9} and Cu(π),¹⁰ square-planar d⁸ Pt(π) based donor–acceptor systems are relatively less extensively studied. It was only until quite recently that Pt(π) based donor–acceptor systems have been explored for their photoinduced electron transfer properties,¹¹ mainly encouraged by the development of the Pt(π) polypyridine alkynyl chromophores that display enhanced ³MLCT excited state behavior through the enlargement of the d–d orbital splitting by the incorporation of an alkynyl ligand that leads to a higher-lying d–d ligand-field state.¹² In the present study, we develop a series of donor–chromophore–acceptor systems based on the bipyridine Pt(π) bisalkynyl chromophore. Herein, we report the synthesis, electrochemical and photophysical

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studies of a series of donor-chromophore-acceptor triads $(Cbz)_2-Pt(bpy)-C_{60}$ and $({}^{t}BuCbz)_2-Pt(bpy)-C_{60}$ as well as their relevant model compounds, $(Cbz)_2-Pt(bpy)$, $({}^{t}BuCbz)_2-Pt(bpy)$, $CbzC_6H_4-C\equiv C-Ph$ and ${}^{t}BuCbzC_6H_4-C\equiv C-Ph$ (Chart 1), using a variety of experimental techniques including electronic absorption and emission spectroscopy, cyclic voltammetry, femtosecond and nanosecond time-resolved transient absorption spectroscopy, and the photochemical processes are identified and the rate constants are determined. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were performed to provide further insights into the origin of the electronic absorption and emission properties.

Results and discussion

Synthesis

The synthesis of $(Cbz)_2$ -Pt(bpy)-C₆₀ and $({}^tBuCbz)_2$ -Pt(bpy)-C₆₀ is shown in Scheme 1. N-(4-Ethynylphenyl)carbazole and N-(4-ethynylphenyl)-3,6-di-tert-butyl-carbazole were first prepared by the Ullmann-type reaction between carbazoles and 1-bromo-4-iodobenzene, followed by the palladium-catalyzed Sonagashira coupling with (trimethylsilyl)acetylene (TMSA), and the subsequent removal of the TMS group with potassium carbonate in tetrahydrofuran-methanol solution. On the other hand, according to literature procedures,¹³ the fullereneappended bipyridine derivative was obtained by the oxidation of 4,4'-dimethyl-2,2'-bipyridine with selenium oxide yielding 4-methyl-2,2'-bipyridine-4'-carboxaldehyde, followed by the incorporation of fullerene with the Prato reaction.¹⁴ The fullerene-appended bipyridine derivative was reacted with [PtCl₂(DMSO)₂] to afford the dichloroplatinum(II) precursor, which was then reacted with alkynes using copper-catalyzed coupling reaction to yield (Cbz)₂-Pt(bpy)-C₆₀ and (^tBuCbz)₂- $Pt(bpy)-C_{60}$, with their identities confirmed by ¹H NMR spectroscopy, FAB mass spectrometry and elemental analysis.

Electronic absorption and emission spectroscopy

The electronic absorption spectra of (Cbz)₂-Pt(bpy) and (^tBuCbz)₂-Pt(bpy) exhibit an intense absorption band at *ca*. 280-360 nm and a moderately intense band at ca. 360-450 nm with a λ_{max} at *ca*. 400 nm in dichloromethane (Fig. 1). The high-energy intense absorptions are the π - π * transitions of the carbazole, bipyridine and alkynyl moieties, whereas the less intense absorptions in the visible region are attributed to an admixture of platinum-to-bipyridine metal-to-ligand charge transfer (MLCT) and alkynyl-to-bipyridine ligand-to-ligand charge transfer (LLCT) transitions.^{12b,i,j} With the C₆₀ moiety appended in $(Cbz)_2$ -Pt(bpy)-C₆₀ and $({}^tBuCbz)_2$ -Pt(bpy)-C₆₀, an absorption tail extending to 700 nm, which can also be observed in the electronic absorption spectrum of N-methylfulleropyrrolidine,^{3b} is tentatively assigned to the π - π * transitions of C60. TDDFT calculations were performed on selected complexes (Cbz)₂-Pt(bpy) and (Cbz)₂-Pt(bpy)-C₆₀ to provide further insight into the nature of the electronic transitions for the complexes. To reduce the computational cost, the dodecyl group of N-dodecylpyrrolidine on C₆₀ for (Cbz)₂-Pt(bpy)-C₆₀ was replaced by a methyl group and was labeled as (Cbz)₂-Pt- $(bpy)-C_{60}$ (see Computational details). Selected singlet-singlet transitions for the complexes are listed in Table S1[†] and the molecular orbitals involved in the transitions are shown in Fig. 2 and S1.[†] The first two transitions computed at 484 and 451 nm for (Cbz)₂-Pt(bpy) are predominantly the LLCT $[\pi(C \equiv C-Ph-Cbz) \rightarrow \pi^*(bpy)]$ transitions, slightly mixed with the MLCT[$d\pi(Pt) \rightarrow \pi^*(bpy)$] character (Table S1[†]). For (Cbz)₂-Pt-(bpy)– C_{60} , the several transitions computed to be less intense in the lower-energy region are the IL π - π * transitions of the C₆₀. The LLCT $[\pi(C = C-Ph-Cbz) \rightarrow \pi^*(C_{60})]$ excited state is the S_2 state which is close in energy to the lowest-energy IL(C_{60}) state. When compared with (Cbz)2-Pt(bpy), the LLCT $[\pi(C \equiv C-Ph-Cbz) \rightarrow \pi^{*}(bpy)]/MLCT[d\pi(Pt) \rightarrow \pi^{*}(bpy)]$ transitions for (Cbz)₂-Pt(bpy)-C₆₀' are found to be red-shifted.

On photoexcitation, $(Cbz)_2$ -Pt(bpy) and $({}^tBuCbz)_2$ -Pt(bpy) display observable emission in dichloromethane (Fig. 3), while fullerene-appended complexes (Cbz)₂-Pt(bpy)-C₆₀ and (^tBuCbz)₂- $Pt(bpy)-C_{60}$ are non-emissive under identical conditions. The emission is red-shifted after the introduction of the di-tertbutyl groups at the 3,6-positions of carbazole in (^tBuCbz)₂-Pt-(bpy). The emission of $(Cbz)_2$ -Pt(bpy) and $({}^tBuCbz)_2$ -Pt(bpy) was found to be strongly quenched with their luminescence quantum yields determined to be 0.03 and 0.01, respectively, much lower than 0.50 for a platinum(II) diimine bis(alkynyl) chromophore.^{12a} The weak emissive nature of the carbazolecontaining complexes may possibly be due to the occurrence of a quenching process in the excited state. A possible interpretation of this is that a competitive process of photoinduced electron transfer between the carbazole moiety and the Pt(n) bipyridine chromophore that leads to photochemical charge separation has taken place. Similarly, the nonemissive nature of the fullerene-containing complexes could again be ascribed to photoinduced electron transfer processes.



Scheme 1 Synthesis of donor-chromophore-acceptor triads, $(Cbz)_2-Pt(bpy)-C_{60}$ and $({}^tBuCbz)_2-Pt(bpy)-C_{60}$. Reagents and conditions: (i) 4-bromoiodobenzene, K₂CO₃, 18-crown-6, Cu, DMF, reflux; (ii) PdCl₂(PPh₃)₂, Cul, PPh₃, TMSA, Et₃N, reflux; (iii) K₂CO₃, MeOH-THF, r.t.; (iv) SeO₂, dioxane, reflux; (v) *N*-dodecyl glycine, C₆₀, PhMe, reflux; (vi) PtCl₂(DMSO)₂, CH₂Cl₂, r.t.; (vii) Cul, Et₃N, CH₂Cl₂, r.t.

Electrochemistry

In order to evaluate the free energy changes associated with the CS and CR processes in (Cbz)₂-Pt(bpy)-C₆₀ and (^tBuCbz)₂-Pt(bpy)-C₆₀, cyclic voltammetry was carried out in 0.1 M n-Bu₄NPF₆ solution in deaerated dichloromethane. The first and second reduction couples in the triads are assigned to the reduction of the C60 moiety, with the observed reduction potentials $E^{\circ}(C_{60}/C_{60}$.⁻) and $E^{\circ}(C_{60}$.⁻/ C_{60} .²⁻), at -0.59 V and -0.98 V (vs. SCE). Furthermore, the third reduction couple, which is assigned as the bipyridine ligand-centred reduction, $E^{\circ}[Pt(bpy)/Pt(bpy)^{-}]$, is observed at -1.32 V, anodically shifted by 50-60 mV compared to that of (Cbz)₂-Pt(bpy) and (^tBuCbz)₂-Pt(bpy). On the other hand, the first oxidation couple in the triads is found to be associated with the oxidation of the carbazole unit with the potential for oxidation of +1.36 V for (Cbz)₂-Pt(bpy)-C₆₀. The introduction of the di-tertbutyl group at the 3,6-positions of carbazole shifts the potentials to +1.24 V in (^{*t*}**BuCbz**)₂-**Pt(bpy**)-C₆₀. The redox potentials of the investigated compounds are summarized in Table 1.

The free energy changes for CS and CR processes in (Cbz)₂– Pt(bpy)–C₆₀ and (^tBuCbz)₂–Pt(bpy)–C₆₀ are evaluated with the corrections of the Coulombic interactions between the centres of positive and negative charges using the Weller equations¹⁵

$$\Delta G_{\rm CR} = \left[E^{\rm o}(A/A^{\bullet-}) - E^{\rm o}(D^{\bullet+}/D) + \frac{e}{4\pi \varepsilon_0 \varepsilon_{\rm S} R_{\rm DA}} \right] \, \mathrm{eV} \qquad (1)$$

with the distances $R_{Pt-C_{60}} = 9.80$ Å, $R_{D-Pt} = 10.49$ Å, $R_{D-C_{60}}$ (*cis*-) = 15.08 Å and $R_{D-C_{60}}$ (*trans*-) = 19.51 Å obtained from the optimized structure of (**Cbz**)₂-**Pt(bpy)**-**C**₆₀'. The calculated free energy changes for the CS and CR processes are listed in Table 2. The energy differences of the ³MLCT/LLCT excited state and the ground state (E_{00}) are estimated from the intersection of the emission and excitation spectra of (**Cbz**)₂-**Pt(bpy**) and (^tBuCbz)₂-**Pt(bpy**) measured at room temperature



Fig. 1 UV-Visible absorption spectra of $(Cbz)_2-Pt(bpy)-C_{60}$ and $({}^{t}BuCbz)_2-Pt(bpy)-C_{60}$ as well as their model compounds $(Cbz)_2-Pt(bpy)$ and $({}^{t}BuCbz)_2-Pt(bpy)$ in CH_2Cl_2 .

in deaerated dichloromethane, and are estimated to be 2.51 eV and 2.42 eV, respectively.

Transient absorption spectroscopy

The photoinduced electron transfer reactions in $(Cbz)_2$ -Pt(bpy)-C₆₀ and (^tBuCbz)₂-Pt(bpy)-C₆₀ were studied by femtosecond transient absorption spectroscopy and the resulting spectra were subjected to global fitting with a sequential model¹⁶ to yield evolution-associated difference spectra (EADS) and with a parallel model to yield decay-associated difference spectra (DADS) (Fig. 4 and 5). $(Cbz)_2$ -Pt(bpy)-C₆₀ and (^tBuCbz)₂-Pt(bpy)-C₆₀ behave similarly upon photo-excitation at 400 nm in dichloromethane with the first resolved component depicting the formation of the ³MLCT/LLCT excited state (Fig. 4b and 5b). The ³MLCT/LLCT excited state is generated within the instrumental response time with a time constant of $\tau < 150$ fs *via* ISC of the initially populated ¹MLCT/ LLCT excited state upon laser irradiation. The first EADS



Fig. 2 Spatial plots (isovalue = 0.03) of selected molecular orbitals of (Cbz)₂-Pt(bpy)-C₆₀' obtained from PBE0/CPCM calculation.



Fig. 3 Normalized emission spectra of $(Cbz)_2-Pt(bpy)$ and $({}^tBuCbz)_2-Pt(bpy)$ in deaerated CH_2Cl_2 .

Table 1 Standard potentials (vs. SCE, in V)^a of $(Cbz)_2-Pt(bpy)-C_{60}$ and $({}^{t}BuCbz)_2-Pt(bpy)-C_{60}$, and their model compounds $CbzC_6H_4-C\equiv C-Ph$, ${}^{t}BuCbzC_6H_4-C\equiv C-Ph$, $(Cbz)_2-Pt(bpy)$ and $({}^{t}BuCbz)_2-Pt(bpy)$ in CH_2Cl_2

	E°/V (vs. SCE) in CH ₂ Cl ₂			
Molecule	D*+/D	C ₆₀ /C ₆₀ *-	C_{60} · -/ C_{60}^{2-}	Pt(bpy)/ Pt(bpy)'
CbzC ₆ H₄-C≡C-Ph	$+1.35^{b}$	_	_	_
^t BuCbzC ₆ H ₄ -C=C-Ph	+1.21	_	_	_
$(Cbz)_2 - Pt(bpy)$	$+1.33^{b}$	_	_	-1.37
(^t BuCbz) ₂ -Pt(bpy)	+1.24	_	_	-1.38
$(Cbz)_2$ -Pt(bpy)-C ₆₀	$+1.36^{b}$	-0.59	-0.98	-1.32
(^t BuCbz) ₂ -Pt(bpy)-C ₆₀	+1.24	-0.59	-0.98	-1.32

^{*a*} The standard potentials were determined as $E^{\circ} = (E_{pa}^{\circ} + E_{pc}^{\circ})/2$ by cyclic voltammetry in CH₂Cl₂ using *n*-Bu₄NPF₆ (0.1 M) as the supporting electrolyte; scan rate = 100 mV s⁻¹. ^{*b*} Quasi-reversible couple.

shows a broad absorption between 550 and 700 nm, which is attributed to the ³MLCT excited state.^{12*b*,*i*} A positive absorption at wavelengths shorter than 475 nm as well as a broad absorption in the near-infrared region ($\lambda > 900$ nm) are also observed.

These absorptions are different from the characteristic signal of Cbz^{•+} ($\lambda_{max} \sim 750 \text{ nm}$).¹⁷ This may be due to the charge delocalization across the Pt-C=C-Ph and the Cbz/^tBuCbz units in the ³LLCT excited state, (Cbz)₂^{•+}-Pt(bpy)^{•-}-C₆₀ and (^tBuCbz)₂^{*+}-Pt(bpy)^{*-}-C₆₀ (see HOMO and HOMO-1 of (Cbz)₂-Pt(bpy) in Fig. S1[†]), leading to absorptions quite similar to that observed for the cation radical of a Cbz dimer, $(Cbz)_2^{*+.17}$. Subsequent to the formation of the ³MLCT/LLCT excited state is the electron transfer reaction generating the fully CS species, namely (Cbz)₂^{•+}-Pt(bpy)-C₆₀^{•-} and (^tBuCbz)₂^{•+}-Pt-(bpy)–C₆₀, with a rise time $\tau_1 = 185$ fs and 221 fs, respectively. The formation of the CS states is characterized by the strong transient absorption at ca. 1000 nm, which is the characteristic signal of C_{60} . It should be noted that the formation of the CS states is very fast, much faster than that of the vibrational relaxation of the ³MLCT/LLCT excited state which was determined to be ~ 4 ps.^{12*i*} As a result, the photoinduced electron transfer reaction is expected to occur at a vibrationally unrelaxed ³MLCT/LLCT excited state,¹⁸ and the subsequent vibrational relaxation of the resulting CS state occurs at a time constant $\tau_2 = 1.7$ ps for $(Cbz)_2$ -Pt(bpy)-C₆₀ and 1.5 ps for $({}^{t}BuCbz)_{2}$ -Pt(bpy)-C₆₀. The lifetime of the CS states is determined to be $\tau_3 = 56$ ps for $(Cbz)_2$ -Pt(bpy)-C₆₀ and $\tau_3 = 331$ ps for $({}^{t}BuCbz)_{2}$ -Pt(bpy)-C₆₀. On the other hand, laser irradiation at 400 nm also populates the ${}^{1}C_{60}$ excited state, where the extinction coefficient (ε) of *N*-methylfulleropyrrolidine at 400 nm is *ca*. 5000 dm³ mol⁻¹ cm⁻¹.^{3b} Therefore, the first four resolved EADS components of both complexes depict the presence of the ${}^{1}C_{60}$ excited state with absorption features at λ_{max} = 510 and 890 nm.^{3b} The ${}^{1}C_{60}^{*}$ eventually proceeds to the ${}^{3}C_{60}*$ through ISC at time constants of τ_{4} = 896 ps and τ_{4} = 943 ps for $(Cbz)_2$ -Pt(bpy)-C₆₀ and $({}^tBuCbz)_2$ -Pt(bpy)-C₆₀, respectively. The final resolved component with strong transient absorption between 550 and 750 nm (λ_{max} = 680 nm) is attributed to the ${}^{3}C_{60}^{*}$ with a lifetime $\tau_{5} > 6$ ns. 3b,5e,19 In order to investigate reactions at times over 6 ns, nanosecond transient absorption spectroscopy was carried out on both triads and their observed absorption difference spectra taken at t =5 µs after laser irradiation at 355 nm in dichloromethane are shown in Fig. 4d and 5d. These spectra match the EADS of the final component of both complexes with strong transient absorption between 550 and 750 nm (λ_{max} = 680 nm), which

Table 2 Free energy changes ΔG (eV) for electron-transfer reactions in CH₂Cl₂ calculated from the electrochemical potentials after correction for the Coulomb interaction between the charges^a

Reaction	CS	CR
$\begin{array}{l} (Cbz)_2 - Pt(bpy) - C_{60} \rightarrow (Cbz)_2^{*+} - Pt(bpy)^{*-} - C_{60} \\ (Cbz)_2^{*+} - Pt(bpy)^{*-} - C_{60} \rightarrow (Cbz)_2^{*+} - Pt(bpy) - C_{60}^{*-} \\ (^{t}BuCbz)_2 - Pt(bpy) - C_{60} \rightarrow (^{t}BuCbz)_2^{*+} - Pt(bpy)^{*-} - C_{60} \\ (^{t}BuCbz)_2^{*+} - Pt(bpy)^{*-} - C_{60} \rightarrow (^{t}BuCbz)_2^{*+} - Pt(bpy) - C_{60}^{*-} \end{array}$	$-0.69 (-0.66)^b$ $-0.69 (-0.66)^b$	$\begin{array}{c} -2.53 \\ -1.84 \ (-1.87)^b \\ -2.41 \\ -1.72 \ (-1.75)^b \end{array}$

 ${}^{a}\Delta G_{CR} = E^{\circ}(A/A^{-}) - E^{\circ}(D^{+}/D) + e/4\pi\varepsilon_{0}\varepsilon_{s}R_{DA}$ is for charge-recombination where R_{DA} is the charge-separation distance determined from DFT; ΔG_{CS} is the driving force for charge-separation. The parameters used are $\varepsilon_{0} = 8.85$, $\varepsilon_{s} = 8.93$ for $CH_{2}Cl_{2}$, $R_{Pt-C_{60}} = 9.80$ Å, $R_{D-Pt} = 10.49$ Å, $R_{D-C_{60}}$ (*cis*-) = 15.08 Å, $R_{D-C_{60}}$ (*trans*-) = 19.51 Å with the distances taken from the DFT optimized structure of (Cbz)₂-Pt(bpy)-C₆₀'. ^b Driving forces for radical ion pairs in the *trans*-position.



Fig. 4 Transient absorption difference spectra of $(Cbz)_2 - Pt(bpy) - C_{60}$ following excitation at 400 nm in CH_2Cl_2 : (a) contour plot of the spectroscopic responses following femtosecond laser pulse irradiation; (b) EADS (top) and DADS (bottom) derived from the global analysis; (c) time decay profiles of optical density at 460 nm, 680 nm and 1020 nm; and (d) taken at 5 µs after nanosecond laser pulse excitation at 355 nm in deaerated CH_2Cl_2 , with the time-decay profile of optical density at 690 nm (inset).

is the characteristic signal of the ${}^{3}C_{60}^{*}$.^{3b,5e,19} The ${}^{3}C_{60}^{*}$ eventually decays to the ground state at time constants of $\tau = 28$ and 22 µs, respectively, for $(Cbz)_2$ -Pt(bpy)-C₆₀ and $({}^{t}BuCbz)_2$ -Pt(bpy)-C₆₀ (Fig. 4d and 5d), close to that found for a functionalized C₆₀ of 25 µs.²⁰ The energetic and kinetic data for $(Cbz)_2$ -Pt(bpy)-C₆₀ and $({}^{t}BuCbz)_2$ -Pt(bpy)-C₆₀ are summarized in Scheme 2.

It is noteworthy that the CS states, $(Cbz)_2^{*+}-Pt(bpy)-C_{60}^{*-}$ and $({}^{t}BuCbz)_2^{*+}-Pt(bpy)-C_{60}^{*-}$, are produced *via* photoinduced electron transfer from the ³MLCT/LLCT excited state, and therefore are in the triplet manifold. As the CR processes occur in a few hundred picoseconds, CR should therefore proceed through a spin-allowed process to the lower-lying ${}^{3}C_{60}^{*}$ state instead of a much slower spin-forbidden direct recombination process to the singlet ground state. In addition, with large driving forces ($\Delta G = -1.84$ eV for (Cbz)₂-Pt(bpy)-C₆₀ and -1.72 eV for (${}^{t}BuCbz)_2$ -Pt(bpy)-C₆₀) and the small reorganization energy in C₆₀-containing complexes,^{14,15} CR processes are expected to be in the Marcus inverted region,²¹ and hence the direct recombination to the lower-lying ${}^{3}C_{60}^{*}$ state is further supported experimentally in that the diminishing of the CS transient absorption is accompanied by the rise of the ${}^{3}C_{60}$ * absorption at a similar rate (Fig. 4c and 5c).

Conclusions

Donor-chromophore-acceptor triads, (Cbz)2-Pt(bpy)-C60 and (^tBuCbz)₂-Pt(bpy)-C₆₀, were synthesized and their photophysical and electrochemical properties were studied. The photoinduced electron transfer processes were investigated by femtosecond and nanosecond transient absorption spectroscopy. Laser irradiation at 400 nm predominantly excites the MLCT/LLCT transition, followed by an ultrafast ISC to generate the ³MLCT/LLCT excited state, from which CS occurs within a picosecond. The triplet CS state decays to the energetically lower-lying spin-allowed ³C₆₀* state in a few hundred picoseconds instead of the spin-forbidden singlet ground state. The resulting long-lived ³C₆₀* state decays to the ground state in the microsecond timescale. The ultrafast ISC in the triads through the strong spin-orbit coupling mediated by the platinum(II) centre and the subsequent ultrafast electron transfer, which eventually generates the CS state in the triplet



Fig. 5 Transient absorption difference spectra of $({}^{t}BuCbz)_{2}-Pt(bpy)-C_{60}$ following excitation at 400 nm in CH₂Cl₂: (a) contour plot of the spectroscopic responses following femtosecond laser pulse irradiation; (b) EADS (top) and DADS (bottom) derived from the global analysis; (c) time decay profiles of optical density at 460 nm, 680 nm and 1020 nm; and (d) taken at 5 μ s after nanosecond laser pulse excitation at 355 nm in deaerated CH₂Cl₂, with the time-decay profile of optical density at 680 nm (inset).

manifold, establishes another strategy for the development of new donor-acceptor systems that are capable of effectively generating triplet CS states with long CS lifetimes.

Experimental section

General

¹H NMR spectra were recorded on a Bruker AVANCE 300 (300 MHz) or Bruker AVANCE 400 (400 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane (Me_4Si). Positive-ion FAB mass spectra were recorded on a Thermo Scientific DFS high-resolution magnetic sector mass spectrometer. Elemental analyses of the newly synthesized complexes were performed using a Flash EA 1112 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing. Ultraviolet-visible spectra were recorded on a Varian Cary 50 UV-vis spectrophotometer in spectroscopic grade CH_2Cl_2 . Steady-state emission spectra were recorded on a Spex Fluorolog-3 Model FL3-211 spectro-fluorometer equipped with a R2658P PMT detector. All solu-

tions for photophysical studies were deaerated on a highvacuum line in a two-compartment cell that consisted of a 10 mL Pyrex bulb and a 1 cm path length quartz cuvette and sealed against the atmosphere with a Bibby Rotaflo HP6 Teflon stopper. The solutions were rigorously degassed with at least four successive freeze-pump-thaw cycles. The luminescence quantum yield was measured at room temperature using [Ru(bpy)₃]Cl₂ as a standard ($\Phi_{\rm em} = 0.06$).²²

Electrochemical measurements

The cyclic voltammetry measurements were performed on a CHI 620A electrochemical analyzer in deaerated dichloromethane containing 0.10 M n-Bu₄NPF₆ as the supporting electrolyte at 298 K. A glassy carbon working electrode was polished with Linde polishing alumina suspension and rinsed with deionized water followed by dichloromethane before use. A platinum wire was used as a counter electrode and an Ag/ AgNO₃ (0.1 M in acetonitrile) was used as a reference electrode. All experiments were followed by the addition of ferrocene and the ferrocene/ferricenium redox potential was used as an internal reference.

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Scheme 2 Schematic energy diagram for photoinduced electron transfer of $(Cbz)_2-Pt(bpy)-C_{60}$ and $({}^tBuCbz)_2-Pt(bpy)-C_{60}$ in CH_2Cl_2 . a Energies of ${}^1C_{60}^*$ and ${}^3C_{60}^*$ excited states are obtained from ref. 19a. b Energy for radical ion pairs in the *trans*-position.

Transient absorption (TA) measurements

The fs time-resolved experiments were performed based on a commercial Ti:Sapphire regenerative amplifier laser system and home-built TA spectrometers. The sample solutions were excited using a 400 nm pump laser; the subsequent excited state processes taking place on the fs to several ns time-scale were detected by a second probe pulse induced by an 800 nm laser in the TA method. The 400 nm pump laser was the second harmonic of the 800 nm fundamental (1 kHz repetition rate, ~35 fs duration) produced with a BBO crystal. In the fs-TA experiments, the excited states were probed by a white light continuum (WLC) pulse produced by focusing part of the 800 nm laser onto a rotating quartz plate. The TA signals were collected by a monochromator and detected with a thermoelectric cooled CCD detector. The spectral window for the TA covers 450-740 nm and 600-1050 nm regions. TA signals at wavelengths from 740 nm to 880 nm were masked by the 800 nm fundamental and thus were not shown in the fs-TA in Fig. 4 and 5. Temporal delay of the probe relative to the pump pulse was controlled by an optical delay line in the fs-TA system. The instrument response function (IRF) of the ultrafast system is wavelength-dependent. As the detection wavelength varies from 1050 to 450 nm, the IRF changes from ~150 to 250 fs. For the fs-TA spectra, corrections have been made to eliminate the wavelength-dependent time shift caused by the group velocity dispersion. The fs-TA spectra were analyzed

by global analysis¹⁶ with the graphical interface program Glotaran²³ (http://glotaran.org/).

Nanosecond transient absorption spectroscopy experiments were performed using an LP920-KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments Ltd, Livingston, UK) at ambient temperature. The excitation source was the 355 nm output (third harmonic) of an Nd:YAG laser (Spectra-Physics Ouanta-Ray Lab-130 Pulsed Nd:YAG Laser) and the probe light source was a Xe900 450 W xenon arc lamp. The transient absorption spectra were recorded using an image-intensified CCD camera (Andor) with a PC plug-in controller, fully operated by the L900 spectrometer software. The absorption kinetics were determined using a Hamamatsu R928 photomultiplier tube and recorded using a Tektronix Model TDS3012B (100 MHz, 1.25 GS s^{-1}) digital oscilloscope. Samples were freshly prepared and degassed with at least four freeze-pump-thaw cycles on a high-vacuum line in a two compartment cell that consisted of a 10 mL Pyrex bulb and a 1 cm path length quartz cuvette.

Computational details

Calculations were carried out using the Gaussian 09 software package.²⁴ The ground-state geometries of (Cbz)₂-Pt(bpy) and (Cbz)₂-Pt(bpy)-C₆₀' were fully optimized by the density functional theory (DFT) with the hybrid Perdew, Burke, and Ernzerhof functional (PBE0).²⁵ Vibrational frequency calculations were performed for all stationary points to verify that each was a minimum (NIMAG = 0) on the potential energy surface. On the basis of the ground state optimized geometries, the timedependent density functional theory (TDDFT)²⁶ calculation at the same level of theory associated with the conductor-like polarizable continuum model (CPCM)²⁷ using CH₂Cl₂ as the solvent was employed to compute the singlet-singlet transitions for the complexes. For all the calculations, the Stuttgart effective core potentials (ECPs) and the associated basis set were applied to describe Pt²⁸ with f-type polarization functions $(\zeta = 0.993)$ ²⁹, while the 6-31G(d,p) basis set³⁰ was used for all other atoms. The DFT and TDDFT calculations were performed with a pruned (99 590) grid.

Synthesis

3,6-Di-*tert*-butylcarbazole,³¹ *N*-(4-bromophenyl)carbazole,³² *N*-(4-bromophenyl)-3,6-di-*tert*-butylcarbazole,³² *N*-(4-ethynylphenyl)carbazole,³³ *N*-(4-ethynylphenyl)-3,6-di-*tert*-butylcarbazole,³³ 9-(4-(2-phenylethynyl)phenyl)carbazole (**CbzC₆H₄-C**=**C**-**Ph**),³⁴ 3,6-di-*tert*-butyl-9-(4-(2-phenylethynyl)phenyl)carbazole (^t**BuCbzC₆H₄-C**=**C**-**Ph**)³⁴ and fullerene-appended bipyridine¹³ were prepared according to literature procedures.

General procedure for platinum(II) complexation

4,4'-Dimethyl-2,2'-bipyridine/fullerene-appended bipyridine and $[PtCl_2(DMSO)_2]$ were stirred in dichloromethane under N₂ for 15 h. The solvent was then reduced in volume and diethyl ether was added. The resulting precipitate, dichloroplatinum(n) precursor, was filtered and dried. Dichloroplatinum(n) precursor and arylacetylene (2.5 equiv.) were added to deaerated dichloromethane. Triethylamine (\sim 1 mL) was added, followed by the addition of copper iodide (\sim 2 mg). The reaction mixture was stirred at room temperature under N₂ for 15 h. The reaction was filtered and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel using chloroform-1% methanol as the eluent, and then recrystallized from chloroform-diethyl ether or chloroform-methanol.

(Cbz)₂-Pt(bpy). Yield: 68%. ¹H NMR (400 MHz, CDCl₃): δ /ppm 9.64 (d, J = 5.7 Hz, 2H), 8.14 (d, J = 7.7 Hz, 4H), 7.92 (s, 2H), 7.76 (d, J = 8.5 Hz, 4H), 7.43 (m, 14H), 7.28 (m, 4H), 2.55 (s, 6H). FAB-MS (m/z): [M + H]⁺ 912.2. Elemental analysis calcd (%) for C₅₂H₃₆N₄Pt·2H₂O: C 65.88, H 4.25, N 5.91; found: C 66.18, H 3.95, N 6.04.

(^tBuCbz)₂–Pt(bpy). Yield: 62%. ¹H NMR (400 MHz, CDCl₃): δ /ppm 9.57 (d, J = 5.6 Hz, 2H), 8.13 (d, J = 1.3 Hz, 4H), 7.96 (s, 2H), 7.73 (d, J = 8.5 Hz, 4H), 7.48 (d, J = 1.6 Hz, 2H), 7.45 (d, J =8.5 Hz, 6H), 7.38 (d, J = 8.5 Hz, 6H), 2.55 (s, 6H), 1.47 (s, 36H). FAB-MS (m/z): [M]⁺ 1135.4. Elemental analysis calcd (%) for C₆₈H₆₈N₄Pt·H₂O: C 70.75, H 6.11, N 4.85; found: C 70.79, H 6.02, N 4.81.

(Cbz)₂-Pt(bpy)-C₆₀. Yield: 39%. ¹H NMR (400 MHz, C₂D₄Cl₂, 75 °C): δ /ppm 9.93 (d, J = 5.7 Hz, 1H), 9.67 (d, J = 5.7 Hz, 1H), 8.69 (s, 1H), 8.19 (d, J = 6.3 Hz, 1H), 8.12 (d, J = 7.7 Hz, 4H), 8.09 (s, 1H), 7.66 (t, J = 7.9 Hz, 4H), 7.45 (d, J = 8.3 Hz, 4H), 7.40 (m, 9H), 7.26 (m, 4H), 5.43 (s, 1H), 5.20 (d, J = 9.6 Hz, 1H), 4.26 (d, J = 9.6 Hz, 1H), 3.19 (m, 1H), 2.78 (m, 1H), 2.53 (s, 3H), 2.51 (m, 1H), 2.01 (m, 1H), 1.92 (m, 1H), 1.72 (m, 1H), 1.58 (m, 1H), 1.46 (m, 3H), 1.29 (bs, 12H), 0.88 (t, J = 6.8 Hz, 3H). FAB-MS (m/z): [M – H]⁺ 1826.6. Elemental analysis calcd (%) for C₁₂₅H₆₁N₅Pt·3/2CH₃OH·1/2CHCl₃: C 78.80, H 3.51, N 3.62; found: C 78.65, H 3.71, N 3.99.

(^t**BuCbz**)₂–**Pt(bpy)**–**C**₆₀. (Yield: 33%). ¹H NMR (400 MHz, C₂D₂Cl₄, 90 °C): δ /ppm 10.01 (d, *J* = 4.1 Hz, 1H), 9.79 (d, *J* = 4.1 Hz, 1H), 8.58 (s, 1H), 8.20 (d, *J* = 5.5 Hz, 1H), 8.15 (s, 4H), 7.95 (s, 1H), 7.75 (t, *J* = 7.5 Hz, 4H), 7.51 (d, *J* = 7.5 Hz, 9H), 7.42 (d, *J* = 6.8, 4H), 5.34 (s, 1H), 5.26 (d, *J* = 9.6 Hz, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 3.24 (m, 1H), 2.83 (m, 1H), 2.60 (s, 3H), 2.55 (m, 1H), 2.09 (m, 1H), 2.01 (m, 1H), 1.77 (m, 1H), 1.67 (m, 1H), 1.50 (s, 39H), 1.34 (bs, 12H), 0.94 (t, *J* = 6.8 Hz, 3H). FAB-MS (*m/z*): [M - 2H]⁺ 2049.5. Elemental analysis calcd (%) for C₁₄₁H₉₃N₅Pt·CH₃OH·1/2CHCl₃: C 79.83, H 4.58, N 3.27; found: C 79.89, H 4.95, N 3.55.

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