



Photoinduced processes of newly synthesized bisferrocene- and bisfullerene-substituted tetrads with a triphenylamine central block

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ABSTRACT

Photoinduced electron transfer processes of two newly synthesized tetrads with a triphenylamine (TPA) as central building block, to which bisfullerenes (C_{60}) and bisferrocenes (Fc) are covalently connected, have been studied. One of them has a TPA linked with one C_{60} moiety and two ferrocene moieties C_{60} -TPA-(Fc)₂ and another tetrad has a TPA linked with two C_{60} moieties and one ferrocene unit (C_{60})₂-TPA-Fc. The photophysical properties of (C_{60})_m-TPA-(Fc)_n have been investigated by applying the picosecond time-resolved fluorescence and nanosecond transient absorption techniques in both polar and nonpolar solvents. The charge separation process via the excited singlet state of the C_{60} moiety of the C_{60} -TPA-(Fc)₂ is more efficient than that of the (C_{60})₂-TPA-Fc. It is found that the ratio of Fc-donor to the C_{60} -acceptor affects charge separation efficiency via the excited singlet state of the C_{60} moiety.

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1. Introduction

The construction of artificial photosynthetic models to mimic natural photosynthesis through the designing of covalently linked electron-donor and electron-acceptor moieties is the object of great interest. The interest lies in the development of efficient organic solar cells [1–4] and other areas of nanotechnology such as photonics or sensors [5–8]. In this respect, C_{60} has been employed as an excellent electron-acceptor [9,10], similar to quinones, and its visible light absorption allows efficient photo-sensitizer inducing such events as energy transfer (EN) and electron transfer (ET) via the excited state of C_{60} moiety in fullerene-donor molecular systems [11,12].

The donor ability determines the nature of the photophysical events in these fullerene-donor systems; ferrocene (Fc) units allow an efficient electron transfer event that generates the radical ion pair [13–17]. Moreover, triphenylamine (TPA) derivatives also have been recognized as good electron-donors with respect to the photo-excited C_{60} [18,19].

In the strategic view points of synthesis, fullerenes such as C_{60} are attractive cores due to their easy chemical functionalizations, which allow the incorporation of most functional groups [20]. Furthermore, the TPA derivatives are also attractive building blocks to connect the donor unit and acceptor unit, in addition to their electron-donor character [21].

In the present report, we synthesized two tetrads with a TPA as a central block, to which fullerenes (C_{60}) and ferrocenes (Fc) are covalently connected. One tetrad has a TPA linked with one C_{60} moiety and two Fc moieties, C_{60} -TPA-(Fc)₂ and another tetrad has a TPA linked with two C_{60} moieties and one ferrocene unit, (C_{60})₂-TPA-Fc as shown in Fig. 1. These new compounds are thought to be dendrimer-like light-harvesting molecules, which have received increased attentions in recent years [22–25]. Some ferrocene-substituted fulleropyrrolidine derivatives with multi-ethylene bridges have been reported to provide a very efficient photoinduced energy transfer [26–28]. Thus, it is interesting to compare the photophysical properties of these bisferrocene- and bisfullerene-substituted molecules with a TPA central block.

The photophysical properties of these compounds have been studied by the time-resolved spectroscopic techniques and compared with those of the single donor-acceptor triad (C_{60} -TPA-Fc) reference molecule. These molecular systems are expected to present efficient photoinduced electron transfer (PET) processes to give long-lived radical ion pairs.

2. Results and discussion

2.1. Synthesis and characterization

The two target tetrads C_{60} -TPA-(Fc)₂ **2** and (C_{60})₂-TPA-Fc **3** as well as the reference triad C_{60} -TPA-Fc **1** have been synthesized according to the procedures depicted in Scheme 1.

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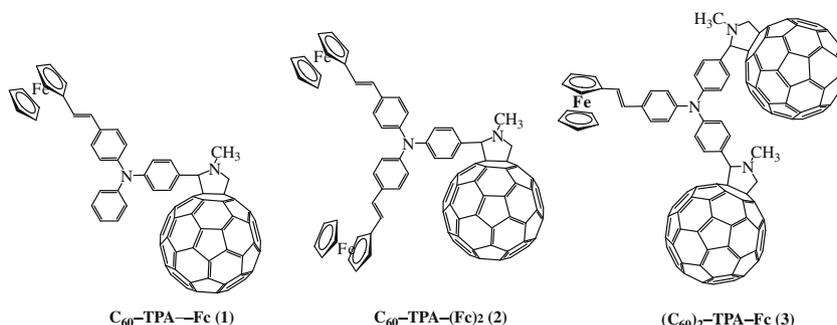


Fig. 1. Molecular structures of compounds **1**, **2** and **3**.

Every step of the reaction sequence proceeded smoothly and efficiently to give a good-or-moderate yield of the product (see Section 4 for synthetic details).

Commercially available diphenylamine was coupled with 1-bromo-4-iodobenzene by Buchwald–Hartwig method [29,30] to give 4-bromotriphenylamine (**4**) in 57.5% and subsequently Vilsmeier formylation [31,32] was carried out to produce aldehyde **5** in 91.0%.

Coupling of ferrocenylvinyl group to **5** was catalyzed by the Heck reaction [33,34] using Pd_2dba_3 catalyst complex with dppf to afford **6** in 65.0%, and finally, fulleropyrrolidine formation was achieved by 1,3-dipolar cycloaddition reaction between aldehyde **6** and C_{60} in the presence of excess *N*-methylglycine (sarcosine) under the condition described by Prato et al. [35] to give C_{60} -TPA-Fc (**1**) in 15.3%. C_{60} -TPA-(Fc)₂ tetrad (**2**) was also prepared in a very similar way. However, in the synthetic course of $(\text{C}_{60})_2$ -TPA-Fc tetrad (**3**), direct double formylation of TPA by the Vilsmeier reaction proved to be difficult due to the deactivation effect of the first carbonyl group on TPA, and mainly gave a monoformylated TPA under normal stoichiometry of POCl_3/DMF (up to 3.5 equiv.). With a large excess of POCl_3/DMF (~10 equiv.), the diformylated TPA **10** was produced with a yield of 42.0%. Subsequent bromination of **10** was performed using bromine to give **11** in 87.0%, and then Heck reaction between **11** and vinylferrocene was carried out using $\text{Pd}(\text{OAc})_2$ as catalyst to afford **12** in 40.0%. Finally, fulleropyrrolidine formation was achieved by Prato's method [35] to give the $(\text{C}_{60})_2$ -TPA-Fc tetrad (**3**) in 50.0%. Although the tetrad **3** should be obtained as a stereo-isomeric mixture due to the formation of two asymmetric centres in twofold cycloaddition reaction, high resolution ^1H NMR spectrum (400 MHz) of tetrad **3** showed the presence of only one stereoisomer. The same results for similar derivatives were often observed by our group [21,36] (see also Section 4).

C_{60} -TPA-Fc (**1**), C_{60} -TPA-(Fc)₂ (**2**) and $(\text{C}_{60})_2$ -TPA-Fc (**3**) are very soluble in aromatic solvents (i.e., toluene (TN), *o*-dichlorobenzene (DCB), benzonitrile (PhCN)) and other common organic solvents (i.e., carbon disulfide, acetone, CH_2Cl_2 , CHCl_3 , THF). The structure and purity of the new compounds were confirmed by ^1H NMR, ^{13}C NMR and IR spectroscopies, MALDI-TOF mass spectroscopy, and elemental analysis.

^1H NMR spectra of **1**, **2** and **3** in CDCl_3 are consistent with the proposed structures, showing the expected features with the correct integration ratios. The signals of pyrrolidine protons in **1**, **2** and **3** appeared as two doublets (geminal protons), and a singlet in the $\delta = 4.60$ – 4.92 ppm region, which is consistent with the spectra obtained for similar derivatives [37]. Protons of the ferrocene moiety showed typical three singlets in the $\delta = 4.04$ – 4.43 ppm region. ^{13}C NMR spectra contained the signals corresponding to the sp^2 and sp^3 atom of C_{60} and the expected signals corresponding to the organic addends. The MALDI-TOF mass spectra provided a

direct evidence for the structures of **1**, **2** and **3**, showing a peak at $m/z = 1233.1$ $[\text{M}+2]^+$ for **1**, a peak at $m/z = 1439.8$ $[\text{M}-\text{H}]^+$ for **2**, and a peak at $m/z = 1825.49$ $[\text{M}-\text{Fc}]^+$ for **3**, respectively. Further confirmation of the hybrid $(\text{C}_{60})_n$ -TPA-(Fc)_n structures was obtained from UV-Vis spectra of **1**, **2** and **3**, which contain a dihydrofullerene absorption band at around 430 nm together with the expected ferrocene and TPA-bands at around 330–360 nm.

2.2. Electrochemistry

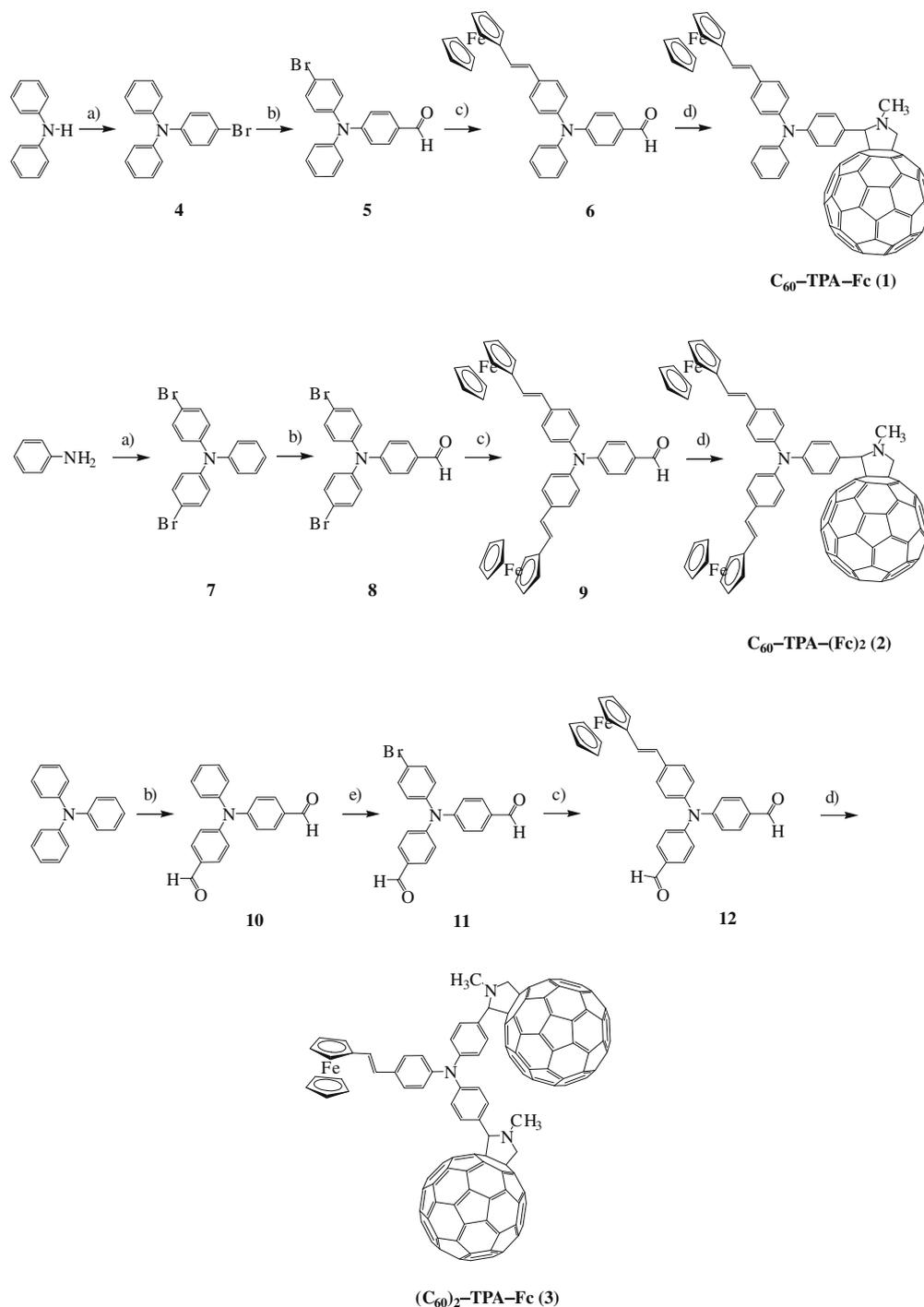
The electrochemical properties of C_{60} -TPA-(Fc)₂, $(\text{C}_{60})_2$ -TPA-Fc and C_{60} -TPA-Fc were probed by cyclic voltammetry in DCB solvent and *n*-Bu₄NClO₄ as a supporting electrolyte. As a general feature, these compounds gave rise to three reversible one-electron reduction waves in the cathodic observation window; they were attributed to three reduction potentials ($E_{\text{red}}^{\text{C}_{60}}$) of the C_{60} cage; the first $E_{\text{red}}^{\text{C}_{60}}$ value was -0.82 V vs. Fc/Fc^+ [21,36]. In the anodic region, single reversible oxidation potential of Fc ($E_{\text{ox}}^{\text{Fc}}$) was observed at -0.07 V; additional reversible oxidation was observed at $+0.80$ V for TPA ($E_{\text{ox}}^{\text{TPA}}$). The free energies (ΔG_{CR}) of the radical ion pairs were calculated from the Rhem–Weller equation [38–40]. For example, the ΔG_{CR} value of $\text{C}_{60}^{\cdot-}$ -TPA-Fc⁺ was evaluated to be -0.75 eV and the ΔG_{CR} value of $\text{C}_{60}^{\cdot-}$ -TPA⁺-Fc was -1.62 eV in DCB. From these ΔG_{CR} values and excited energies (E_{00}) of C_{60} ($=1.70$ eV), the free energy changes of the charge separation process (ΔG_{CS}) via the excited singlet state of C_{60} ($^1\text{C}_{60}^*$) were calculated to be -0.95 and -0.08 eV, respectively, in DCB. For other C_{60} -TPA-(Fc)₂ and $(\text{C}_{60})_2$ -TPA-Fc, almost the same values were evaluated. For TPA⁺- $\text{C}_{60}^{\cdot-}$, the ΔG_{CR} and ΔG_{CS} values were calculated to be -1.62 and -0.08 eV, respectively.

2.3. Steady-state absorption studies

The absorption spectra of C_{60} -TPA-Fc are shown in Fig. 2. The absorption spectrum of C_{60} -TPA-Fc exhibits a sharp absorption band at 430 nm and a weak one at 700 nm, which are attributed to the C_{60} moiety, whereas the weak band of the Fc unit may be hidden near the 400 nm band of the C_{60} moiety, and the TPA unit shows the absorption band near 330 nm. Thus, the remaining broad band in the whole visible region can also be attributed to the C_{60} moiety. Similar spectral features were observed for C_{60} -TPA-(Fc)₂ and $(\text{C}_{60})_2$ -TPA-Fc, in which the latter shows twice intense bands in the visible region.

2.4. Fluorescence studies

The fluorescence spectra of the reference C_{60} compounds show the emission peaks at 710 nm as a mirror image of the 700 nm absorption. As shown in Fig. 3, C_{60} -TPA-(Fc)₂, showed weak fluorescence at 710 nm in nonpolar toluene, whose fluorescence inten-



Scheme 1. Synthesis of compounds **1**, **2** and **3**. (a) 1-Bromo-4-iodobenzene, Pd₂dba₃, dppf, NaO^tBu, toluene, 100 °C, 15 h, 57.5% for **4**, 48.5% for **7**. (b) DMF, POCl₃, 1,2-dichloroethane, reflux, 24 h, 91.0% for **5**, 42.7% for **8**, 42.0% for **10**. (c) vinyl ferrocene, K₂CO₃, Bu₄NBr, Pd(OAc)₂, DMF, 95 °C, 24 h, 65.0% for **6**, 56.3% for **9**, 40.0% for **12**. (d) C₆₀, N-methylglycine, toluene, reflux, 48 h, 15.3% for **1**, 24 h, 17.7% for **2**, 48 h, 50.0% for **3**. (e) Br₂, dichloromethane, r.t., 3 h, 87.0%.

sity was decreased very much compared with the reference C₆₀. The origin of the C₆₀-fluorescence quenching is mainly attributed to the Fc moiety attached to the TPA moiety, since such quenching was not observed for C₆₀-TPA in toluene [21].

In polar PhCN, almost all the fluorescence intensity of C₆₀-TPA-(Fc)₂ was quenched. Since these observations are quite similar to C₆₀-TPA [21], the origin of the C₆₀-fluorescence quenching is mainly attributed to the attached TPA moiety to the C₆₀ moiety.

The fluorescence time profiles observed by applying the 410 nm pulsed laser light in the time range 0–1.2 ns are shown for C₆₀-

TPA-Fc in Fig. 4. The fluorescence time profile of the reference C₆₀ exhibited a single exponential decay with a lifetime (τ_f) of 1.4 ns, which matches well with the reported value [41–43].

The fluorescence lifetimes (τ_f) of the ¹C₆₀ moiety of C₆₀-TPA-Fc could be evaluated from curve-fitting of the fluorescence time profile with two exponential components, in which the main lifetimes are shorter than 100 ps as summarized in Table 1, whereas the minor long life times are about 1.3–1.4 ns. The τ_f values in polar solvents are shorter than those in toluene, suggesting that attachment of the TPA to the C₆₀ moiety introduces a new quenching

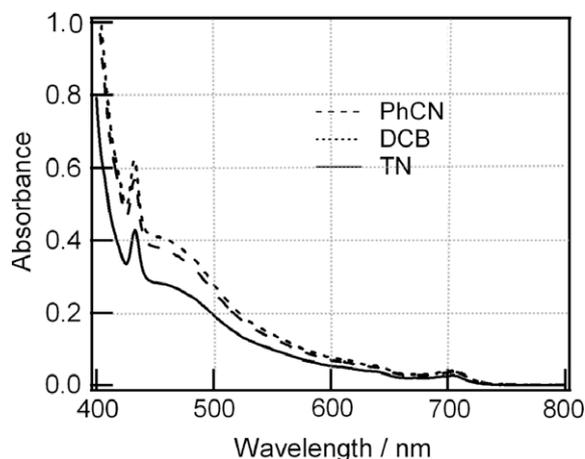


Fig. 2. Steady-state absorption spectra of C_{60} -TPA-Fc; PhCN (benzonitrile), DCB (*o*-dichlorobenzene), and TN (toluene).

pathway for the ${}^1C_{60}^*$ moiety. In addition, attachment of the Fc moiety to TPA influences indirectly the C_{60} -fluorescence quenching. From the solvent dependence of the τ_f values, we infer a charge separation (CS) quenching of the ${}^1C_{60}^*$ moiety. The CS process from the ${}^1C_{60}^*$ moiety to the attached electron-donors can be supported by the negative ΔG_{CS} values. In toluene, appreciable shortening of the τ_f values was observed, which is a strong contrast to the τ_f values of C_{60} -TPA, showing $\tau_f = 1.4$ ns in toluene. Thus, the observed short τ_f values for C_{60} -TPA-Fc are induced by the attachment of the Fc moiety to TPA, which implies that the Fc moiety makes the CS process possible, generating $C_{60}^{\cdot-}$ -TPA-Fc $^+$ even in nonpolar toluene. Similar tendencies were observed for $(C_{60})_2$ -TPA-Fc and C_{60} -TPA-(Fc) $_2$.

The rate constants (k_{CS}) and quantum yields (Φ_{CS}) for CS via the ${}^1C_{60}^*$ moieties were evaluated from the τ_f values as listed in Table 1. Both k_{CS} and Φ_{CS} values for C_{60} -TPA-Fc, $(C_{60})_2$ -TPA-Fc and C_{60} -TPA-(Fc) $_2$ were found to be higher than those for C_{60} -TPA in DCB as well as in toluene, indicating that the additional effect of the Fc group is present in less polar solvents. In highly polar solvents such as PhCN, however, the k_{CS} and Φ_{CS} values are almost the same as C_{60} -TPA, indicating that extremely efficient CS takes place even in C_{60} -TPA without Fc moieties. Bisferrocene tetrad C_{60} -TPA-(Fc) $_2$ shows the larger k_{CS} and higher Φ_{CS} than those of monoferrocene triad C_{60} -TPA-Fc in all solvents used, suggesting that the extra Fc

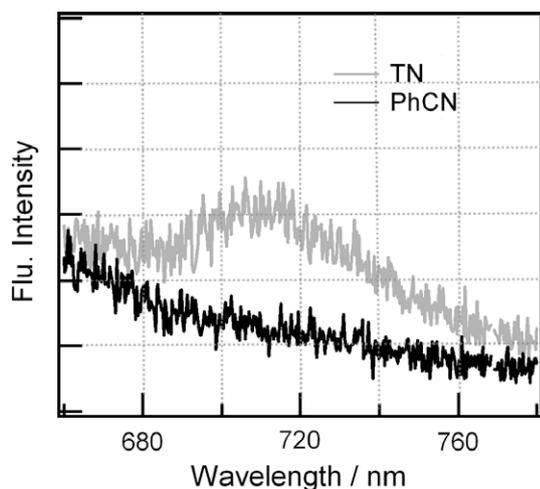


Fig. 3. Steady-state fluorescence spectra of C_{60} -TPA-(Fc) $_2$ in toluene (TN) and benzonitrile (PhCN); $\lambda_{ex} = 410$ nm.

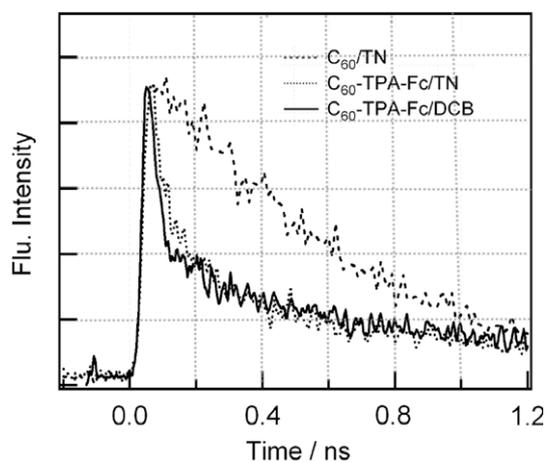


Fig. 4. Fluorescence decay profiles of C_{60} -TPA-Fc in toluene and DCB and C_{60} in toluene as a reference; $\lambda_{ex} = 410$ nm.

moiety accelerates the CS process between C_{60} and TPA as a dendrimer effect [22]. On the other hand, bisfullerene tetrad $(C_{60})_2$ -TPA-Fc shows almost the same k_{CS} and Φ_{CS} values compared to those of monofullerene triad C_{60} -TPA-Fc in the same solvents.

2.5. Nanosecond transient absorption spectra

The nanosecond transient absorption technique in the visible and near-IR regions was performed to confirm the existence of the CS state and to monitor the charge recombination (CR) processes. The transient absorption spectra of $(C_{60})_2$ -TPA-Fc in DCB are shown in Fig. 5, in which three spectra at different times after the laser pulse are shown. Immediately after the laser pulse (10 ns), a sharp peak with quick rise and decay component was observed at 1000 nm, indicating the generation of the short lived $C_{60}^{\cdot-}$ [44,45]. The immediate rise of the 1000-nm band after the laser light pulse supports the very quick CS process, corresponding to the fluorescence decay. From the decay of the 1000-nm band shown in inset of Fig. 5, the CR rate constant (k_{CR}) was evaluated by the first-order curve-fitting to be 6.3×10^7 s $^{-1}$, which corresponds to the lifetime of the radical ion pair (τ_{RIP}) such as $(C_{60})_2^{\cdot-}$ -TPA-Fc $^+$ to be 16 ns in DCB. Since the broad absorption near 700 nm hides the absorption of the counter part of $C_{60}^{\cdot-}$ in the radical ion pair, the absorption due to the Fc $^+$ moiety must be buried.

In toluene, similar transient absorption spectra were observed. The time profiles of the absorption peaks at 1000 and 700 nm consist of two components. The fast decay component at 1000 nm of the $C_{60}^{\cdot-}$ moiety gave the k_{CR} of 2.1×10^7 s $^{-1}$ corresponding to a lifetime for the radical ion pair (τ_{RIP}) of 48 ns in toluene. In PhCN, only weak absorption peak with slow decay was observed at 700 nm due to the ${}^3C_{60}^*$ moiety, but no extra peak due to the CS state was observed, suggesting that the CR process is fast in highly polar solvent. This trend is along the Marcus theory [46]; that is, the CR process belongs to the inverted region of the Marcus parabola due to larger ΔG_{CR} values than the small reorganization energy [47–49]. The τ_{RIP} values for $(C_{60})_2$ -TPA-Fc in toluene and DCB are longer than those of C_{60} -TPA-Fc and C_{60} -TPA-(Fc) $_2$. Compared with other monoferrocene- C_{60} radical ion pairs and multi-ferrocene- C_{60} radical ion pairs [50–52], the $\tau_{RIP} = 48$ ns for $(C_{60})_2$ -TPA-Fc in toluene may be longest.

2.6. Energy diagram

The energy level diagram and photoinduced processes of $(C_{60})_m$ -TPA-(Fc) $_n$ in DCB are shown in Fig. 6. After photoexcitation,

Table 1
Short lifetimes (τ_f) and fractions, rates (k_{CS}) and quantum-yields (Φ_{CS}) of the charge-separation process via ${}^1C_{60}^*$ and k_{CR} of the radical ion pair.

	Solvent	τ_f (ps) ^a	k_{CS} (s ⁻¹) ^b	Φ_{CS} ^b	k_{CR} (s ⁻¹)
C_{60} -TPA-Fc	TN	47 (70%)	2.1×10^{10}	0.97	1.3×10^8
	DCB	33 (85%)	3.2×10^{10}	0.98	– ^c
	PhCN	23 (68%)	4.5×10^{10}	0.98	– ^c
$(C_{60})_2$ -TPA-Fc	TN	98 (67%)	9.5×10^9	0.93	2.1×10^7 (9.6×10^5) ^d
	DCB	49 (65%)	2.0×10^{10}	0.97	6.3×10^7
	PhCN	36 (57%)	2.5×10^{10}	0.97	– ^c
C_{60} -TPA-(Fc) ₂	TN	48 (67%)	2.0×10^{10}	0.97	– ^c
	DCB	25 (25%)	3.9×10^{10}	0.98	– ^c
	PhCN	<10	$>1 \times 10^{11}$	>0.99	– ^c

^a In parentheses, fraction of the short lifetime component.

^b $k_{CS} = (1/\tau_f)_{\text{sample}} - (1/\tau_f)_{\text{ref}}$ and $\Phi_{CS} = [(1/\tau_f)_{\text{sample}} - (1/\tau_f)_{\text{ref}}]/(1/\tau_f)_{\text{sample}}$. The minor long lifetimes were evaluated in the range of 1.0–1.3 ns. For C_{60} -TPA, 1300 ps in toluene, 107 ps in DCB, and <50 ps in PhCN [21].

^c Too weak to detect or too fast.

^d This value may be affected by the triplet decay.

direct CS process takes place via ${}^1C_{60}^*$ to Fc over TPA (k_C), as supposed by the observed ${}^1C_{60}^*$ -fluorescence quenching [53,54]. In less polar solvents, the energy level of $(C_{60})_m^{\cdot-}$ -TPA-(Fc)_n^{·+} is between ${}^1(C_{60})_m^* \text{-TPA-(Fc)}_n$ and ${}^3(C_{60})_m^* \text{-TPA-(Fc)}_n$; thus, the CR process from $(C_{60})_m^{\cdot-}$ -TPA-(Fc)_n^{·+} to ${}^3(C_{60})_m^* \text{-TPA-(Fc)}_n$ is possible with k_{CR} , as supported by the observation of huge transient absorption at 700 nm (Fig. 5). Then, ${}^3(C_{60})_m^* \text{-TPA-(Fc)}_n$ goes back to the neu-

tral molecule, in addition to the triplet energy transfer to $(C_{60})_m \text{-TPA-(Fc)}_n^*$, because of the lower triplet energy level of Fc [55,56]. In polar solvents, since the energy level of $(C_{60})_m^{\cdot-}$ -TPA-(Fc)_n^{·+} is lower than ${}^3(C_{60})_m^* \text{-TPA-(Fc)}_n$, the CR process to ${}^3Fc^*$ (k_{CR}) and to the ground state may be predominant.

3. Conclusion

Photoinduced electron transfer processes of two newly synthesized tetrads with a TPA moiety as a central building block and fullerene (C_{60}) as an electron-acceptor and ferrocene (Fc) as an electron-donor have been studied by the time-resolved spectroscopic techniques. In this paper, we succeeded in the syntheses of bis-Fc tetrad C_{60} -TPA-(Fc)₂, and bisfullerene tetrad $(C_{60})_2$ -TPA-Fc. Even in mono-Fc triad, efficient CS takes place via ${}^1C_{60}^*$ better than the simple dyad C_{60} -TPA. Compared with conventional mono-Fc triad, new bisferrocene tetrad and new bisfullerene tetrad showed efficient CS processes, supporting that the bisferrocene donor effect, a kind of dendrimer effect, is working in the light harvesting photoinduced processes. It was found that the ratio of electron-donor to C_{60} affects the CS efficiency via the excited singlet state of C_{60} .

4. Experimental

4.1. Materials and instruments

Reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed using dry glassware under nitrogen atmosphere. Analytical TLC was carried out on Merck 60 F254 silica gel plate and column chromatography was performed on Merck 60 silica gel (230–400 mesh). Melting points were determined on an Electrothermal IA 9000 series melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with TMS peak as reference. IR spectra were recorded on a Nicolet 550 FT infrared spectrometer and measured as KBr pellets. UV-Vis spectra were recorded on a Jasco V-550 spectrometer. MALDI-TOF MS spectra were recorded with an Applied Biosystems Voyager-DE-STR. Elemental analyses were performed with a Perkin-Elmer 2400 Analyzer.

4.2. Synthesis

4.2.1. Synthesis of 1-bromo-4-diphenylaminobenzene (4)

To a solution of 1-bromo-4-iodobenzene (3.0 g, 10.0 mmol) in toluene (50 ml) were added tris(dibenzylideneacetone)dipalla-

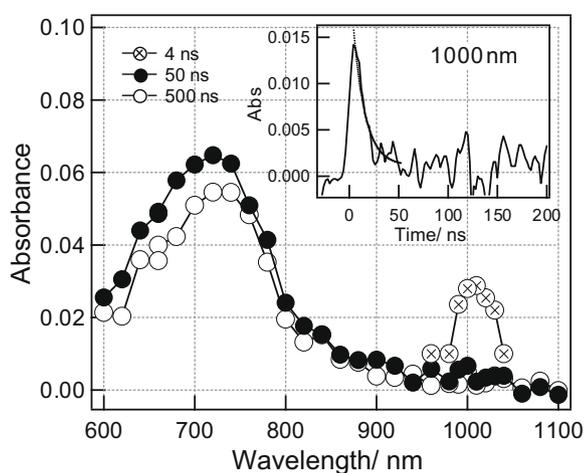


Fig. 5. Transient absorption spectra of $(C_{60})_2$ -TPA-Fc tetrad in Ar-saturated DCB; $\lambda_{\text{ex}} = 532$ nm. Inset: Time profile at 1000 nm.

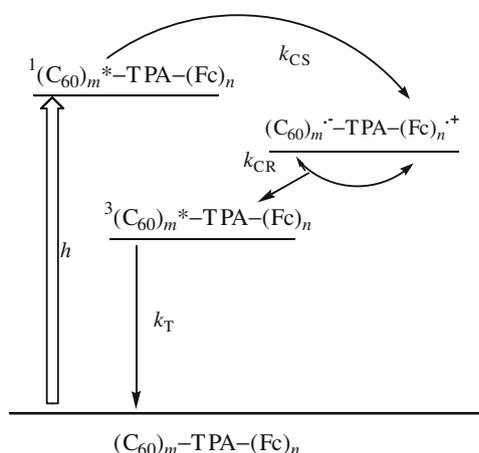


Fig. 6. Energy diagram for $(C_{60})_m$ -TPA-(Fc)_n in DCB.

dium(0) (Pd_2dba_3 , 0.15 g, 0.16 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 0.12 g, 0.21 mmol) and stirred for 15 min. Diphenylamine (1.79 g, 15.01 mmol), NaO^tBu (1.15 g, 11.97 mmol) were added to the reaction mixture and warmed to 100 °C and then stirred for 15 h. After cooling, the solution was filtered and the solvent was removed under reduced pressure. The product was column chromatographed on silica gel with dichloromethane/hexane (1:10) to give compound **4** (2.79 g, 57.5%) in a white solid. M.p. 113–115 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.30 (d, 3H), 7.20 (d, 4H), 7.10 (d, 3H), 6.98 (t, 2H), 6.92 (d, 2H). Anal. Calc. for $\text{C}_{18}\text{H}_{14}\text{NBr}$: C, 66.68; H, 4.35; N, 4.32. Found: C, 66.51; H, 4.66; N, 4.10%.

4.2.2. Synthesis of 4-[N-(4-bromophenyl)-N-phenylamino]benzaldehyde (**5**)

To a solution of compound **4** (1.0 g, 3.08 mmol) in 1,2-dichloroethane (30 ml) were added DMF (0.81 ml, 10.80 mmol), POCl_3 (1.80 ml, 10.80 mmol). The mixture was refluxed for 24 h and cooled to r.t. The solution was poured into water (100 ml) and stirred for 30 min, and then the product was extracted with dichloromethane (3 × 100 ml). The organic layer was dried over MgSO_4 , the solvent was evaporated. The residue was purified by column chromatography over silica gel with dichloromethane/hexane (3:1) to give compound **5** (0.99 g, 91.0%) in a yellow solid. M.p. 103–105 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 9.78 (s, 1H), 7.66 (d, 2H), 7.40 (d, 2H), 7.31 (d, 2H), 7.13 (d, 2H), 7.00 (m, 5H). Anal. Calc. for $\text{C}_{19}\text{H}_{14}\text{NOBr}$: C, 64.79; H, 4.01; N, 3.98. Found: C, 64.66; H, 4.12; N, 3.82%.

4.2.3. Synthesis of 4-[N-(4-(2-ferrocenylvinyl)phenyl)-N-phenylamino]benzaldehyde (**6**)

To a solution of compound **5** (0.71 g, 2.01 mmol) in DMF (50 ml) were added vinyl ferrocene (0.51 g, 2.40 mmol), K_2CO_3 (3.47 g, 25.01 mmol), Bu_4NBr (3.30 g, 0.01 mol), $\text{Pd}(\text{OAc})_2$ (50 mg, 0.25 mmol) and the mixture was warmed to 95 °C, and then stirred for 24 h. The reaction solution was cooled to r.t. and filtered. The solvent was removed under reduced pressure and the crude product was washed with water and dried. The product was purified by column chromatography over silica gel with dichloromethane/hexane (2:1) to give compound **6** (0.63 g, 65.0%) in an orange color solid. M.p. 79–82 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 9.80 (s, 1H), 7.65 (d, 2H), 7.33 (m, 5H), 7.18 (d, 2H), 7.09 (d, 2H), 7.02 (d, 2H), 6.81 (d, 1H), 6.62 (d, 1H), 4.43 (s, 2H), 4.29 (s, 2H), 4.14 (s, 5H); IR (KBr): ν = 3411, 3083, 2805, 2728, 1689, 1585, 1506, 1330 cm^{-1} . Anal. Calc. for $\text{C}_{31}\text{H}_{25}\text{NOFe}$: C, 77.03; H, 5.21; N, 2.90. Found: C, 76.90; H, 5.41; N, 2.84%.

4.2.4. Synthesis of N-[4-(2-ferrocenylvinyl)phenyl]-N-[4-(1-methyl-3,4-fullero-2,3,4,5-tetrahydropyrrol-2-yl)phenyl]-N-phenylamine (**1**)

Compound **6** (0.12 g, 0.23 mmol) and fullerene (0.20 g, 0.28 mmol), sarcosine (0.13 g, 1.40 mmol) were added to toluene (120 ml) and refluxed for 48 h. The reaction mixture was cooled to r.t., and the solvent was removed under reduced pressure. The product was purified by column chromatography over silica gel with toluene/hexane (2:1) to give compound **1** (43 mg, 15.3%) in a black solid. M.p. >400 °C (dec.); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.20–6.90 (m, 13H), 6.62 (d, 1H), 6.54 (d, 1H), 4.89 (d, 1H), 4.85 (d, 1H), 4.82 (s, 1H), 4.34 (s, 2H), 4.17 (s, 2H), 4.04 (s, 5H), 2.78 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3): δ = 156.43, 154.14, 153.79, 153.55, 147.68, 147.45, 146.99, 146.64, 146.52, 146.41, 146.34, 146.30, 146.24, 146.14, 146.08, 145.92, 145.67, 145.59, 145.47, 145.43, 145.39, 145.33, 145.28, 144.85, 144.78, 144.53, 143.31, 143.13, 142.81, 142.39, 142.29, 142.23, 142.19, 141.95, 141.80, 141.76, 140.31, 140.26, 140.05, 139.39, 137.99, 136.86, 136.70, 136.05, 135.93, 132.85, 131.45, 129.18, 128.38, 126.81, 125.73, 125.66, 125.46, 124.41, 83.98, 83.35, 77.78, 70.31, 69.95, 69.50, 69.27,

69.23, 67.05, 40.45; IR (KBr): ν = 2917, 2848, 2777, 1631, 1591, 1506, 1315, 1178, 811, 526 cm^{-1} ; UV-Vis (toluene): λ_{max} = 331, 431 nm; MS (MALDI-TOF): for $\text{C}_{93}\text{H}_{30}\text{N}_2\text{Fe}$ ($M = 1231.09$) m/z : 1233.10[$M+2$] $^+$. Anal. Calc.: C, 90.73; H, 2.46; N, 2.28. Found: C, 90.70; H, 2.35; N, 2.25%.

4.2.5. Synthesis of N,N-bis(4-bromophenyl)aminobenzene (**7**)

To a solution of 1-bromo-4-iodobenzene (6.60 g, 23.60 mmol) in toluene (100 ml) were added Pd_2dba_3 (0.09 g, 0.10 mmol) and stirred for 15 min. Aniline (0.55 g, 5.91 mmol), NaO^tBu (1.36 g, 14.10 mmol) were added to the reaction mixture and warmed to 100 °C and then stirred for 15 h. After cooling, the solution was filtered and the solvent was removed under reduced pressure. The product was column chromatographed on silica gel with dichloromethane/hexane (1:10) to give compound **7** (4.61 g, 48.5%) in a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.31 (d, 3H), 7.24 (t, 3H), 7.04 (d, 3H), 6.91 (d, 4H). Anal. Calc. for $\text{C}_{18}\text{H}_{13}\text{NBr}_2$: C, 53.63; H, 3.25; N, 3.47. Found: C, 53.60; H, 3.31; N, 3.44%.

4.2.6. Synthesis of N,N-bis(4-bromophenyl)aminobenzaldehyde (**8**)

To a solution of compound **7** (0.35 g, 0.87 mmol) in 1,2-dichloroethane (30 ml) were added DMF (0.20 ml, 2.61 mmol), POCl_3 (0.24 ml, 2.61 mmol). The mixture was refluxed for 24 h and cooled to r.t. The solution was poured into water (100 ml) and stirred for 30 min, and then the product was extracted with dichloromethane (3 × 100 ml). The organic layer was dried over MgSO_4 , the solvent was evaporated. The residue was purified by column chromatography over silica gel with dichloromethane/hexane (3:1) to give compound **8** (0.16 g, 42.7%) in a yellow solid. M.p. 158–161 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 9.91 (s, 1H), 7.69 (d, 2H), 7.30 (d, 4H), 6.98 (d, 6H); IR (KBr): ν = 2831, 2744, 1683, 1600, 1486 cm^{-1} . Anal. Calc. for $\text{C}_{19}\text{H}_{13}\text{NOBr}_2$: C, 52.93; H, 3.04; N, 3.25. Found: C, 52.85; H, 3.11; N, 3.12%.

4.2.7. Synthesis of N,N-bis[4-(2-ferrocenylvinyl)phenyl]aminobenzaldehyde (**9**)

To a solution of compound **8** (0.15 g, 0.35 mmol) in DMF (80 ml) were added vinyl ferrocene (0.17 g, 0.81 mmol), K_2CO_3 (1.20 g, 8.68 mmol), Bu_4NBr (1.11 g, 3.47 mol), $\text{Pd}(\text{OAc})_2$ (18 mg, 0.08 mmol) and the mixture was warmed to 95 °C, and then stirred for 24 h. The reaction solution was cooled to r.t. and filtered. The solvent was removed under reduced pressure and the crude product was washed with water and dried. The product was purified by column chromatography over silica gel with dichloromethane/hexane (2:1) to give compound **9** (0.14 g, 56.3%) in an orange color solid. M.p. 103–106 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 9.91 (s, 1H), 7.68 (d, 2H), 7.38 (d, 4H), 7.20–7.03 (m, 6H), 6.82 (d, 2H), 6.64 (d, 2H), 4.45 (s, 4H), 4.29 (s, 4H), 4.14 (s, 10H); IR (KBr): ν = 3089, 3033, 2915, 2724, 1689, 1589, 1506, 1324 cm^{-1} . Anal. Calc. for $\text{C}_{43}\text{H}_{35}\text{NOFe}_2$: C, 74.48; H, 5.09; N, 2.02. Found: C, 74.29; H, 5.31; N, 1.94%.

4.2.8. Synthesis of N,N-bis[4-(2-ferrocenylvinyl)phenyl]-N-[4-(1-methyl-3,4-fullero-2,3,4,5-tetrahydropyrrol-2-yl)phenyl]amine (**2**)

Compound **8** (0.09 g, 0.14 mmol) and fullerene (0.15 g, 0.20 mmol), sarcosine (0.07 g, 0.82 mmol) were added to toluene (120 ml) and refluxed for 24 h. The reaction mixture was cooled to r.t., and the solvent was removed under reduced pressure. The product was purified by column chromatography over silica gel with toluene/hexane (2:1) to give compound **2** (36 mg, 17.7%) in a black solid. M.p. >400 °C (dec.); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.36 (d, 2H), 7.32–7.11 (m, 6H), 6.99 (d, 4H), 6.72 (d, 2H), 6.60 (d, 2H), 5.01 (d, 1H), 4.92 (s, 1H), 4.90 (d, 1H), 4.43 (s, 4H), 4.29 (s, 4H), 4.16 (s, 10H), 2.89 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3): δ = 156.43, 154.14, 153.79, 153.55, 147.68, 147.45, 146.99,

146.64, 146.52, 146.41, 146.34, 146.30, 146.24, 146.14, 146.08, 145.92, 145.67, 145.59, 145.47, 145.43, 145.39, 145.33, 145.28, 144.85, 144.78, 144.53, 143.31, 143.13, 142.81, 142.39, 142.29, 142.23, 142.19, 141.95, 141.80, 141.76, 140.31, 140.26, 140.05, 139.39, 137.99, 136.86, 136.70, 136.05, 135.93, 132.85, 131.45, 129.18, 128.38, 126.81, 125.73, 125.66, 125.46, 124.41, 83.98, 83.35, 77.78, 70.31, 69.96, 69.50, 69.28, 69.22, 67.03, 40.46; IR (KBr): $\nu = 2944, 2915, 2775, 1631, 1596, 1504, 1178, 1105, 811, 526 \text{ cm}^{-1}$; UV-Vis (toluene): $\lambda_{\text{max}} = 366, 429 \text{ nm}$; MS (MALDI-TOF): for $\text{C}_{105}\text{H}_{40}\text{N}_2\text{Fe}_2$ ($M = 1441.14$) m/z : 1439.80 $[M+1]^+$. Anal. Calc.: C, 87.51; H, 2.80; N, 1.94. Found: C, 87.44; H, 2.92; N, 1.88%.

4.2.9. Synthesis of *N,N*-bis(4-formylphenyl)aminobenzene (**10**)

To a solution of triphenylamine (10.0 g, 40.0 mmol) in DMF (100 ml) was slowly added POCl_3 (39.2 ml, 420.0 mmol) at 0 °C. The mixture was warmed to 100 °C and stirred. After 6 h, the mixture was cooled to r.t. and then carefully poured into saturated aqueous Na_2CO_3 solution (300 ml). The mixture was stirred for 30 min, and then the product was extracted with ethyl acetate (3 × 200 ml). The organic layer was dried over MgSO_4 , the solvent was evaporated. The residue was purified by column chromatography over silica gel with ethyl acetate/hexane (1:5) to give compound **10** (5.06 g, 42.0%) in a yellow solid. M.p. 142–145 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 9.90$ (s, 2H), 7.78 (d, 4H), 7.39 (m, 2H), 7.31–7.16 (m, 7H); Anal. Calc. for $\text{C}_{20}\text{H}_{15}\text{NO}_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.80; H, 5.11; N, 4.42%.

4.2.10. Synthesis of *N*-(4-bromophenyl)-*N,N*-bis(4-formylphenyl)amine (**11**)

To a solution of compound **10** (2.80 g, 9.30 mmol) in dichloromethane (100 ml) was slowly added bromine (1.70 g, 11.20 mmol) and the mixture was stirred for 3 h. The solution was washed with water (150 ml), aqueous Na_2CO_3 (2 × 100 ml) and the organic layer was dried over MgSO_4 . The solvent was evaporated to gain compound **11** (3.07 g, 87.0%) in a green solid. M.p. 217 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 9.90$ (s, 2H), 7.80 (d, 4H), 7.51 (d, 2H), 7.18 (d, 4H), 7.06 (d, 2H); IR (KBr): $\nu = 2833, 2740, 1683, 1602, 1486 \text{ cm}^{-1}$. Anal. Calc. for $\text{C}_{20}\text{H}_{14}\text{NO}_2\text{Br}$: C, 63.18; H, 3.71; N, 3.68. Found: C, 63.05; H, 3.88; N, 3.51%.

4.2.11. Synthesis of *N*-{4-(2-ferrocenylvinyl)phenyl}-*N,N*-bis(4-formylphenyl)amine (**12**)

To a solution of compound **11** (3.0 g, 7.80 mmol) in DMF (100 ml) were added vinyl ferrocene (2.0 g, 9.30 mmol), K_2CO_3 (3.50 g, 39.0 mmol), Bu_4NBr (12.0 g, 39.0 mol), $\text{Pd}(\text{OAc})_2$ (0.2 g, 0.90 mmol) and the mixture was warmed to 95 °C, and then stirred for 24 h. The reaction solution was cooled to r.t. and filtered. The solvent was removed under reduced pressure and the crude product was washed with water and dried. The product was purified by column chromatography over silica gel with ethyl acetate/hexane (1:9) to give compound **12** (1.6 g, 40.0%) in a orange color solid. M.p. 133 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 9.91$ (s, 2H), 7.80 (d, 4H), 7.44 (d, 2H), 7.22 (d, 4H), 7.12 (d, 2H), 6.86 (d, 1H), 6.70 (d, 1H), 4.47 (s, 2H), 4.38 (s, 2H), 4.20 (s, 5H); IR (KBr): $\nu = 3088, 3031, 2915, 2724, 1689, 1589, 1508, 1324 \text{ cm}^{-1}$. Anal. Calc. for $\text{C}_{32}\text{H}_{25}\text{NO}_2\text{Fe}$: C, 75.17; H, 4.93; N, 2.74. Found: C, 75.09; H, 5.11; N, 2.54%.

4.2.12. Synthesis of *N*-{4-(2-ferrocenylvinyl)phenyl}-*N,N*-bis[4-(1-methyl-3,4-fullero-2,3,4,5-tetrahydropyrrol-2-yl)phenyl]amine (**3**)

Compound **12** (0.30 g, 0.58 mmol) and fullerene (1.0 g, 1.40 mmol), sarcosine (0.13 g, 6.90 mmol) were added to toluene (30 ml) and refluxed for 48 h. The reaction mixture was cooled to r.t., and the solvent was removed under reduced pressure. The product was purified by column chromatography over silica gel with dichloromethane to give compound **3** (0.58 g, 50.0%) in a

black solid. M.p. >400 °C (dec.); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.58$ (br, 4H), 7.32 (d, 4H), 7.04 (d, 2H), 7.02 (d, 2H), 6.68 (d, 2H), 4.80 (d, 2H), 4.60 (s, 2H), 4.56 (d, 2H), 4.43 (s, 2H), 4.28 (s, 2H), 4.16 (s, 5H), 2.72 (s, 6H); ^{13}C NMR (CDCl_3): $\delta = 148.58, 147.84, 147.49, 147.01, 146.27, 146.09, 145.75, 145.55, 145.12, 144.73, 144.41, 143.05, 142.59, 142.08, 141.58, 131.99, 131.27, 130.82, 129.85, 129.37, 128.75, 127.61, 126.94, 126.71, 126.25, 126.02, 124.95, 124.42, 124.17, 123.48, 121.40, 115.11, 83.98, 83.35, 69.83, 69.58, 69.15, 68.59, 68.11, 66.81, 66.45, 40.01, 38.69$; IR (KBr): $\nu = 2944, 2921, 2775, 1737, 1693, 1590, 1504, 1161, 1105, 818, 526 \text{ cm}^{-1}$; UV-Vis (toluene): $\lambda_{\text{max}} = 328, 414 \text{ nm}$; MS (MALDI-TOF): for $\text{C}_{156}\text{H}_{35}\text{N}_3\text{Fe}$ ($M = 2006.81$) m/z : 1825.49 ($M-\text{Fc}$) $^+$. Anal. Calc.: C, 93.37; H, 1.76; N, 0.70. Found: C, 93.31; H, 1.82; N, 0.68%.

4.3. Electrochemical measurements

Reduction potentials E_{red} and oxidation potentials E_{ox} were measured by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) with a potentiostat BAS CV50W in a conventional three-electrode cell equipped with Pt-working and counter-electrodes with an Ag/AgNO₃ reference electrode at scan rate of 100 mV/s. The E_{red} and E_{ox} were expressed vs. Fc/Fc $^+$ used as an internal reference. In each case, a solution containing 0.2 mM of a sample with 0.05 M of *n*-Bu₄NClO₄ (Fluka purest quality) was deaerated with argon bubbling before measurements.

4.4. 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 photomultiplier tube having high sensitivity in the 700–800 nm region.

4.5. Time-resolved fluorescence measurements

The time-resolved fluorescence spectra were measured by single photon counting method using a streak-scope (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, fwhm = 1.5 ps) as an excitation source. Lifetimes were evaluated with software provided with the equipment.

4.6. Nanosecond transient absorption measurements

Nanosecond transient absorption measurements were carried out using the SHG (532 nm) of an Nd:YAG laser (Spectra Physics, Quanta-Ray GCR-130, fwhm = 6 ns) as excitation source. For the transient absorption spectra in the near IR region (600–1600 nm), the monitoring light from a pulsed Xe-lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834).

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