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Photophysical Properties of the Newly Synthesized Triad Based on [70]Fullerene Studies with Laser Flash Photolysis

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N,N-Dimethylaniline-pyrazolinoC₇₀-ferrocene has been prepared with the 1,3-dipolar cycloaddition reaction of a nitrile imine with C₇₀. Although three regioisomers regarding the position of the pyrazolino group on the C₇₀ were identified in the reaction products, molecular orbital calculations indicate that the stabilities and electronic properties of the three isomers are almost the same, which was confirmed by the sharp redox peaks. The photophysical properties of the triads have been investigated by measuring the time-resolved emission and transient absorption spectra showing that charge separation takes place efficiently via the photoexcited singlet state of the C₇₀ moiety with accepting an electron from the donor moieties. It was found that the pyrazolino ring mediates a charge separation between the donor moieties and the photoexcited C₇₀ moiety.

Introduction

The unique structures and reactivities of fullerenes, C₆₀ and C₇₀, have attracted considerable attention in a variety of research areas.¹ Although the chemistry of C₆₀ has been extensively studied,² the derivatization and study of C₇₀ is still fragmentary³ due to its low abundance and high cost. From the limited data available for C₇₀, some common patterns of reactivity can be identified. The lower symmetry of C₇₀ (*D*_{5h} symmetry) gives rise to a larger number of isomers than C₆₀: whereas C₆₀ contains a single type of [6,6] bond, C₇₀ contains four different [6,6] bonds. In a way similar to C₆₀, the cycloaddition reactions with C₇₀ take place exclusively on [6,6] bonds, and the 1–2 and 5–6 bonds⁴ are the most reactive, in this order.⁵ This fact is supported by theoretical calculations, which show that the product in the 1–2 position is the most stable, followed by the 5–6 isomer.⁶ There are several reports indicating that C₆₀ and C₇₀ differ in their rates of reactivity, and hydroboration,⁷ addition of hydroxide,⁸ or 1,3-dipolar cycloaddition with azomethine ylides⁹ or nitrile oxides¹⁰ proceed more slowly with C₇₀ than with C₆₀.

Although C₆₀ and C₇₀ have similar photophysical and electrochemical¹¹ properties, it was reported that the LUMO of C₇₀ is more stabilized than that of C₆₀ as a consequence of an increase in the molecular size.¹² Consequently, it would be expected that the HOMO_(donor)–LUMO_(fullerene) gap of C₇₀ systems would be lower as compared to analogous C₆₀ compounds.¹³ The photoinduced events of fullerene (C₆₀)-electron donor systems have been the subject of extensive study in the past few years.¹⁴ In contrast, only intermolecular

photoinduced electron transfer between C₇₀ and electron donors have been studied; this was reported by Ito and co-workers.¹⁵ Furthermore, only a few examples have been reported for the intramolecular events in the excited state in donor–C₇₀ dyads.¹⁶ Recently, we reported the photoinduced events of pyrazolino-[60]fullerene covalently linked to ferrocene (Fc) and *N,N*-dimethylaniline (DMA) groups.¹⁷ Because the absorption of C₇₀-based systems in the visible region is markedly stronger than that of C₆₀, we decided to extend our studies to synthesize a new C₇₀-based triad with DMA and Fc as electron donors and a pyrazolino (Pz) ring as donor and bridge by means of the newly described 1,3-dipolar cycloaddition to C₇₀. Steady-state and time-resolved emission as well as nanosecond transient absorption spectral studies were performed to reveal the photoinduced processes and decay of the charge-separated states following initial excitation.

Results and Discussion

Synthesis. The synthesis of the *N,N*-dimethylaniline-pyrazolino C₇₀-ferrocene triad (DMA-PzC₇₀-Fc) **4** was carried out in three steps from previously reported hydrazone **1**¹⁸ and C₇₀ according to Scheme 1. In the first step, the novel 2-pyrazolino-[70]fullerene (PzC₇₀) **2** was prepared by 1,3-dipolar cycloaddition of the in-situ-generated nitrile imine to C₇₀. Although cycloaddition of nitrile imines to C₆₀ is well documented,¹⁹ their reactivity toward C₇₀ remained unexplored.

Monofunctionalization of C₇₀ preferentially affords C(1)–C(2) adducts,² with the (C5)–C(6) adduct being the second most favored. Consequently, three isomers are expected (Figure 1): isomers **2a** and **2b**, by cycloaddition to C(1)–C(2), and **2c**, resulting from reaction at the C(5)–C(6) bond.

Finally, cycloadduct **5**, which was used as a model in electrochemical and photophysical studies (vide infra), was obtained following the procedure described in Scheme 2. (For more details on the synthetic procedures and NMR characterization see the Supporting Information.)

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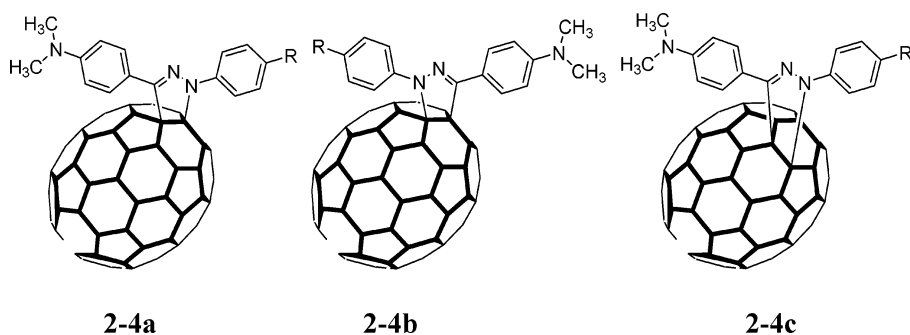


Figure 1. Isomers **2-4a** (C(1)–C(2)), **2-4b**, (C(2)–C(1)), and **2-4c**, (C(5)–C(6)) for **2** (R = NO₂), **3** (R = NH₂), and **4** (R = NH–CO–Fc).

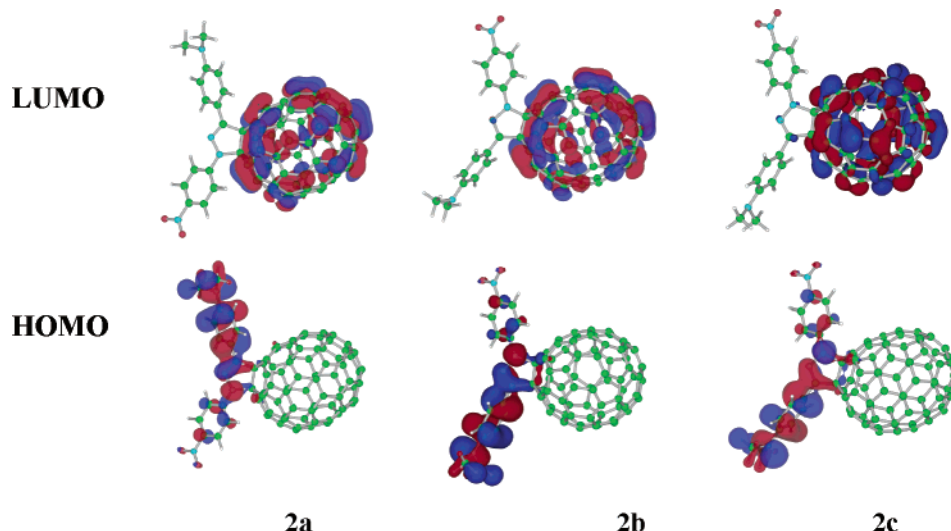
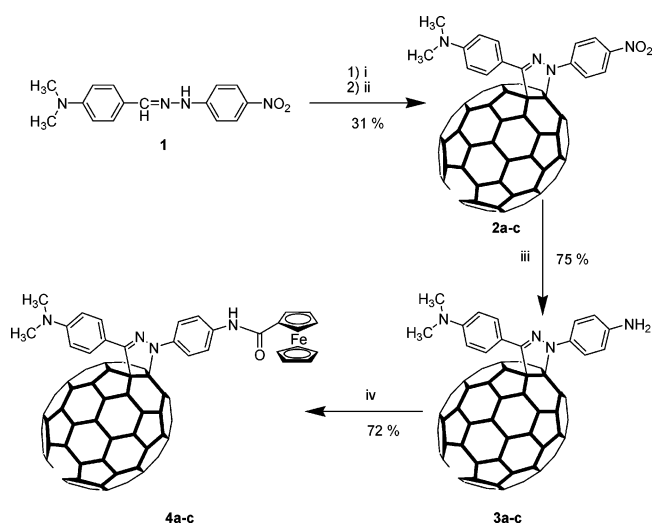


Figure 2. Fully optimized structures of isomers **2a** (C(1)–C(2)), **2b** (C(2)–C(1)), and **2c** (C(5)–C(6)).

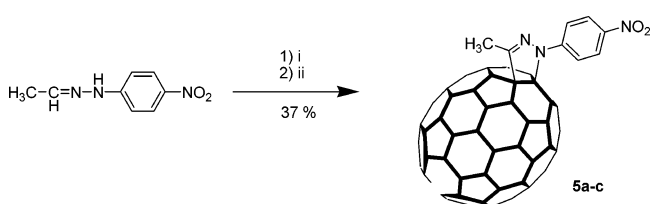
SCHEME 1^a



^a (i) NCS, pyridine, CHCl₃, 20 min, r.t.; (ii) C₇₀, toluene, Et₃N, 3 h, r.t.; (iii) tin powder, HCl, CHCl₃, 3 h, reflux; (iv) ferrocenyl chloride, pyridine, CH₂Cl₂, 3 h, r.t. (only a representative major isomer is shown); isomers a–c refer to Figure 1.

The HOMO and LUMO of **2a–c** were calculated by the Gaussian DTF method (B3LYP/6-31G* level) after optimizing the geometries with PM3, as shown in Figure 2. The three isomers have almost the same HOMO and LUMO energies with HOMO–LUMO gaps in the 2.34–2.42 eV range. The electron density of the LUMO is localized in the C₇₀ sphere, whereas the electron density of the HOMO is delocalized among the DMA and Pz groups. These molecular orbital calculations

SCHEME 2^a



^a (i) NBS, CHCl₃, 20 min, r.t.; (ii) C₇₀, toluene, Et₃N, 7 min, r.t.; isomers a–c refer to Figure 1.

suggest that in the charge-separated state, the electron localizes on the C₇₀ sphere, and the hole (radical cation) is outside the C₇₀ entity. It is notable that the radical cation is delocalized along the DMA and Pz groups, which act as good electron donors.

Electrochemistry. The electrochemical behavior of compounds **2–5** and C₇₀ in *o*-dichlorobenzene (DCB)/acetonitrile (AN) (4:1) was studied by cyclic voltammetry (CV) techniques and by Osteryoung square wave voltammetry (OSWV) at room temperature using tetra(*n*-butyl)ammonium perchlorate, (*n*-C₄H₉)₄NClO₄, as a supporting electrolyte. The CV of **4** is shown in Figure 3, along with the OSWV in the negative potential region. CV shows four sharp reversible peaks in the negative potentials corresponding to the four one-electron reductions of the C₇₀ entity, whereas two sharp reversible peaks in the positive potential correspond to the oxidation of the Fc and DMA entities. These observations provide further evidence of the similarity of the electronic properties of the three isomers. The results are summarized in Table 1.

CV showed that all compounds are electrochemically active in both anodic and cathodic sweep directions between +1.5 and

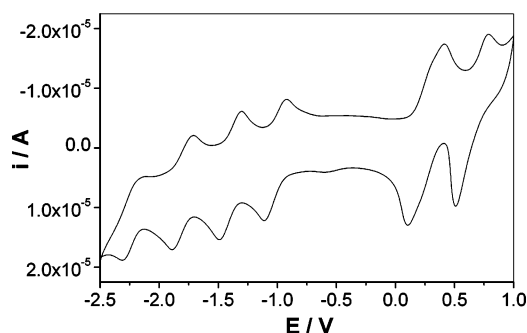


Figure 3. CV of compound **4** in DCB/AN (4:1) solution at room temperature.

TABLE 1: Electrochemical Data (V vs Ag/AgNO₃) for the Redox Processes of Compounds 2–5 Measured by OSWV^a

	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4	E_{red}^5	E_{red}^6	E_{ox}^1	E_{ox}^2
C ₇₀	-0.97	-1.35		-1.78	-2.17			
2	-0.96	-1.35	-1.71 ^b	-1.84	-2.13	-2.19 ^b	0.40 ^c	
3	-1.02	-1.40		-1.80	-2.20		0.11 ^c	0.32 ^{b,c}
4	-1.00	-1.38		-1.78	-2.18		0.26 ^c	0.64 ^c
5	-0.96	-1.35	-1.71 ^b	-1.89	-2.15	-2.31 ^b		

^a Solvent: DCB/AN (4:1) solution (0.1 M (*n*-C₄H₉)₄NClO₄). ^b Irreversible. ^c Measured by CV.

−2.5 V. As a general feature on the reduction side, compounds **2**–**5** gave rise to four quasireversible, one-electron reduction waves (E_{red}^1 , E_{red}^2 , E_{red}^3 , E_{red}^4 , E_{red}^5) attributed to the C₇₀ core.²¹ Compounds **2** and **5** presented two additional nonreversible CV peaks (E_{red}^6 , E_{red}^7), corresponding to the reduction of the *p*-nitrophenyl moiety, which is consistent with related systems. In a way similar to other 2-PzC₆₀ derivatives,²² the first reduction potential (E_{red}^1) is analogous to that of the parent [70]fullerene due to the −I inductive effect of the Pz ring. It is interesting to note that although the different derivatives are formed by a mixture of isomers, as indicated by HPLC and ¹H NMR spectroscopy (see Figures S1–S7), sharp peaks are found in CV and OSWV curves, suggesting that the different regioisomers are not significantly different in terms of electrochemical behavior. This is not surprising, since significant differences in the reduction potentials for regioisomers of other C₇₀ derivatives were not reported in a previous paper on this subject.⁹

On the oxidation side, all compounds except **5** were active. Compound **2** showed a quasireversible wave attributed to the DMA moiety at +0.40 V. In the case of **3**, this potential is cathodically shifted relative to **2** (up to +0.32 V) as a consequence of the presence of the new amino group, suggesting communication between the substituents on both sides of the Pz ring. A nonreversible oxidation wave at +0.11 V, corresponding to the aniline group, was also observed.¹⁶ Finally, in **4**, a broad oxidation wave was observed at +0.26 V; the asymmetry and intensity of this oxidation wave suggest that both the Fc and DMA groups are responsible for this wave. A second oxidation wave at +0.64 V was observed and is assigned to the oxidation of the amido group.

From the first E_{ox} and E_{red} values, the free-energy changes of the charge-separation (− ΔG_{CS}) and charge-recombination (− ΔG_{CR}) processes of Fc^{•+}~PzC₇₀^{•−}, Aniline^{•+}~PzC₇₀^{•−}, and DMA^{•+}~PzC₇₀^{•−} were calculated from the Rehm–Weller equations.²³ From the ΔG_{CS} values listed in Table 2, the charge-separation processes via the excited singlet state of C₇₀ (¹C₇₀^{*}) for **2** (DMA^{•+}~PzC₇₀^{•−}), **3** (aniline^{•+}~PzC₇₀^{•−}) and **4** (DMA^{•+}~PzC₇₀^{•−} and Fc^{•+}~PzC₇₀^{•−}) are exothermic. The charge-separation process via the excited triplet state of C₇₀ (³C₇₀^{*}) is

TABLE 2: Free-Energy Changes of the Charge-Separation Process (ΔG_{CS}) and Charge-Recombination Process (ΔG_{CR}) in DCB/AN (4:1)

compound	solvent	ΔG_{CR}^a eV	ΔG_{CS} eV via ¹ C ₇₀ [*]	ΔG_{CS} eV via ³ C ₇₀ [*]
2	DCB/AN	−1.24 ^b	−0.51 ^b	−0.28 ^b
3	DCB/AN	−1.01 ^c	−0.74 ^c	−0.51 ^c
4	DCB/AN	−1.14 ^d (−1.52) ^b	−0.61 ^d (−0.23) ^b	−0.38 ^d (0.00) ^b

^a $E_{00} = 1.75$ eV for ¹C₇₀^{*}, and $E_{00} = 1.52$ eV for ³C₇₀^{*}. ^b DMA^{•+}~PzC₇₀^{•−}. ^c Aniline^{•+}~PzC₇₀^{•−}. ^d Fc^{•+}~PzC₇₀^{•−}. The − ΔG_{CS} and − ΔG_{CR} were calculated from the Rehm–Weller equations: − $\Delta G_{\text{CS}} = \Delta G_{\text{CR}} + E_{00}$ and − $\Delta G_{\text{RIP}} = E_{\text{ox}} - E_{\text{red}} + \Delta G_{\text{S}}$, where ΔG_{S} refers to the static energy in DCB/AN (4:1) and is calculated according to $\Delta G_{\text{S}} = -e^2/(4\pi\epsilon_0\epsilon_{\text{R}}R_{\text{D-A}})$. The terms e , ϵ_0 and ϵ_{R} refer to elementary charge, vacuum permittivity, and static dielectric constant of the mixed solvent, respectively. In other solvents, $\Delta G_{\text{S}} = e^2/4\pi\epsilon_0[(1/2R_+ + 1/2R_- - 1/R_{\text{D-A}})(1/\epsilon_{\text{S}}) - (1/2R_+ + 1/2R_-)(1/\epsilon_{\text{R}})]$, where $R_+ = 3.0$ Å for Fc, 2.5 Å for DMA; $R_- = 5.2$ Å; and $R_{\text{D-A}}$ = center-to-center distance between the Fc or DMA. The PzC₇₀ moieties were evaluated from Figure S3.

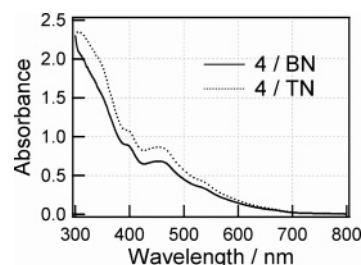


Figure 4. Steady-state absorption spectra of **4** (0.02 mM) in BN and TN.

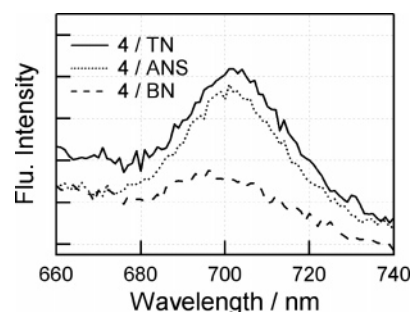


Figure 5. Fluorescence spectra of **5** (0.05 mM) and **4** (0.05 mM) observed with a streak-scope image in DCB and BN. $\lambda_{\text{ex}} = 400$ nm.

also exothermic for **2**, **3**, and **4** (Fc^{•+}~PzC₇₀^{•−}), but iso-free-energetic for **4** (DMA^{•+}~PzC₇₀^{•−}).

Steady-State Absorption Studies. Compared with C₆₀, the absorption of C₇₀ is markedly stronger in the visible region. The absorption spectra of **4** are shown in Figure 4, in which the broad absorption bands can be observed over a wide range in the visible region, with the main peak at 475 nm. The absorption spectrum of **4** is nearly identical to that of pristine C₇₀ due to the low absorptivity of the Fc moiety in the UV–vis region ($\lambda_{\text{max}} = 440$ nm, $\epsilon = 90$ M^{−1} cm^{−1})²⁴ and the shorter than 400 nm wavelength region of the absorption of DMA moiety. The effect of the solvent on the absorption spectra is quite small. Laser flash photolysis was performed with 532 nm laser light, which predominantly excites the C₇₀ entity.

Emission Studies. The photophysical behavior of the studied compounds was investigated, first, by the steady-state emission measurements by applying 400-nm light as the excitation wavelength, which exclusively excites the C₇₀ moiety.²⁵ The emission band at nearly 700 nm in Figure 5 was attributed to the C₇₀ moiety. It was found that the intensity of the C₇₀

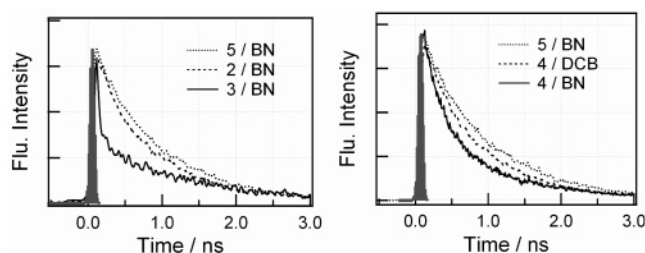


Figure 6. Fluorescence time profiles of (left) **5**, **2**, and **3** in BN and (right) **5** and **4** in DCB and BN; $\lambda_{\text{ex}} = 400$ nm. The concentrations were maintained at 0.05 mM.

TABLE 3: Fluorescence Lifetimes (τ_f) of ${}^1\text{C}_{70}^*$, Rate-Constants (k_{CS}) and Quantum Yields (Φ_{CS}) of the Charge Separation via ${}^1\text{C}_{70}^*$, Charge-Recombination Rate Constants (k_{CR}), and Lifetimes of Radical Ion Pair (τ_{RIP}) of **4 in Various Solvents**

solvent	τ_f of ${}^1\text{C}_{70}^*$ ns	k_{CS}^a s^{-1}	Φ_{CS}^a	ΔG_{CS} eV	k_{CR} s^{-1}	τ_{RIP} ns	ΔG_{CR} eV
BN	0.34 (74%), 1.27 (26%)	1.9×10^9	0.64	-0.75	2.6×10^7	38	-1.00
DCB	0.52 (57%), 1.11 (43%)	0.9×10^9	0.45	-0.59	1.3×10^7	76	-1.16
ANS	0.64 (80%), 1.83 (20%)	0.5×10^9	0.33	-0.40	1.2×10^7	80	-1.35
TN	0.79 (90%), 1.80 (10%)	0.2×10^9	0.17	-0.05	1.0×10^7	100	-1.70

^a k_{CS} and Φ_{CS} of the charge separation process via ${}^1\text{C}_{70}^*$ were calculated from $k_{\text{CS}} = (1/\tau_f) - (1/\tau_0)$ and $\Phi_{\text{CS}} = k_{\text{CS}}/(1/\tau_f)$, where τ_0 and τ_f are the lifetimes of the reference compound and investigating compounds, respectively.

emission band of **4** was slightly quenched as compared with that of **5** owing to the presence of the appended Fc and DMA moieties. By changing the solvent from toluene to a more polar benzonitrile (BN), the overall quenching efficiency was increased (Figure 5), suggesting the charge-separation character for the quenching process. Similar quenching behavior was obtained by using streak scope images.

The time-resolved fluorescence spectral features of the studied compounds track those of the steady-state measurements. The fluorescence decay-time profiles of **2**, **3**, and **5** at 700 nm in benzonitrile are shown in Figure 6 (left panel). The fluorescence time profile of **5** exhibited a single-exponential decay with a lifetime (τ_0) of 0.95 ns, which is almost the same as the C_{70} reference. The lifetimes (τ_f) of **2** and **3** were evaluated by curve-fitting with biexponential decays; the major initial fast decays were evaluated as 0.64 and 0.10 ps for **2** and **3**, respectively. The rate constants (k_{CS}) and quantum yields (Φ_{CS}) via ${}^1\text{C}_{70}^*$ of the charge-separation process were estimated as $5.1 \times 10^8 \text{ s}^{-1}$ and 0.33 (for **2**) and $8.9 \times 10^9 \text{ s}^{-1}$ and 0.89 (for **3**), respectively.²⁶ On the other hand, the charge separation process

for **5** was not observed. From this comparison, it was clear that the charge-separation process for **3** (which contains electron-donating aniline directly attached to the N atom of the Pz group) is more efficient than that of **2** (which has electron-donating DMA and electron-withdrawing nitrobenzene).

Attaching Fc moiety to Pz- C_{70} introduces a new quenching pathway for **4**, as shown in Figure 6 (right panel), as compared with **5** and **2**. This quenching process is due to the charge separation from the Fc and DMA moieties attaching with the Pz group to the ${}^1\text{C}_{70}^*$ moiety. In BN, the rate constant of the charge separation of **4** is faster than that of **2**, but slower than that of **3**; this trend matches well with the electron-donating ability of the group attached to the sp^2 N atom of the Pz moiety. It was observed that the fluorescence decay-time profiles of **4** tend to become shorter with an increase in the solvent polarity, as shown in Figure 6 (right panel), where the major initial fast decay components gave the lifetime (τ_f) of C_{70} as 340, 520, 640, and 790 ps in BN, DCB, anisole (ANS), and toluene (TN), respectively. As listed in Table 3, it was found that both the k_{CS} and Φ_{CS} values decrease with a decrease in the solvent polarity, which is in agreement with the steady-state emission measurement.

Further studies involving the nanosecond transient absorption technique have been performed to confirm the charge separation process in the studied compounds.

Nanosecond Absorption Spectra. The nanosecond transient absorption spectra were obtained by 532 nm laser-light, which excites the C_{70} moiety predominantly. The transient spectra of **5** (with nitrobenzene) in Ar-saturated DCB (see Figure S12) exhibited the absorption band at 1000 nm, which is unambiguously assigned to ${}^3\text{C}_{70}^*$ ($\tau_{\text{T}} = 1.5 \mu\text{s}$).^{1,27,28} The absence of electron-donating moieties in **5** made it difficult to produce the radical ion pair.

The transient absorption spectra of **2**, which incorporate the DMA and nitrobenzene moieties, in DCB are shown in Figure 7, left panel. The transient absorption band of ${}^3\text{C}_{70}^*$ was observed at 1000 nm with a shoulder at 1380 nm, in which the latter band can be assigned to the radical anion of the C_{70} entity.²⁹ From this observation, the DMA group may act as an electron donor with respect to the ${}^1\text{C}_{70}^*$ entity. The DMA group conjugates with the Pz rings to increase the electron-donating ability. The time profile at 1020 nm shows two-component decay, suggesting that the absorption of the radical ion pair is overlapped with that of the ${}^3\text{C}_{70}^*$ entity at this wavelength. The fast decay corresponds to the decay of the radical ion pair, which is faster than the ${}^3\text{C}_{70}^*$ entity of **2**.

In the case of **3**, in which DMA and aniline are attached to increase the electron-donating ability, the transient absorption spectrum at 0.1 μs (Figure 7, right panel) shows broad absorption

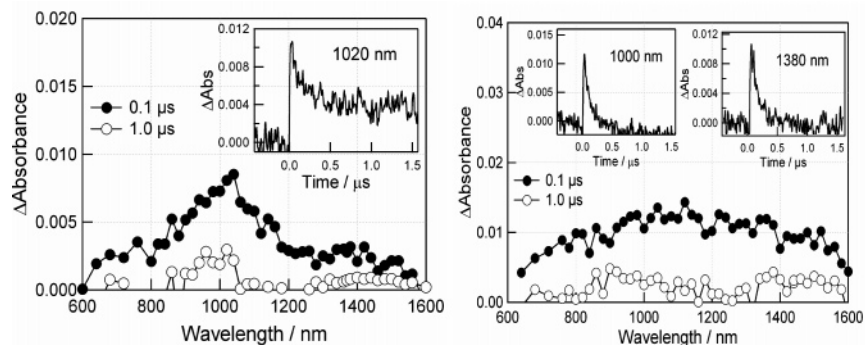


Figure 7. Transient absorption spectrum of **2** (left panel) and **3** (right panel) in Ar-saturated DCB obtained by 532 nm laser photolysis. Inset: time profiles at 980 and 1380 nm.

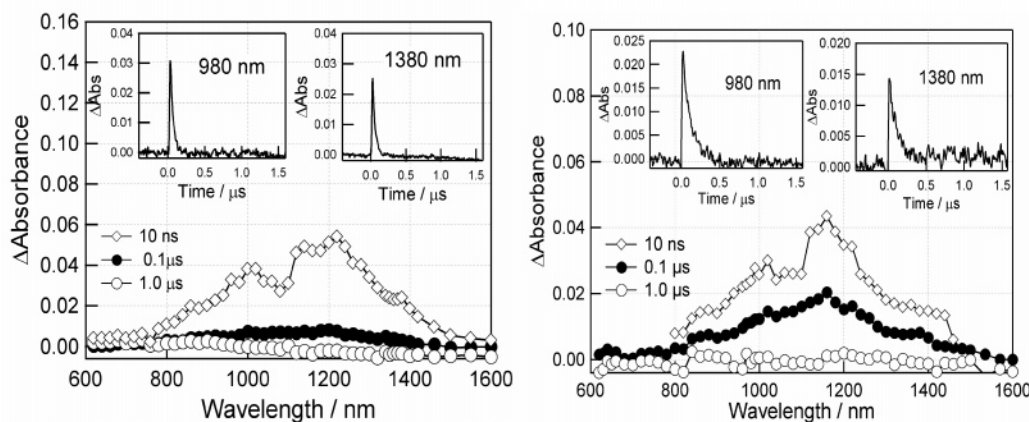


Figure 8. Transient absorption spectra obtained by 532 nm laser excitation of **4** (0.1 mM) in Ar-saturated BN (left panel) and TN (right panel). Inset: time profiles at 980 and 1380 nm.

over the whole region of 600–1600 nm. This broad absorption in the visible and near-IR regions can be attributed to the C₇₀ radical anion with the Pz moiety bearing two electron-donating substituents (such assignment was supported by the record steady-state absorption of the one-electron reduced form of **4** (see Figure S16)). The time profiles at 1000 and 1380 nm show quick decay, which suggests that the decay of the radical ion pair is quite fast.

The transient absorption spectra of **4** in Ar-saturated solvents are shown in Figure 8. In BN (left panel), the transient absorption bands that appeared over the wide wavelength region from 800 to 1600 nm with two maxima at 1200 nm were assigned to the radical cation (DMA-Pz-Fc)^{•+}, according to previous studies in analogous C₆₀ derivatives¹⁷ and 1380 nm, which is assigned to the radical anion of C₇₀. The other peak also appeared at 980 nm, which is a position that is similar to that of the ³C₇₀^{*} entity. On the other hand, the one-electron oxidized form of the Fc unit was not clearly observed at 625 nm because of the small extinction coefficient of Fc^{•+} (500 dm³ mol⁻¹ cm⁻¹).^{3,30} From these observations, it is clear that the charge separation takes place within **4** in BN via the ¹C₇₀^{*} moiety. Similar transient absorption spectra were observed in DCB and ANS, confirming the charge separation via ¹C₇₀^{*}.

The transient absorption spectra of **4** in toluene (Figure 8 (right panel)) exhibited the same characteristic absorption bands as in BN, suggesting that the charge separation takes place even in a nonpolar solvent; nevertheless, the decrease in the fluorescence lifetime was only slight (Table 3).

From the decays of the 1200–1400 nm bands, the lifetimes of the radical ion pairs of **4** were evaluated to be in the range of 38–100 ns, showing a tendency to increase with decreasing solvent polarity (Table 3). This tendency suggests that the charge-recombination process is in the deep inverted region of the Marcus parabola.³¹ It is reasonable to believe that the final charge-separated state can be considered as Fc^{•+}~PzC₇₀^{•-}; thus, the charge recombination may occur between the cationic center of the Fc entity and the anionic center of the C₇₀ entity of **4**. It can be seen from Figure 8 that the decay rates of ³C₇₀^{*} are almost the same as the *k*_{CR} values, suggesting that the charge-separated state and the triplet state are in rapid equilibrium, which in turn implies that the radical ion pair gains the triplet spin character.

Energy Diagram. From the thermodynamic data and excited energy levels, the energy diagrams of **4** can be drawn as shown in Figure 9. The charge separation via the excited singlet state is possible in all solvents employed in the present study;

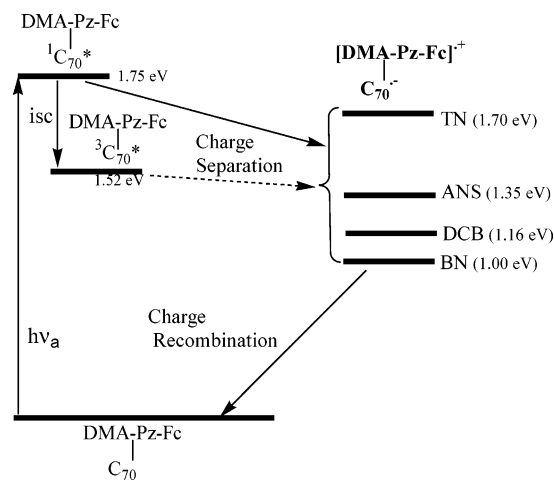


Figure 9. Energy diagram of **4** in different solvents.

however, both the *k*_{CS} and Φ_{CS} values increase with an increase in the absolute values of Δ*G*_{CS} via the ¹C₇₀^{*} entity, suggesting that the charge-separation process occurs in the normal region of the Marcus parabola.³² On the other hand, the *k*_{CR} values decrease with the absolute value of Δ*G*_{CR}, suggesting that the charge-recombination process occurs in the inverted region of the Marcus parabola.³² Since the energy level of ³C₇₀^{*} (1.53 eV)³³ is located higher than that of the charge-separated states in polar solvents, the charge separation via the ³C₇₀^{*} entity is thermodynamically possible. However, this process is not kinetically favorable because of the higher Φ_{CS} values in polar solvents.

Comparison with C₆₀ Derivatives. From the comparison of **4** with the previously reported DMA-PzC₆₀-Fc,¹⁷ we could mention the following points: (i) The *k*_{CS} (3.0 × 10⁹ s⁻¹) and Φ_{CS} (0.88) values of DMA-PzC₆₀-Fc in DCB are comparable to those of **4**. (ii) The lifetime of the radical ion pair of **4** is significantly longer than that of the DMA-PzC₆₀-Fc (30 ns in DCB). The longer-lived radical ion pair of **4**, as compared to the DMA-PzC₆₀-Fc, may be caused by the stabilization of the radical anion with larger C₇₀ sphere as compared to that of C₆₀. Since thermodynamic driving forces for the electron transfer of DMA-PzC₇₀-Fc are almost equal to those of DMA-PzC₆₀-Fc triads, the possible reasons for the difference in τ_{RIP} values might be the smaller reorganization energy and weaker electronic coupling in DMA-PzC₇₀-Fc than those of DMA-PzC₆₀-Fc.

Conclusions

C₇₀-based triads have been synthesized, and their photoinduced events have been studied for the first time. Cycloadditions of nitrile imines to C₇₀ have been carried out, and this demonstrates the application of this reaction for the functionalization of C₇₀. As examples, 2-pyrazolino[70]fullerenes with ferrocene and *N,N*-dimethylaniline moieties as donors have been prepared by this procedure. Electrochemical investigations show that there are no differences in the redox behavior of the different C₇₀ regioisomers. Photophysical properties of newly synthesized 2-pyrazolino[70]fullerene triads have been investigated by measuring the time-resolved fluorescence spectra and transient spectra in polar and nonpolar solvents. In the C₇₀ triads with the pyrazoline ring as a linker, the charge separation takes place efficiently between the photoexcited C₇₀ moiety and the ferrocene moiety in polar and nonpolar solvents. It was revealed that the pyrazoline ring mediates charge separation between the ferrocene moiety and the photoexcited C₇₀ moiety. Comparison of the behavior of the C₇₀-based triad with the C₆₀-based triad indicates that the lifetime of the charge separated state is longer in the former.

Experimental Section

General. All chemicals were purchased from Aldrich and used without further purification. All the solvents (BN, DCB, ANS, and TN) were purchased from Aldrich and used as received. The UV-vis spectral measurements were carried out with a Jasco model 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.

The electrochemical behavior of compounds 2–5 and C₇₀ in *o*-dichlorobenzene/acetonitrile (4:1) was studied by cyclic voltammetry techniques and by Osteryoung square wave voltammetry at room temperature using tetra(*n*-butyl)ammonium perchlorate, (n-C₄H₉)₄NClO₄, as a supporting electrolyte.

The lifetime measurements were measured by a single-photon counting method using a second harmonic generation (SHG, 400 nm) of a Ti:sapphire laser (Spectra-Physica, Tsunami 3950-L2S, 1.5 ps fwhm) and a streak scope (Hamamatsu Photonics) equipped with a polychromator (Action Research, SpectraPro 150) as an excitation source and a detector, respectively. Lifetimes were evaluated with software attached to the equipment. The nanosecond transient absorption measurements in the near-IR region were measured by means of laser-flash photolysis; 532 nm light from a Nd:YAG laser (Spectra-Physics and Quanta-Ray GCR-130, 6 ns fwhm) was used as an excitation source. For transient absorption spectra in the near-IR region (600–1600 nm), monitoring light from a pulsed Xe lamp was detected with a Ge-avalanche photodiode module (Hamamatsu Photonics). All the samples in a quartz cell (1 × 1 cm) were deaerated by argon's bubbling through the solution for 20 min.

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Supporting Information Available: Detailed experimental procedures, new compound characterizations (NMR, mass

spectra), and supplementary transient absorption spectra of 4 and 5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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