[60]Fullerene-perchlorotriphenylmethide anion triads. Synthesis and study of photoinduced intramolecular electron-transfer processes[†]

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Received 20th October 2005, Accepted 7th November 2005 First published as an Advance Article on the web 17th November 2005 DOI: 10.1039/b514882k

For the first time an anionic donor, the perchlorotriphenylmethide anion (PTM⁻), has been covalently bonded to C_{60} , generating the C_{60} –(PTM⁻)₂ triad that is reversibly oxidized to the corresponding C_{60} –perchlorotriphenylmethyl radical triad C_{60} –(PTM⁻)₂. For the triad C_{60} –(PTM⁻)₂, photoinduced charge-separation can be confirmed to occur *via* the excited singlet states of the C_{60} moiety and the PTM anion in polar and nonpolar solvents from quenching of their fluorescence intensities in the region of 700–750 nm and 560–630 nm, respectively. The charge-separation state was confirmed by the nanosecond transient absorption spectra in the visible and near-IR spectral regions. After charge-separation, back electron transfer takes place with a lifetime of about 80 ns. Steady-state concentration of the highly persistent PTM radical was observed after repeated laser light irradiation.

Introduction

Since C_{60} has been revealed as a very attractive electron acceptor with unique photo-physical and electrochemical properties,^{1–3} considerable efforts have been devoted in recent years to develop systems in which C_{60} is covalently linked to electron donors,^{4–15} in addition to the blend systems consisting of C_{60} and donors.^{16–23} Donor–acceptor systems including C_{60} are of particular interest, because they exhibit characteristic electronic properties in the excited states with interesting photo-physical properties attributed to the small reorganization energy of C_{60} in electron transfer processes due to its spherical rigid molecular shape.²⁴ Thus, a lot of research has been conducted for a better understanding of photoinduced electron-transfer processes in dyads and triads including C_{60} .^{4–15} These phenomena open the potential applications in the realization of new artificial photosynthetic systems, molecular electronic devices, and photovoltaic cells.^{4,6,7}

Among the wide variety of donor molecules that have been covalently linked to C_{60} , most donors are neutral molecules such as aromatic amines, carotene, tetrathiafulvalenes, ferrocenes, porphyrins, phthalocyanines, oligothiophenes, π conjugated phenyl oligomers, *etc.* These dyads generated the radical anion-radical cation pairs, some of them showing quite persistent charge-separated state in polar solvents, since the

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charge-recombination processes enter the inverted region of the Marcus parabola.

In the present study, for the first time an anionic donor, the perchlorotriphenylmethide anion (PTM⁻), has been covalently bonded to a C₆₀ derivative, generating the C₆₀–perchlorotriphenylmethide anion triad 1 shown in Fig. 1.

Triphenylmethide anions have been reported to be quite stable when the hydrogen atoms of the triphenyl groups are substituted by chlorine atoms.²⁵ The stability is not only due to the electron-withdrawing character of the substituents, but also to an effective steric shielding of the central carbon wrapped by the six bulky chlorine atoms in the *ortho* positions of the phenyl rings. In addition, PTM anions are reversibly oxidized to highly persistent perchlorotriphenylmethyl radicals (PTM[•]) at low potential (around -0.55 V, *versus* Fc/Fc⁺) being therefore very good donors.²⁶

For the target triad C_{60} -(PTM⁻)₂ (1) we expected the occurrence of an electron transfer from the anionic part to the photoexcited C_{60} moiety, generating the neutral perchloro-triphenylmethyl radical (PTM[•]) and the radical anion of the



Fig. 1 Molecular structure of C_{60} –(PTM⁻)₂.

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E-mail: ito@tagen.tohoku.ac.jp † Electronic supplementary information (ESI) available: CV of compounds 1 and 5, minimized geometry of compound 1, timeresolved fluorescence spectra, transient spectrum and time profiles in polar solvents. See DOI: 10.1039/b514882k

 C_{60} moiety. This represents a completely new situation in this kind of donor-acceptor systems since the charge-recombination takes place between the C_{60} radical anion and a neutral radical, which may show quite different behavior from the usual charge-separated states generating oppositely charged species.

Results and discussion

Synthesis of C₆₀-(PTM⁻)₂

The synthesis of the target triad 1 consisting of two donor units, the perchlorinated triphenylmethide anions, and the C_{60} moiety as the acceptor unit, was achieved by a multi-step synthetic procedure in which the bis-acylation of the C₆₀-diol 4^{27} using the PTM acid chloride 3 is the key step. The new acid chloride derivative 3 was obtained in good yield (80%) following the same procedure used in the synthesis of its radical counterpart²⁸ through refluxing 4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoic acid²⁹ in an excess of thionyl chloride. We carried out the esterification reaction in refluxing CH₂Cl₂ under an argon atmosphere in the presence of dimethylaminopyridine (DMAP). Note that this reaction affords compound 5, the precursor of the target compound 1, in quite good yield ($\sim 60\%$), although two bulky groups are attached to the fullerene moiety through the neighboring alcohol groups. In fact the yield is very similar to that obtained in the esterification of C₆₀-diol 4 with a TTFacid chloride with long alkyl chains that afford high flexibility to the linkage.³⁰ As shown in Scheme 1 the deprotonation of the bis α -H precursor 5 yields quantitatively the target triad 1, by converting the non electroactive α -H triphenylmethane addends to electroactive carbanions that are very good donors. Compound 1 was isolated as the pure tetrabutylammoniun salt by washing the dark purple precipitate with hexane several times.

According to the donor characteristics of bisanion 1, when a CH₂Cl₂ solution of this salt containing an excess of AgNO₃ as oxidant is shaken for a few minutes, the bistriphenylmethyl radical **6** was obtained as a deep red solid in quantitative yield after filtration (Scheme 2). The reaction was followed by UV-Vis spectroscopy; Fig. 2 shows the evolution of the spectra over time. The disappearance of the intense band centered at 518 nm corresponding to the PTM⁻ anion^{26e} was accompanied by the increasing of the characteristic bands of the PTM radical at 364 and 384 nm.²⁶ The presence of the clean transformation of C₆₀-(PTM⁻)₂ (1) into C₆₀-(PTM⁺)₂ (6).

Bisradical **6** was characterized by EPR spectroscopy. The X-band isotropic spectrum of **6** in toluene–CH₂Cl₂ at room temperature consists of a signal with a central intense line and small satellite overlapped lines corresponding to the coupling of the unpaired electron with the naturally abundant ¹³C isotope at the α and aromatic positions of the PTM[•] addends. The g_{iso} value, 2.0023, as well as the isotropic coupling constant values, a_1 (¹³C_{α}) = 30 G and a_2 (¹³C_{arom}) = 12 G, are usual values for the monoradicals of the PTM family.²⁶ The spectrum of bisradical **6** in frozen toluene–CH₂Cl₂ solution does not show the characteristic fine structure nor the forbidden $\Delta m_s = 2$ transition characteristic of the triplet species. All these features indicate that the two radical units in the C₆₀–(PTM[•])₂ triad are not interacting.

Electrochemical measurements

The redox behavior of all new compounds was studied by cyclic voltammetry and the $PTM^{-}[18\text{-}crown-6]^{+}$ salt and

Scheme 1 Synthesis of C₆₀-(PTM⁻)₂(NBu₄⁺)₂. Conditions: *i*) SOCl₂, reflux; *ii*) DMAP, CH₂Cl₂, 35 °C; *iii*) NBu₄OH, THF, room temperature.





Scheme 2 Synthesis of C_{60} -(PTM[•])₂ (6).



Fig. 2 UV-Vis spectra obtained upon oxidation of bisanion 1 in CH_2Cl_2 .

pristine C_{60} were also studied under the same conditions as the reference compounds. As expected, triad **5**, in which only the C_{60} moiety is electroactive, presents the characteristic reversible reduction waves of the substituted C_{60} compounds. By contrast, unexpected results were obtained in the cyclic voltammogram of the triad C_{60} -(PTM⁻)₂, **1**, which contains two different electroactive moieties. In all conditions assayed, only one reversible oxidation wave appears clearly (see ESI[†] Fig. SI1 and SI2) whereas the waves expected for the C_{60} moiety are quite weak. The wave corresponding to the redox characteristics of the anionic PTM moieties appears at the same potential as the reference PTM⁻[18-crown-6]⁺, indicating that there is no influence of one anionic moiety on the other and that there is no interaction with the C_{60} moiety.

The reversibility observed in the cyclic voltammogram of compound 1 is in accordance with the stability of the free bisradical $C_{60}(PTM^{-})_2$, 6. In Table 1, the $E_{1/2}$ values for C_{60} , $C_{60}-(PTM^{-})_2$ 1, $PTM^{-}[18\text{-}crown-6]^+$ and $C_{60}-(PTMH)_2$ 5 are summarized. Weak reduction peaks of the C_{60} unit in charged triad 1 were always observed under different conditions, the phenomenon being independent of the concentration, excluding an intermolecular phenomenon, the nature of the

Table 1 Redox potentials of C_{60} -(PTM⁻)₂ and references ($E_{1/2}$ vs. Fc/Fc⁺ in *o*-DCB-CH₃CN (95 : 5))

Compound	$E_{\rm ox}/{\rm V}$	E^{1}_{red}/V	$E^2_{\rm red}/V$	E^{3}_{red}/V
C ₆₀		-1.03	-1.42	-1.87
PTM ⁻ C··-(PTMH)-	-0.54	-1.10	-1.49	
C_{60} – (PTM ⁻) ₂	-0.52	-1.12^{a}	-1.50^{a}	
^a Very weak sign	al.			

electrode (platinum, gold and carbon vitreous), excluding a phenomenon of adsorption to the electrode, and the solvent (CH₂Cl₂ and *o*-dichlorobenzene (*o*-DCB)). The unexpected behavior of compound **1** is not understood and new studies on other negative charged compounds are underway in order to know if the negative charges present in the addends of C_{60} can be responsible for this.

In order to calculate, from the Weller equations,³¹ the freeenergy changes for charge-separation ($\Delta G_{\rm CS}$) and chargerecombination ($\Delta G_{\rm CR}$) for C₆₀–(PTM⁻)₂ the first reduction potential ($E_{\rm red}$) value of the C₆₀ moiety and the first oxidation potential ($E_{\rm ox}$) of the PTM⁻ moiety are needed. From these $E_{\rm ox}$ and $E_{\rm red}$ values, the $\Delta G_{\rm CS}$ and $\Delta G_{\rm CR}$ values were calculated using eqn (1)–(3):

$$-\Delta G_{\rm CS} = \Delta E_{0.0} - (-\Delta G_{\rm CR}) \tag{1}$$

$$-\Delta G_{\rm CR} = E_{\rm ox} - E_{\rm red} + \Delta G_{\rm S} \tag{2}$$

$$-\Delta G_{\rm s} =$$

$$\frac{e^2}{4\pi\varepsilon_0} \left[\left(\frac{1}{2R^+} + \frac{1}{2R^-} - \frac{1}{R_{\rm CC}} \right) \left(\frac{1}{\varepsilon_{\rm s}} \right) - \left(\frac{1}{2R^+} + \frac{1}{2R^-} \right) \left(\frac{1}{\varepsilon_{\rm r}} \right) \right]^{(3)}$$

where $\Delta E_{0.0}$ is the energy of the 0-0 transition of C_{60} , R^+ the radius of the PTM radical,²⁶ R^- the radius of the radical anion of C_{60} and R_{cc} the distance between the two electroactive sites;³² e, ε_0 , ε_s , and ε_r are the elementary charge, vacuum permittivity, and static permittivities of the solvents used for rate measurements and redox potential measurements, respectively. The ΔG_{CS} and ΔG_{CR} values for C_{60} –(PTM⁻)₂ in different solvents are summarized in Table 2. In polar solvent such as PhCN, charge-separation processes *via* excited singlet states of the C_{60} moiety (${}^{1}C_{60}^{*}$) and the PTM⁻ (1 (PTM⁻)*) are

Table 2 Free-energy changes for charge separation $(-\Delta G_{CS})$ *via* the excited states of C_{60} in $C_{60-}(PTM^-)_2$ and charge recombination $(-\Delta G_{CR})$ of C_{60} ^{•-}- $(PTM^{•})(PTM^-)$

Solvent	$-\Delta G^{\rm S}{}_{\rm CS}/{\rm eV}^a$	$-\Delta G^{\mathrm{T}}{}_{\mathrm{CS}}/\mathrm{eV}^{a}$	$-\Delta G_{\rm CR}/{\rm eV}^a$
Toluene	0.92	0.70	0.82
o-DCB	1.26	1.06	0.46
PhCN	1.33	1.13	0.39
CH ₃ CN	1.34	1.14	0.38
^{<i>a</i>} Calculate	d from eqns (1) -(3	b) employing ΔE_{0-0}	$= 1.72 \text{ eV for } {}^{1}\text{C}_{60}$

 $\Delta E_{0.0} = 1.52 \text{ eV}$ for ${}^{3}C_{00}^{*}$, $E_{\text{ox}} = -0.52 \text{ V}$ for PTM^{-} , and $E_{\text{red}} = -1.12 \text{ V}$ for C_{60} vs. Fc/Fc^{+} in *o*-DCB-CH₃CN 95 : 5. $R^{+} = 7.4 \text{ Å}$ for PTM⁻, and $R^{-} = 4.7 \text{ Å}$ for C₆₀, and $R_{\text{CC}} = 10 \text{ Å}^{.32}$ Permittivities of toluene, *o*-DCB, and PhCN are 2.38, 9.93, 25.2, and 37.5 respectively.

exothermic and predicted to occur easily. In toluene, the charge-separation process is also exothermic and can occur. The charge-separation process *via* the excited triplet state of C_{60} (${}^{3}C_{60}^{*}$) is also exothermic in polar and nonpolar solvents.

Steady-state absorption measurements

Steady-state absorption spectra of C_{60} -(PTMH)₂ **5**, C_{60} -(PTM⁻)₂ **1**, and PTM⁻ in PhCN are shown in Fig. 3. For C_{60} -(PTMH)₂, the peaks at 700 and 430 nm bands are attributed to the characteristic bands of the functionalized C_{60} . In the case of C_{60} -(PTM⁻)₂, the broad absorption band at 518 nm is characteristic of the PTM⁻ moiety, as shown in

Fig. 2. The absorption bands of the C_{60} moiety appear at 700 nm and in the shorter wavelength than 400 nm. Since this spectrum is almost the same as the one resulting from the summed spectrum of the components PTM⁻ and C_{60} , an appreciable interaction between moieties may not be present in the ground state. For the transient absorption measurements, a 355 nm laser light was used, which excites the C_{60} moiety about 90% and 10% of to the PTM⁻ moiety. For time-resolved fluorescence measurement, a 400 nm laser light was used, which excites both the C_{60} moiety (75%) and the PTM⁻ moiety (25%).

Fluorescence measurements

Steady-state fluorescence spectra of PTM⁻, C₆₀-(PTMH)₂, C₆₀-(PTM⁻)₂ in toluene and *o*-DCB are shown in Fig. 4. The fluorescence peak ($\lambda_{\rm f}$) for C₆₀-(PTM⁻)₂ appeared at 600 nm (Fig. 4b), which is almost the same as that of PTM⁻ (Fig. 4a). Therefore, the origin of the observed fluorescence at 600 nm of C₆₀-(PTM⁻)₂ is attributed to the PTM⁻ moiety. From the cross point of the fluorescence band and absorption band after normalizing both intensities, the lowest excited singlet energy (E_{0-0}) of the PTM⁻ moiety was estimated to be 2.1 eV.

The fluorescence of the C_{60} moiety would be expected to appear at 720 nm as shown for C_{60} -(PTMH)₂ (Fig. 4a). In the case of C_{60} -(PTM⁻)₂, however, the fluorescence of the C_{60}



Fig. 3 Steady-state absorption spectra of (a) C_{60} -(PTMH)₂ (0.1 mM) in PhCN and (b) C_{60} -(PTM⁻)₂ and PTM⁻ (0.025 mM) in PhCN.



Fig. 4 Steady-state fluorescence spectra of (a) PTM⁻ (0.05 mM) and C_{60} -(PTMH)₂ (0.05 mM), and (b) C_{60} -(PTM⁻)₂ (0.05 mM) in toluene and *o*-DCB; $\lambda_{ex} = 550$ nm.



Fig. 5 Fluorescence time profiles at 560–630 nm in *o*-DCB and PhCN; $\lambda_{ex} = 400$ nm.

moiety may be hidden by the huge fluorescence tail of ${}^{1}(PTM^{-})^{*}$. Further quantitative analyses on the fluorescence properties were carried out based on fluorescence lifetime measurements.

Time-resolved fluorescence spectra and fluorescence lifetimes

The peak position and shape of time-resolved fluorescence spectra of ${}^{1}(\text{PTM}^{-})^{*}$ (see ESI†) are quite similar to those of the steady-state spectra. Within the fluorescence lifetime, the spectral shape is almost the same. The time profiles of the fluorescence peak position are shown in Fig. 5. The fluorescence time profile of ${}^{1}(\text{PTM}^{-})^{*}$ showed slow fluorescence decay obeying a single exponential function, yielding a fluorescence lifetime of 4100 ps in toluene and *o*-DCB.^{20a} In PhCN, a shorter lifetime (1000 ps) was evaluated, suggesting differences in the excited state of ${}^{1}(\text{PTM}^{-})^{*}$ in this polar solvent from that in nonpolar and less polar solvents.

Also for C_{60} –(PTMH)₂, the time-resolved fluorescence spectra (see ESI[†]) are in good agreement with the steady-state fluorescence spectrum. Within the fluorescence lifetime of C_{60} –(PTMH)₂ the spectral shape is unchanged. Time profiles of the fluorescence intensity at the peak position in toluene and *o*-DCB are shown in Fig. 6. In slightly polar *o*-DCB, the fluorescence lifetime of the ${}^{1}C_{60}^{*}$ moiety is almost the same to



Fig. 6 Fluorescence decays of C_{60} -(PTMH)₂ at 700–750 nm in toluene and *o*-DCB; $\lambda_{ex} = 410$ nm.



Fig. 7 Fluorescence time profiles at (a) 560–630 nm and (b) 710–750 nm, respectively, in toluene and *o*-DCB; $\lambda_{ex} = 400$ nm.

that in non-polar toluene within experimental errors, in which both decays are the same as that of pristine ${}^{1}C_{60}^{*}$, as expected for a compound with no donor moieties that can not present charge-separation.

Time profiles of the fluorescence peak position of C_{60^-} (PTM⁻)₂ in toluene and *o*-DCB are shown in Fig. 7. Slight blue shift of the florescence peak was observed in the timeresolved fluorescence spectra of C_{60^-} (PTM⁻)₂ (see ESI[†]) on going from toluene to *o*-DCB, which is the same trend as observed in steady-state measurements. The fluorescence lifetimes of the ¹(PTM⁻)* moiety in C_{60^-} (PTM⁻)₂ at 560– 630 nm (Fig. 7) are quite shorter than that of ¹(PTM⁻)* in all studied solvents (Fig. 5). This finding indicates that a quenching process from the ¹(PTM⁻)* moiety to the C_{60} moiety takes place for $C_{60^{-1}}$ (PTM⁻)* (PTM⁻). Even in nonpolar solvents like toluene, the fluorescence decay rate of the ¹(PTM⁻)* moiety in $C_{60^{-1}}$ (PTM⁻)*(PTM⁻) was faster than that of the isolated ¹(PTM⁻)*, it is possible to consider that both energy transfer and charge separation occur *via* ¹(PTM⁻)*.

From the $(\tau_f)_{\text{sample}}$ value of the ¹(PTM⁻)* moiety in C₆₀-(PTM⁻)₂, the intramolecular quenching rate-constant (k_q^S) was evaluated using eqn (4):

$$k_{q}^{S} = (1/\tau_{f})_{sample} - (1/\tau_{f})_{ref}$$
 (4)

where $(\tau_f)_{ref}$ is the fluorescence lifetime of PTM⁻ in toluene.^{20e} The kinetic data are summarized in Table 3, which indicates

Table 3 Fluorescence lifetimes (τ_f) at 710–730 nm, quenching rate-constants (k_q^S) and quenching quantum yields (Φ_q^S) via $C_{60}^{-1}(PTM^-)*(PTM^-)$, and rate constants (k_{CS}^S) and quantum yields (Φ_{CS}^S) for charge separation via ${}^{1}C_{60}*-(PTM^-)_{2}$ at room temperature

Solvent	$\tau_{\rm f}^{\ b}$ /ps via ¹ (PTM ⁻)*	k_{q}^{Sa}/s^{-1} via ¹ (PTM ⁻)*	$\Phi^{S_{q}a}_{q}$ via ¹ (PTM ⁻)*	$\tau_{\rm f}^{\ b}/\text{ps}$ via $^1\text{C}_{60}*$	$k_{\rm CS}^{\rm S} a/{\rm s}^{-1}$ via ${}^{1}{\rm C}_{60}^{*}$	$\Phi^{\rm S}{}_{\rm CS}{}^a$ via ${}^1{ m C}_{60}{}^*$
Toluene	150 (70%)	6.4×10^{9}	0.96	100 (85%)	9.3×10^{9}	0.93
o-DCB	79 (85%)	1.3×10^{10}	0.98	83 (94%)	1.1×10^{10}	0.94
PhCN	$257(70\%)^{c}$	$(3.7 \times 10^9)^c$	$(0.94)^c$	95 (88%)	9.8×10^{9}	0.93
^a Calculat	ted by using eqn (4) and	d (5). The values of $(\tau_f)_{ref}$	were employed to be 4	130 ps for PTM	and 1390 for C_{60} . ^b Fl	luorescence decays of

¹ Calculated by using eqn (4) and (5). The values of $(\tau_{f})_{ref}$ were employed to be 4150 ps for PTM and 1390 for C₆₀. ² Fluorescence decays of ¹(PTM⁻)* and ¹(C₆₀)* were fitted with biexponential functions and the k_q^S , ϕ_q^S , k_{CS}^S and ϕ_{CS}^S values were calculated from the shorter lifetimes with the major fraction. ^c Effect of impurity in PhCN may be included.

efficient energy/electron transfer quenching processes of the PTM⁻ moiety in C₆₀-(PTM⁻)₂; thus, in the evaluated k_q^S values, both energy transfer rate constant ($k_{\rm EN}^S$) and charge-separation rate constant ($k_{\rm CS}^S$) may be included. For clear evidence of the energy transfer process, a rise of the fluorescence of the ${}^1C_{60}^*$ moiety at 720 nm would be expected, but this was difficult to observe due to the quick decay of ${}^1C_{60}^*$ even in toluene (Fig. 7b).

The fluorescence quenching quantum yields of (Φ^{S}_{q}) via the ¹(PTM⁻)* moiety in C₆₀-(PTM⁻)₂ in polar and nonpolar solvents were evaluated from eqn (5):

$$\Phi_{q}^{S} = [(1/\tau_{f})_{sample} - (1/\tau_{f})_{ref}]/(1/\tau)_{sample}$$
(5)

Thus, $\Phi_q^S = 0.96-0.98$ was calculated for $C_{60}^{-1}(PTM^-)*(PTM^-)$. Similarly, Φ_q^S may contain both quantum yields of energy transfer (Φ_{EN}^S) and quantum yields of charge separation (Φ_{CS}^S).

In PhCN, the fluorescence decay rate was slower than those in toluene and *o*-DCB, probably because of the presence of some impurity in PhCN, which was quite difficult to eliminate.

By contrast with the fluorescence decay of the C_{60} –(PTMH)₂ moiety yielding the fluorescence lifetime (τ_f) of 1390 ps in toluene (Fig. 6),²⁰ the time profiles of the fluorescence at 720 nm of the C_{60} moiety in C_{60} –(PTM⁻)₂ (Fig. 7b) show biexponential decay in *o*-DCB and toluene. The major component decayed with the τ_f values in the 83 ps (94%)–100 ps (85%) region, whereas the minor slow-decay components gave τ_f values of 1300 ps. The τ_f values of the major components are summarized in Table 3.

The difference between the $\tau_{\rm f}$ values evaluated from the main fluorescence decays in 710-750 nm in polar and nonpolar solvents can be attributed predominantly to charge separation via the ${}^{1}C_{60}^{*}$ moiety in $C_{60}^{-}(PTM^{-})_{2}$ generating the radical ion-pair states (C_{60} · -(PTM ·)(PTM -)). From the τ_f value of the ${}^{1}C_{60}$ * moiety in C_{60} -(PTM⁻)₂, the intramolecular chargeseparation rate constants (k_{CS}^{S}) in polar and nonpolar solvents were evaluated from eqn (4) as summarized in Table 3. Thus, the $k^{\rm S}_{\rm CS}$ values for the C₆₀-(PTM⁻)₂ were evaluated to be $(9.3-11.0) \times 10^9 \text{ s}^{-1}$ which indicate that charge separation *via* the ${}^{1}C_{60}$ * moiety is an effective process in polar and nonpolar solvents. The quantum yields of charge separation (Φ^{S}_{CS}) via the ${}^{1}C_{60}$ * moiety in C₆₀–(PTM⁻)₂ were evaluated from eqn (5). Thus, $\Phi^{S}_{CS} = 0.93-0.94$ were calculated for the C₆₀-(PTM⁻)₂ (Table 3) in polar and nonpolar solvents, respectively, which indicates that the charge separation via the ${}^{1}C_{60}^{*}$ moiety is the main process, overwhelming the intersystem crossing (ISC) process to the ${}^{3}C_{60}$ * moiety even in toluene.

Nanosecond transient absorption measurements

Transient absorption spectra observed upon nanosecond laser excitation (355 nm) of C_{60} -(PTMH)₂ in toluene are shown in Fig. 8. The 355 nm laser light excites the C_{60} and PTMH moieties. The broad absorption bands were observed in the region of 600–850 nm, which is the absorption region of ${}^{3}C_{60}*$ (peak = 700 nm).^{20e} The decay time profile is quite slow on the time scale of 1.5 µs. Even the PTMH moiety was excited, the energy transfer gives the ${}^{1}C_{60}*$ moiety, which is finally converted to ${}^{3}C_{60}*$ by ISC.

Transient absorption spectra observed by the nanosecond laser excitation (355 nm) of C_{60} -(PTM⁻)₂ in toluene are shown in Fig. 9. Broad absorption bands were observed in the region of 600-1200 nm, which can be attributed to the absorption of the C_{60} moiety,^{20e} although the absorption bands are broader compared with the pristine C_{60} .⁻ and other C_{60} .⁻ derivatives. This broadening may be caused by the interaction between the C_{60} · moiety and the (PTM ·)(PTM –) moiety, in which anion, radical and halogen atoms may be the candidate of the interactions. From the decay time-profile at 1020 nm, the charge-recombination rate constant (k_{CR}) between C_{60} . and PTM of C60 -(PTM)(PTM) was evaluated to be $1.23 \times 10^7 \text{ s}^{-1}$, from which the lifetime (τ_{RIP}) of the chargeseparated state was calculated to be 81 ns at room temperature. Since the 355 nm laser light predominantly excites the C₆₀ moiety, the process photoinduced by the excitation of PTM⁻ can be neglected.

Similarly, transient absorption-time profiles at 1020 nm were observed in *o*-DCB and PhCN (see ESI[†]), although the



Fig. 8 Nanosecond transient absorption spectra of 0.1 mM C_{60} -(PTMH)₂ observed by 532 nm laser irradiation at 100 ns (\bullet) and 1000 ns (\bigcirc) in PhCN. Inset: Absorption–time profiles at 720 nm.



Fig. 9 Nanosecond transient absorption spectra of 0.05 mM C_{60} -(PTM⁻)₂ observed by 355 nm laser irradiation at 100 ns (\bullet) and 1000 ns (\bigcirc) in toluene. Inset: Absorption–time profiles at 1020 nm.

transient absorption spectra were distorted in *o*-DCB and PhCN by laser irradiation (see ESI† Fig. SI-8). From the decay time-profiles at 1020 nm, the charge-recombination rate constants (k_{CR}) were evaluated to be 1.30 × 10⁷ and 1.72 × 10⁷ s⁻¹ for *o*-DCB and PhCN, from which the τ_{RIP} values of the charge-separated states were calculated to be 77 and 58 ns, respectively, at room temperature as listed in Table 4.

The solvent polarity effect on the τ_{RIP} values was small; for polar and nonpolar solvents, almost similar lifetimes (τ_{RIP}) are found. However, C_{60} ^{•-}–(PTM[•])(PTM⁻) in toluene gives a long lifetime.

Repeated laser irradiation

By excitation of C_{60} -(PTM⁻)₂ with the 355 nm light, the absorption band of PTM⁻ decreased; instead, a sharp peak appeared at 390 nm (Fig. 10), which is attributed to the PTM[•] moiety (see Fig. 2). This observation indicates that after the photoinduced charge-separation the stable C_{60} -(PTM[•])(PTM⁻) species was generated, probably because the C_{60} [•] moiety may be quenched by some reactions such as donation of an electron to the impurity in the solution.

Energy diagram

Fig. 11 shows an energy diagram of C_{60} -(PTM⁻)₂ when PTM⁻ and C_{60} are excited. Energy levels of the radical ionpairs C_{60} ^{•-}-(PTM[•])(PTM⁻) are deduced from Table 2. In toluene, *o*-DCB and PhCN, the charge-separation takes place *via* C_{60} -¹(PTM⁻)*(PTM⁻) and ${}^{1}C_{60}$ *-(PTM⁻)₂ as indicated by the weak fluorescence intensity and the short fluorescence lifetime, since the energy levels of C_{60} ^{•-}-(PTM[•])(PTM⁻) are

Table 4 Charge-recombination rate constant (k_{CR}) of C_{60} ⁻⁻-(PTM⁻)(PTM⁻) at room temperature

Solvent	$k_{\rm CR}/{\rm s}^{-1}$	$\tau_{\rm RIP}/\rm ns$
Toluene o-DCB PhCN	$\begin{array}{ccc} 1.23 \ \times \ 10^{7} \\ 1.30 \ \times \ 10^{7} \\ 1.72 \ \times \ 10^{7} \end{array}$	81 77 58



Fig. 10 Steady-state absorption spectra of 0.10 mM C_{60} -(PTM⁻)₂ in PhCN before and after 355 nm laser light (LS) irradiation.



Fig. 11 Schematic energy diagram for electron-transfer processes of C_{60} -(PTM⁻)₂.

lower than these excited singlet states even in toluene. Thus, the generation of ${}^{3}C_{60}^{*}$ -(PTM⁻)₂ through the ISC process from ${}^{1}C_{60}^{*}$ -(PTM⁻)₂ is not possible, because the Φ^{S}_{CS} values are almost unity in all solvents. Furthermore, with excitation of PTM⁻, an energy-transfer process is also possible from the 1 (PTM⁻)* moiety to generate the ${}^{1}C_{60}^{*}$ moiety.

Summary

We have succeeded, for the first time, in synthesizing a C_{60} based triad which bears an anionic donor as addend, the

perchlorotriphenylmethide anion (PTM⁻), thus generating the C_{60} -(PTM⁻)₂ triad 1. For this triad, photoinduced charge separation via both $C_{60}^{-1}(PTM^{-})^{*}(PTM^{-})$ and ${}^{1}C_{60}^{*}$ – (PTM⁻)₂ were observed in polar and nonpolar solvents through photoexcitation at room temperature. The efficiency and rate of the charge-separation process are quite high. The longest lifetime for C₆₀^{•-}-(PTM[•])(PTM⁻) was 81 ns in toluene at room temperature, which is quite long and comparable with other C_{60} based dyads and triads such as C₆₀-fluorene-diphenylamine,³³ C₆₀-bridgedimethylaniline,⁵ C₆₀-extended TTF³⁴ or C₆₀-long flexible bridge-TTF.³⁰ Even though the properties of C₆₀ perchlorotriphenylmethide anion based triads are not so good like the best ones found in some C60-porphyrins and C60-chlorines based dyads,³⁶ the present study provides a new possibility for functional fullerenes based on the perchlorotriphenylmethide anion, which can be added to other known functional materials based on the parent perchlorotriphenylmethyl radical that works as an acceptor and has permitted the development of multifunctional switchable molecular systems.^{26e,35} We believe that the present study gives valuable information not only about the photo-induced electrontransfer chemistry of fullerene-triad systems, but also about the materials science of perchlorotriphenylmethide anion functional compounds.

Experimental

General information

Reagents were purchased from commercial suppliers and used without further purification. Compounds **2**, PTM⁻[18-crown-6]⁺, and **4** were synthesized as previously described.^{25,27,28} All solvents were spectrophotometric grade and were distilled before use. Column chromatography was performed using Merck silica gel 60. The NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (500 MHz for ¹H, 125.5 MHz for ¹³C). IR spectra were run on a FT-IR spectrometer BIO-RAD FTS 155, the solid compounds being studied in KBr pellets. UV-Vis spectra were recorded on a Cary 5 E Varian Spectrometer. MALDI-TOF mass spectra were obtained on a Bruker Biflex III spectrometer, equipped with a N₂ laser (337 nm) using dithranol as a matrix. The ESI-MS spectra were obtained with a JEOL, JMS 700 B/E mass spectrometer.

Electrochemical measurements

Oxidation potentials (E_{ox}) and reduction potentials (E_{red}) were measured by a voltammetric analyzer (EGG PAR 273A) in a conventional three-electrode cell equipped with Pt working electrodes and counter electrodes. A silver wire served as a quasi-reference electrode; its potential was checked against the ferrocene/ferrocenium couple (Fc/Fc⁺) before and after each experiment, at a scan rate of 100 mV s⁻¹. In each case, the solution contained ~0.5 mM sample and 0.1 M tetra *n*-butylammonium hexafluorophosphate (Bu₄NPF₆) dissolved in a mixture of *o*-dichlorobenzene–acetonitrile 95 : 5 or other solvents. The experiments were performed in a glove box.

Synthesis of 4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoyl chloride (3)

A solution of 4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoic acid (2)²⁹ (149.7 mg; 0.194 mol) in thionyl chloride (3 mL) was refluxed for 24 h. Excess SOCl₂ was removed under reduced pressure. The resulting solid was purified by chromatography (silica gel, chloroform). Compound **3** was obtained in 80% yield as a beige solid. IR (KBr): 675, 764, 810, 1780 (COCl) cm⁻¹. Anal. Calc. for $C_{20}HCl_{15}O_2$: C, 29.84; H, 0.12; Cl, 66.06. Found: C, 29.67; H, 0.14; Cl, 66.36%.

Synthesis of 2,2-bis{4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzoyloxymethyl}-1,2-propano-1,2dihydro[60]fullerene (5)

A mixture of compound 4^{27} (68.3 mg; 0.083 mmol), compound 3 (150 mg; 0.190 mmol) and dimethylaminopyridine (35.5 mg; 0.290 mmol) in freshly distilled dichloromethane (10 mL) was stirred under argon atmosphere at 38 °C for 5 days. The solvent was evaporated and the residue was purified by column chromatography (silica gel, hexane then hexane-CH₂Cl₂ 2 : 1). Compound **5** was obtained in 59% yield as a brown solid. ¹H NMR (250 MHz, CDCl₃): 3.97 (s, 4H, CH₂-C₆₀), 5.41 (s, 4H, CH₂-O-CO-), 7.06 (s, 2H, CH). IR (KBr): 527(C₆₀), 810 (C-Cl), 1749 (C=O) cm⁻¹. UV-Vis (CH₂Cl₂): λ_{max} (ε) = 430 (4625), 326 (32800), 305 (38900), 255 nm (167000 L mol⁻¹ cm⁻¹). MS (MALDI-TOF): *m/z* calcd for the maximum peak of C₁₀₅H₁₀O₄Cl₂₈ = 2327.17, observed maximum [M]⁺ = 2327.25.

Synthesis of C_{60} -(PTM⁻)₂(NBu₄)₂ (1)

Tetrabutylammonium hydroxide, 40 wt% solution in water, ~1.5 M (31.5 µl; 47.25 µmol) was added to a solution of compound **5** (20 mg; 8.59 µmol) dissolved in freshly distilled THF (2.5 mL). This mixture immediately became garnet-red and was stirred for 2 hours in a light protected place. The compound precipitates after addition of deoxygenated distilled hexane. The resulting solid was purified by centrifugation, and washed several times with deoxygenated distilled hexane. The garnet-red compound **1** was obtained quantitatively. IR (KBr): 518 (C₆₀), 810 (C–Cl), 1738 (C=O) cm⁻¹. UV (THF), $\lambda_{max} (\varepsilon) =$ 518 nm (75000 L mol⁻¹ cm⁻¹). MS (ESI⁻): *m/z* calcd for the maximum peak of C₁₀₅H₈O₄Cl₂₈ = 1163.58, observed maximum 1162.45.

Steady-state measurements

Steady-state absorption spectra in the visible and near-IR regions were measured on a Jasco V570 DS spectrophotometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer equipped with a photomultiplier tube having high sensitivity in the 700–800 nm region.

Time-resolved fluorescence measurements

The time-resolved fluorescence spectra were measured by single photon counting method using a streakscope (Hamamatsu

Photonics, C4334-01) as a detector and the laser light (second harmonic generation (SHG), 400 nm) of a Ti : sapphire laser (Spectra-Physics, Tsunami 3950-L2S, 150 fs fwhm) as an excitation source.³⁶ Lifetimes were evaluated with software attached to the equipment.

Nanosecond transient absorption measurements

Nanosecond transient absorption measurements were carried out using THG (355 nm) of a Nd : YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 5 ns fwhm) as an excitation source. For transient absorption spectra in the near-IR region (600–1200 nm) and the time-profiles, monitoring light from a pulsed Xe lamp was detected with a Ge-APD (Hamamatsu Photonics, B2834). For the measurements in the visible region (400–1000 nm), a Si-PIN photodiode (Hamamatsu Photonics, S1722-02) was used as a detector.^{20,36}

Acknowledgements

The present work was supported by a Grant-in-Aid on Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, Dirección General de Investigación, Spain (Project BQU2003-00760), DGR, Generalitat de Catalunya (Centre de Referencia CeRMAE and Project 2001SG00362), EU COST D14 and CNRS (France).

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- 32 The distance was evaluated from the minimized structure of the triad 1 obtained using semiempirical AM1 calculations (see ESI† Fig. SI-3). Three resulting minimized geometries were obtained in which the distance between the PTM unit and C₆₀ are different. The geometry used was the conformation with the lower formation enthalpy (ΔH_f). Distances between the center of C₆₀ and PTM⁻ were evaluated to be 10 Å from this optimized structure.
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