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Synthesis and Photoinduced Intramolecular Processes of Fulleropyrrolidine–Oligothienylenevinylene–Ferrocene Triads

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Abstract: Two new triads based on *N*-methylfulleropyrrolidine, oligothienylenevinylenes (*n*TV) and ferrocene (Fc), namely C_{60}-*n*TV-Fc ($n=2$, 4) have been synthesized. A HOMO–LUMO gap as low as 1.09–1.11 eV was experimentally determined by cyclic voltammetry. In both polar and nonpolar solvents, photoinduced charge-separation (CS) processes in C_{60}-*n*TV-Fc predominantly take place from the singlet excited states of C_{60} and *n*TV; this result was indicated by steady and time-resolved emission spectroscopy. In the case of C_{60}-4TV-Fc, the CS state was indicated by the nanosecond transient absorption spectra. In C_{60}-2TV-Fc, although the CS process was also confirmed by the fluorescence quenching in nonpolar and polar solvents, the lifetimes of the CS states were shorter than those of C_{60}-4TV-Fc. It was revealed that the introduction of Fc donor moiety at the end of the longer *n*TV chain in the C_{60}-*n*TV dyad systems effectively increases the CS efficiency and the lifetimes of CS states.

Keywords: electron transfer · ferrocene · fullerenes · oligothienylenevinylenes

Introduction

Fullerenes have been shown to be good electron acceptors due to their low reduction potentials and low reorganization energy involved in electron-transfer reactions.[1] Considerable efforts have been devoted to develop the systems, in which C_{60} is covalently linked to electron donors,[2–7] in addition to the mixture systems of C_{60} and donors.[8,9] These characteristics of fullerene derivatives open potential applications in the realization of new artificial photosynthetic systems, molecular electronic devices, and photovoltaic cells.[2–4]

The preparation of photovoltaic cells based on blends of polymers and soluble C_{60} derivatives has received a lot of attention during the last decade, and efficiencies of up to 3% have been reached.[10] Furthermore, recent years have witnessed an increase of research aimed at the synthesis of C_{60}-derivatized π-conjugated oligomers.[11] At the same time, the well-defined chemical structures of oligomers make it possible to investigate the effect of extension of π-conjugation on the photophysical processes (light absorption, and energy or electron transfer).[12] Nierengarten[13] and Jansen[14] have studied C_{60} derivatives bearing oligophenylenvinylene (*n*PV) chains finding competition between energy- and electron-transfer processes. More recently, Martín, Guldi, et al. prepared and studied C_{60}-*n*PV-donor triads with extended-TTF[15] or porphyrins[16] as donors observing strong electronic coupling realized through the π-conjugation of the *n*PV chain.

One important factor governing charge separation is the oxidation potential of the donor, which should be low in order to stabilize the charge-separated state. Recently, dyads involving C_{60} and oligothienylenevinylenes (*n*TV) were synthesized[17] and, as *n*TVs exhibit low oxidation potentials[18] in comparison to *n*PVs with comparable chain lengths;[5a,19] their photophysical properties have been studied.[20]

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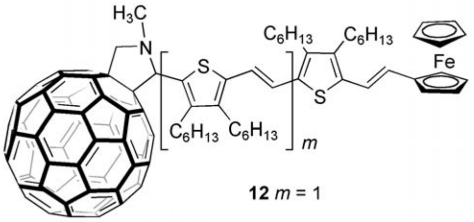
Ferrocene (Fc) derivatives have also high electron-donor abilities. Fc derivatives have been employed as hole traps for multistep charge-separation systems of triad and tetrad molecules, in which Fc moieties act as final hole centers.[3c,4b,21,22]

Thus, in the present study, two kinds of novel fullerene–oligothienylenevinylene–ferrocene triads (C_{60}-*n*TV-Fc; $n=2$ and 4) were designed and synthesized to develop photoinduced intramolecular processes and compared with the C_{60}-*n*TV dyads.[17,18]



12 *m* = 1

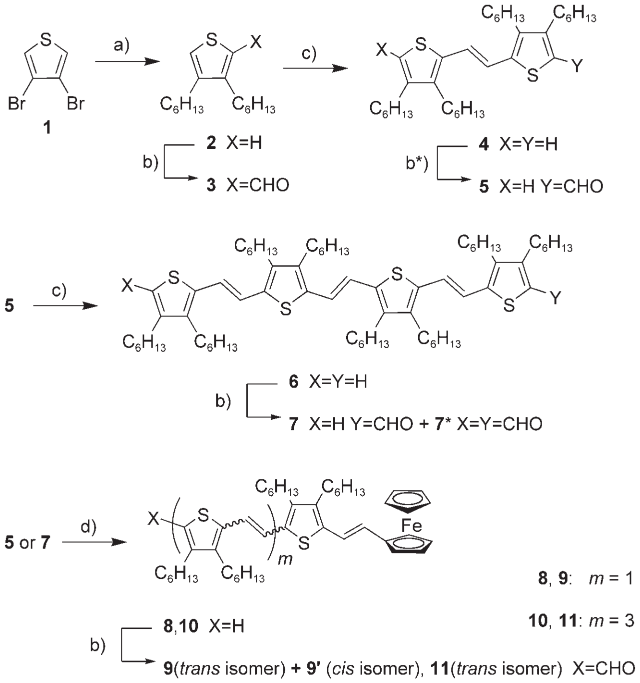
13 *m* = 3

It is expected that the Fc and oligothienylenevienylene moieties act as electron donors to the singlet excited state of C_{60}, acting as an electron acceptor. The charge-separation and charge-recombination processes were investigated by the time-resolved fluorescence and absorption spectra in the visible and near-IR regions. Additionally, the effect of introduction of Fc into the dyad systems and effect of length of the *n*TV group on these processes were also observed by varying solvent polarity.

Results and Discussion

Synthesis: The synthetic route for the two target ferrocene–thienylenevinylenes (*n*TV-Fc) **9** and **11**, carrying alkyl chains to enhance solubility and formyl group at the end of the *n*TV system to make available further transformations, is depicted in Scheme 1. We followed the strategy employed by Roncali[23,18] for the preparation of **4**. Compound **2** was prepared from 3,4-dibromothiophene in 84 % yield by following the Kumada coupling procedure.[24] Formylation of **2** followed by McMurry coupling afforded dimer **4**. It is worth noting that compound **5** was prepared by a modification of the previously described procedure due to the formation of a *cis*/*trans* isomeric mixture during the Vilsmeier formylation. However, quantitative conversion of the *cis* to the *trans* isomer was achieved by refluxing the mixture in toluene in the presence of a catalytic amount of iodine.

Tetramer **6** was obtained in 70 % yield from **5** by using a McMurry coupling reaction. Then aldehyde **7** was obtained, together with the corresponding dialdehyde **7′**, through a Vilsmeier formylation. Both aldehydes, **7** and **7′**, were easily separated by column chromatography affording **7** in 52 % and **7′** in 34 % yield.



Scheme 1. Synthesis of *n*TVs: a) $C_6H_{13}MgBr$, [$NiCl_2$(dppp)], dry THF, reflux; b) $POCl_3$, dry DMF/DCE, reflux; b*) 1) $POCl_3$, dry DMF/DCE, reflux; 2) I_2, dry toluene, reflux; c) $TiCl_4$, Zn/dry THF, reflux; d) $TiCl_4$, Zn/dry THF, ferrocenecaboxaldehyde, reflux.

The McMurry cross-coupling reaction between **5** or **7** and ferrocenecarboxaldehyde afforded *n*TV-Fc dyads **8** or **10** in quantitative and 47 % yield, respectively. Finally, a new Vilsmeier formylation gave the target *n*TV-Fc carboxaldehydes **9** and **11** in quantitative and 29 % yields, respectively.

During the formation of **9**, a *cis*/*trans* isomerization of the tiophene–thiophene double bond was observed, yielding **9** (*trans* isomer) and **9′** (*cis* isomer) in a 5:2 proportion according to ^1H NMR spectroscopy. Further purification by column chromatography (silicagel, CH_2Cl_2/Hexane 1:1) afforded pure **9** in sufficient quantity for analytical purpose, but due to major decomposition of the compounds in these conditions (as well as when using neutral or basic alumina instead of silica gel), this technique could not be employed for the purification of **9** in a synthetic scale. Furthermore, due to the presence of the ferrocene, the previously used method for the isomerization of the *cis* compound into the corresponding *trans* isomer could not be used without complete degradation of the starting material. Thus, the synthesis of triad **12** was performed by using the *E*/*Z* isomeric mixture (**9**+**9′**).

The fullerene–oligothienylenevinylene–ferrocene triads (C_{60}-*n*TV-Fc), **12** and **13**, were prepared by 1,3-dipolar cycloaddition among **9** (*E*/*Z* isomers) or **11**, *N*-methylglycine and C_{60} in refluxing toluene in 24 and 25 % yield, respectively, following the procedure described by Prato (Scheme 2).[25] Compound **12** was obtained as an *E*/*Z* isomeric mixture (proportion unchanged respecting to the starting mixture). At this stage, the stability of the final adduct allowed further

$\mathbf{9+9'}$ $m = 1$ $\xrightarrow{\text{a)}}$ $\mathbf{12+12'}$ $m = 1$

$\mathbf{11}$ $m = 3$ $\quad$ $\mathbf{13}$ $m = 3$

Scheme 2. Synthesis of triads **12** and **13**: a) C_{60}, sarcosine, dry toluene, reflux

purification by column chromatography (silicagel). Elution, using hexane/toluene 6:4, afforded first **12** (*trans*) in its pure form then a mixture of **12** and **12′** (*cis*). Despite the use of several columns, **12′** could not be obtained in its pure form.

The all-*trans* isomers of **12** and **13** were used in the ulterior studies.

All new compounds were fully characterized by MALDI mass spectrometry as well as ^{1}H NMR, ^{13}C NMR, FT-IR, and UV-Visible spectroscopy. In all cases, the molecular ions were observed in the mass spectra (positive ion mode). The ^{1}H NMR spectra of C_{60}-2TV-Fc (**12**) and C_{60}-4TV-Fc (**13**) reveal the presence of ferrocene as shown by proton signals between $\delta = 4.1$ and 4.5 ppm, in addition to the pyrrolidine ring signature as two doublets and one singlet between $\delta = 4.2$ and 5.3 ppm. Finally, the *trans* configuration of the vinyl protons of the *n*TV is clearly seen ($J \approx 15$ Hz); the alkyl chains in the aliphatic region of the spectra are observed as well.

Compound **14** (C_{60}-2TV) was synthesized, according to procedures described by Roncali, as a model compound for the different studies.[17]

Conformational studies were performed on compound **14**. In principle, two diastereoisomeric conformers can exist for compound **14** by rotation of the thiophene moiety around the thiophene–pyrrolidine bond. However, the ^{1}H NMR spectra recorded at temperatures from −40 to 40 °C are all similar, showing that this rotation does not occur under these conditions. The steric hindrance resulting from the introduction of an alkyl chain in *ortho* position (with respect to the thiophene–pyrrolidine bond) seems to be sufficient enough to increase the rotational energy barrier to the point at which free rotation is almost impossible and reveals no dynamic exchange between two possible conformers. This last observation shows that only one of the two possible conformers exists for **14**. This fact is also supported by computational studies performed on the reference compound **15** (C_{60}–bisalkylthiophene) to evaluate the relationship between potential energy and the dihedral angle between the pyrrolidinofullerene moiety and one substituted thiophene (to simplify calculation). The molecular geometry was optimized at the AM1 semiempirical level with fixed value of the torsion angle for rotation around the considered bond. The resulting energy diagram is shown in Figure 1.

As shown in Figure 1, two conformers can exist. On the basis of assignment of proton resonances of compound **14**, by one- and two-dimensional experiments such as gCOSY, 1D-NOESY and 2D-NOESY experiments (see Supporting Information, Figure S8), it was possible to determine unambiguously that **14** adopts a conformation in which the *n*-hexyl chain is in the *cis* position with respect to CH group of pyrrolidine ring. NOE cross-peaks were observed for the following pairs of protons: Me–N group/all protons pyrrolidine ring, between both H/H protons of CH_2 group pyrrolidine ring, only one of these protons/CH pyrrolidine ring, and CH pyrrolidine ring/first CH_2 group of *n*-hexyl chain in *ortho* position thiophenes–pyrrolidine bond, are in full agreement with the proposed conformation.

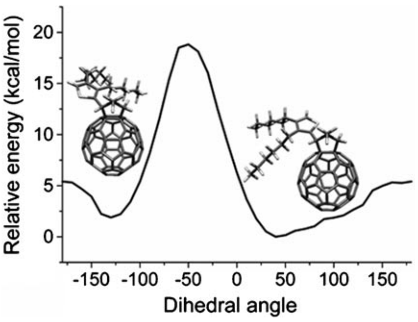


Figure 1. Calculated potential energy diagram for the rotation around the thiophene–pyrrolidine bond and the theoretical structure of the two conformers corresponding to the minima of **15**.

Electrochemical measurements: The electrochemical characteristics of C_{60}-*n*TV-Fc triads were examined by using cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV) at room temperature in *ortho*-dichlorobenzene (*o*-DCB)/acetonitrile 4:1 as solvent and $(n\text{-Bu})_4N^+ClO_4^-$ as a supporting electrolyte. The redox potentials for C_{60}-*n*TV-Fc, **12** and **13**, are listed in Table 1 along with those of *n*TV (**4**, **6**), *n*TV-Fc (**8**, **10**), C_{60}-2TV (**14**), ferrocene, *N*-methylfulleropyrrolidine ($NMPC_{60}$) and C_{60} as reference compounds. As an example, the CV plot for **12** (C_{60}-2TV-Fc) is shown in Figure 2.

Table 1. Electrochemical data (E [V vs. Ag/AgNO$_3$]) for redox processes detected by CV/OSWV in *o*-DCB/acetonitrile (4:1).[a]

	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E^1_{ox}	E^2_{ox}	E^3_{ox}
C_{60}	−0.96	−1.37	−1.83				
2TV (**4**)				−2.32	0.30[e]	0.61[e]	
4TV (**6**)				−2.10	0.17	0.35	
ferrocene					0.06		
2TV-Fc (**8**)				−1.99	0.16[b]	0.58[c,e]	
4TV-Fc (**10**)				−1.98	0.08[b]	0.27[d]	0.49[d]
$NMPC_{60}$	−1.05	−1.45	−1.99				
C_{60}–2TV (**14**)	−1.06	−1.48	−2.01				0.61[c,e]
C_{60}-2TV-Fc (**12**)	−1.07	−1.48	−2.01		0.04[b]		0.45[c]
C_{60}-4TV-Fc (**13**)	−1.00	−1.41	−1.96		0.09[b]	0.25[d]	0.50[d]

[a] OSWVs were obtained using a sweep width of 25 mV, a frequency of 15 Hz, a step potential of 4 mV, and a quiet time of 2 s on a Windows-driven Autolab PGSTAT 30 electrochemical analyzer. [b] For Fc moiety. [c] For 2TV moiety. [d] For 4TV moiety. [e] Irreversible.

As previously described,[17] the CV of 2TV (**4**) shows two irreversible oxidation waves. The irreversibility of the oxidation wave observed in the case of **4** is attributed to electropolymerization, a consequence of the activation of free α-position on the thiophene ring during the first oxidation step. However, rapid inhibition of this phenomenon occurs

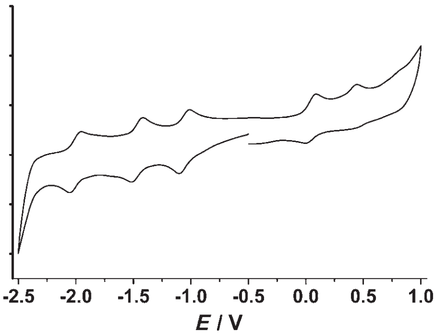


Figure 2. Cyclic voltammogram of C_{60}-2TV-Fc (**12**) in *o*-DCB/acetonitrile 4:1 containing 0.1 M (n-Bu)$_4$NClO$_4$. Scan rate 100 mV s^{-1}.

with chain extension and steric hindrance. Thus 4TV (**6**) exhibits two reversible oxidations waves negatively shifted relative to **4** in good agreement with the literature. The reversibility is also observed in the case of compounds bearing the ferrocene moiety.

Concerning *n*TV-Fc, **8** and **10**, one reversible oxidation peak appears at 0.16 V and 0.08 V, respectively, and was attributed, by direct comparison, to the ferrocene moiety. Other oxidation peaks provided by the *n*TV moiety were observed (see Table 1). Introduction of the ferrocene causes a positive shift of the *n*TV-based waves. In the case of **8**, due to this shift, only one peak, corresponding to the TV moiety, is detected in the observation window.

On the cathodic side of the observation window, compounds **12** and **13** show three reversible reduction waves. The first two waves can be attributed to the fullerene moiety; the third reduction potential was assigned to both the fullerene cage and the reduction of the *n*TV-Fc moiety by comparison with the reduction potentials of **8** and **10**. Similar to other fulleropyrrolidines described in the literature[25] and to reference compound NMPC$_{60}$, an anodic shift of around 100 mV for the first reduction wave was observed in comparison with the parent C_{60}. On the anodic side, one reversible oxidation peak appears between 0.04 V for **12** and 0.09 V for **13**. Thus, considering the similar redox potential values for ferrocene and *n*TV-Fc, these lowest oxidation waves of the C_{60}-*n*TV-Fc triads can be assigned to the ferrocene component. For Fc oxidation potential, the value of 4TV-Fc (**10**) is almost the same as that of C_{60}-4TV-Fc (**13**), whereas a significant change was observed from 0.16 V for 2TV-Fc (**8**) to 0.04 V for C_{60}-2TV-Fc (**12**). The next oxidation waves observed are attributable to the *n*TV moiety. The 4TV oxidation peaks (0.17–0.27 V) are less positive than that of 2TV (0.30 –0.45 V).

The experimentally measured HOMO–LUMO gaps are as low as 1.11 eV for **12** and 1.09 eV for **13**, making these systems good candidates to act as molecular rectifiers (diodes).

Steady-state absorption spectra: Figure 3a shows an absorption spectrum of **12** (C_{60}-2TV-Fc) in toluene as well as those of **8** (2TV-Fc) and NMPC$_{60}$.

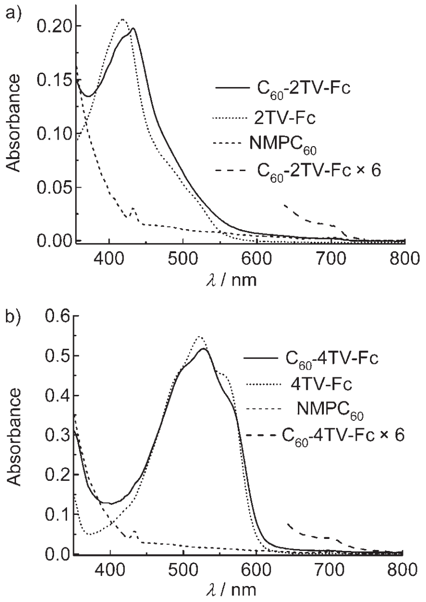


Figure 3. Steady-state absorption spectra of a) **12** (C_{60}-2TV-Fc) and b) **13** (C_{60}-4TV-Fc) in toluene. Absorption spectra of **8** (2TV-Fc), **10** (4TV-Fc), and NMPC$_{60}$ are also included.

With respect to the peak of 2TV-Fc at 420 nm, a slight red-shift of the absorption band at 432 nm, corresponding to the 2TV moiety in C_{60}-2TV-Fc (**12**), is observed indicating quite weak interaction between the C_{60} and 2TV due to the close distance of these two moieties. In Figure 3b, the spectrum of **13** (C_{60}-4TV-Fc) shows the absorption maxima at 532 nm corresponding to 4TV, which is also slightly red-shifted compared with the absorption maxima at 527 nm of **10** (4TV-Fc). In addition, the absorption maximum at 700 nm of **13** is found to be red-shifted by about 10 nm relative to the 690 nm peak of NMPC$_{60}$. Due to chain extension, which leads to an increase of the π-conjugation, the main absorption maximum at 532 nm of **13** (C_{60}-4TV-Fc) is shifted from that at 432 nm of **12** (C_{60}-2TV-Fc). In the present laser flash photolysis study, excitations of C_{60}-*n*TV-Fc triads were carried out by the 532 nm laser light, which is absorbed by the C_{60} and *n*TV-Fc moiety in about 1:2 for C_{60}-2TV-Fc (**12**), and 1:10 for C_{60}-4TV-Fc (**13**). The 355 nm laser light is absorbed by both 2TV-Fc and C_{60} moieties for **12** (C_{60}-2TV-Fc), whereas predominantly absorbed by the C_{60} moiety for **13** (C_{60}-4TV-Fc).

Steady-state fluorescence measurement: As reported earlier, *n*TVs show intense fluorescence in the visible region; 2TV at 500 nm and 4TV at 575 nm.[18] On attachment of Fc to 2TV, the fluorescence intensity was almost the same as 2TV, whereas for 4TV the fluorescence was significantly quenched, suggesting the intercommunication between ^{1}4TV* and Fc, that is, energy transfer or charge separation. On further attachment of C_{60} to 2TV-Fc, fluorescence quenching of 2TV was observed as shown in Figure 4a, suggesting energy transfer from ^{1}2TV* to C_{60}. In the case of 4TV, slight fluorescence quenching was observed with re-

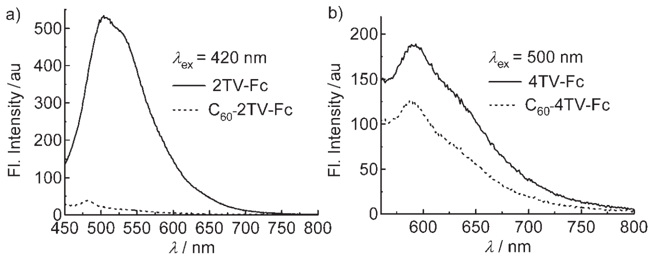


Figure 4. Fluorescence spectra of a) **12** (C_{60}-2TV-Fc) and **8** (2TV-Fc) and b) **13** (C_{60}-4TV-Fc) and **10** (4TV-Fc) in *o*-DCB.

spect to 4TV-Fc as shown in Figure 4b, suggesting that the charge separation from ^{1}4TV* to C_{60} was accelerated.

In the steady-state fluorescence spectra of C_{60}-*n*TV-Fc in toluene, the fluorescence peak at 715 nm was attributed to the C_{60} moiety, since the spectral shape of the fluorescence band of **12** (C_{60}-2TV-Fc) is almost the same as that of $NMPC_{60}$ in the same solvent. The fluorescence intensity of **12** in toluene was found to be much decreased relative to that of $NMPC_{60}$, (matched absorbance at the excitation wavelength). It is also reported that the fluorescence intensity of **14** (2TV-C_{60}) was quenched relative that of $NMPC_{60}$.[20] Thus, attaching the Fc moiety to 2TV in **14** induces the charge-separation process via the $^{1}C_{60}$* state through 2TV; energy transfer cannot be considered because of the low energy of $^{1}C_{60}$*. In polar solvents such as PhCN, the fluorescence intensity of **12** was found to be drastically quenched compared with that in toluene, supporting the charge-separation process via the $^{1}C_{60}$* state; this process is more efficient in polar solvent.

The fluorescence intensity of $^{1}C_{60}$*-4TV-Fc was also found to be remarkably lower even in toluene than that of $NMPC_{60}$, as shown in Figure 5. This quenching of the fluorescence can be ascribed to a charge separation from the 4TV-Fc moiety to the $^{1}C_{60}$* moiety. In addition, the fluorescence intensity of **13** (C_{60}-4TV-Fc) in PhCN almost disappeared completely.

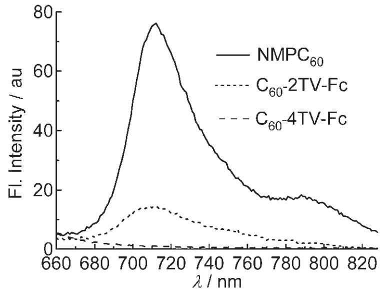


Figure 5. Fluorescence spectra of **12** (C_{60}-2TV-Fc), **13** (C_{60}-4TV-Fc) and $NMPC_{60}$ in toluene; excitation at 430 nm.

Picosecond time-resolved emission measurements: Since the 2TV fluorescence lifetime was reported to be very short,[20] we did not try to measure the lifetimes of *n*TV moiety in **12** and **13**. On the other hand, the time-resolved emission spectrum of the C_{60} moiety of **12** was observed (see Supporting Information, Figure S9), which tracked that of steady-state fluorescence spectrum. For **13** quite weak time-resolved fluorescence spectra, showing a peak near 720 nm, were found in toluene and *o*-DCB (see Supporting Information, Figure S9); such peak was also observed in spectra measured in PhCN.

Figure 6a shows the emission-decay/time profiles of **12** (C_{60}-2TV-Fc) in toluene and PhCN. The fluorescence/time profile of the $^{1}C_{60}$* moiety shows faster decay than that of $NMPC_{60}$. These decay profiles follow a bi-exponential function with lifetimes of 232 (70%) and 1300 ps (30%) in toluene. The shortening of the fluorescence lifetime indicates a charge separation from the donor moieties to the C_{60} moiety in the triad. In PhCN, a similar fluorescence/time profile with shorter lifetimes than those in toluene (listed in Table 2) was observed for **12** (C_{60}-2TV-Fc), indicating faster charge separation in polar solvent.

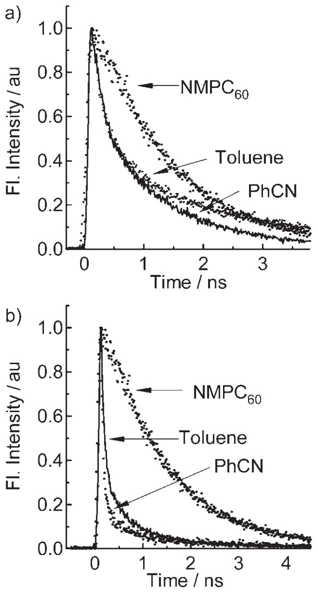


Figure 6. Fluorescence decays at 700–740 nm range of a) **12** (C_{60}-2TV-Fc) and b) **13** (C_{60}-4TV-Fc) in toluene and PhCN; $\lambda_{ex} = 400$ nm, fluorescence decay of $NMPC_{60}$ is also included.

For **13** (C_{60}-4TV-Fc), the quick fluorescence decays of the $^{1}C_{60}$* moiety are shown in Figure 6b. The fluorescence decays of the $^{1}C_{60}$* moiety follow bi-exponential functions, giving two fluorescence lifetime (τ_f) values, even in nonpolar solvents. Figure 6b also clearly shows that the fluorescence decays increase with an increase of the solvent polarity. These findings strongly suggest that photoinduced charge separation takes place from the 4TV-Fc moieties to the $^{1}C_{60}$* moiety, yielding a charge-separated state.[26]

The charge-separation rate (k^{S}_{CS}) and quantum yield (ϕ^{S}_{CS}) via the $^{1}C_{60}$* moiety were evaluated from the short τ_f components according to Equations (1) and (2),[21c,27] in which the reference $(\tau_f)_{ref}$ is τ_f of $NMPC_{60}$.

Table 2. Free-energy changes (ΔG_{CS}^{S} and ΔC_{CR} in eV)[a] fluorescence lifetimes (τ_f, fraction)[b] of $^1C_{60}$*, rate constants (k_{CS}; in s^{-1}) and quantum yield (ϕ_{CS}) of charge-separation via $^1C_{60}$*, rate constants of charge-recombination (k_{CR}; in s^{-1}) and lifetime of the radical ion pair (τ_{RIP}; in ns) of C_{60}-*n*TV-Fc (**12** and **13**) in toluene, *o*-DCB and PhCN.

	solvent	ΔG_{CS}^{S}	τ_f/ps	k_{CS}^{S}	ϕ_{CS}^{S}	ΔG_{CR}	k_{CR}	τ_{RIP}
12	toluene	0.04	232 (70 %)	2.3×10^9	0.63	−1.76	–[c]	–[c]
	o-DCB	−0.17	198 (74 %)	4.3×10^9	0.84	−1.55	–[c]	–[c]
	PhCN	−0.32	181 (72 %)	6.2×10^9	0.87	−1.40	–[c]	–[c]
13	toluene	−0.08	101 (72 %)	9.3×10^9	0.93	−1.64	1×10^8[d]	10[c]
	o-DCB	−0.27	74 (75 %)	1.3×10^{10}	0.96	−1.45	5×10^7[d]	20
	PhCN	−0.42	57 (76 %)	1.7×10^{10}	0.98	−1.30	2×10^7[d]	50

[a] The $-\Delta G_{CS}$ values were calculated according to equations; $-\Delta G_{CS=} \Delta E_{00}-e(E_{ox}+E_{red})-\Delta G_S$; in which ΔE_{00} is the 0–0 transition energy (1.70 eV for $^1C_{60}$*). ΔG_S refers to the static energy calculated according to $-\Delta G_S = e^2/(4\pi\varepsilon_0\varepsilon_R R_{CC})$ in PhCN, while in DMF, DCB and toluene, $-\Delta G_S = -e^2/(4\pi\varepsilon_0))\ [(1/(2R_+)+1/(2R_-)-(1/R_{CC})/\varepsilon_S-(1/(2R_+)+1/(2R_-))/\varepsilon_R)]$, in which ε_R and ε_S refer to solvent dielectric constants for electrochemistry and electron-transfer, respectively. R_+, R_- and R_{CC} are radii of the radical cation and radical anion and their distance evaluated from the optimized structures, respectively; they are 3.8, 4.2, and 11.4 Å for C_{60}–2TV-Fc (**12**) and 7.2, 4.2, and 14.35 Å for C_{60}–4TV-Fc (**13**), respectively (see Supporting Information). [b] Goodness-of-fit parameters (χ^2) were 1.00–1.17. The values of the second lifetimes with minor fractions were 1300 ps (**12**) and 500–750 ps (**13**). [c] Too fast to observe. [d] Slower k_{CR}.

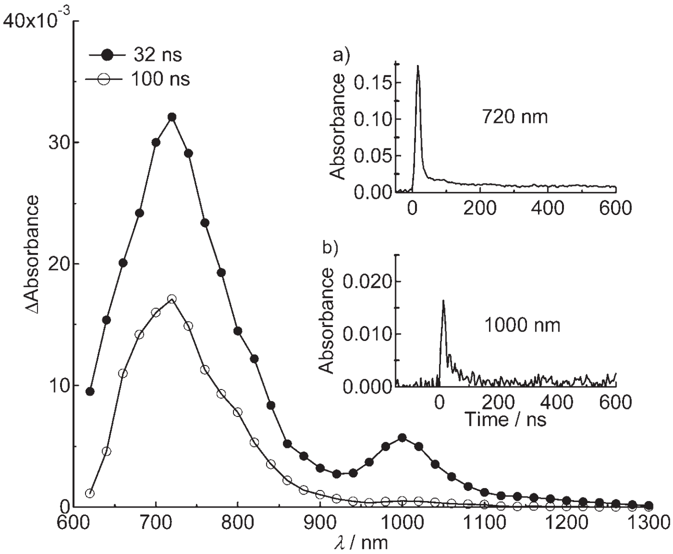


Figure 7. Transient absorption spectra of **13** (C_{60}-4TV-Fc) (0.10 mM) in Ar-saturated PhCN by 355 nm laser light excitation. Insert: Time profiles at a) 720 nm and b) 1000 nm.

$$k_{CS}^{S} = (1/\tau_f)_{sample} - (1/\tau_f)_{ref} \quad (1)$$

$$\phi_{CS}^{S} = [(1/\tau_f)_{sample} - (1/\tau_f)_{ref}]/(1/\tau_f)_{sample} \quad (2)$$

The calculated k_{CS}^{S} and ϕ_{CS}^{S} values are listed in Table 2. The k_{CS}^{S} and ϕ_{CS}^{S} for **13** (C_{60}-4TV-Fc) were found to be $1.7\times10^{10}\,s^{-1}$ and 0.98 in PhCN, respectively, indicating the occurrence of efficient charge separation within **13**. Furthermore, by comparison with **12** (C_{60}-2TV-Fc) in PhCN, the CS process for **13** is rapid and efficient in both polar and nonpolar solvents, indicating that the 4TV-Fc moiety enhances the donor ability with respect to that of 2TV-Fc. With an increase of the solvent polarity, the k_{CS}^{S} and ϕ_{CS}^{S} values tend to increase. It is also notable that the k_{CS}^{S} value of **13** is larger than that of C_{60}-2TV-Fc **12**; that is, k_{CS}^{S} increases with the increase in the length of *n*TV moiety. This finding suggests that the lower E_{ox} value of 4TV with respect to that of 2TV accelerates the charge-separation process.

From the ΔG_{CS} values listed in Table 2 (calculated on the basis of the electrochemical data listed in Table 1), the observed charge-separation processes via $^1C_{60}$* for both **12** (C_{60}-2TV-Fc), in polar solvents, and **13** (C_{60}-4TV-Fc), in all solvents, are supported. The larger $-\Delta G_{CS}$ values in **13** (C_{60}-4TV-Fc) indicate that the charge-separation process is more favorable in **13** than in **12**.

Nanosecond transient absorption studies: Nanosecond transient spectra of **13** (C_{60}-4TV-Fc) observed with 355 nm laser excitation in deaerated PhCN are shown in Figure 7. Absorption bands appear at 720 and 1000–1100 nm at 32 ns after the 6 ns laser pulse excitation. Similar transient absorption spectra are also observed with 532 nm laser light excitation for **13**, in which the 4TV-Fc moiety is predominantly excited in a ratio of 10:1 with respect to the C_{60} excitation. The intense absorption band at 720 nm is mainly due to the $^3C_{60}$* moiety. The transient absorption band around 660–750 nm, attributed to ^{3}4TV* moiety (see Supporting Information, Figures S10 and S11) and which could be observed by the laser excitation of 4TV-Fc (see Supporting Information), was not detected, suggesting rapid energy transfer from 4TV-Fc to C_{60}. The 1000–1100 nm band can be attributed to the $C_{60}^{\bullet-}$ moiety. These observations indicate the generation of a charge-separated state, such as $C_{60}^{\bullet-}$-4TV-$Fc^{\bullet+}$. Because of the low absorption intensity of $Fc^{\bullet+}$, it is difficult to confirm $Fc^{\bullet+}$. In addition the absorption of $4TV^{\bullet+}$ may be overlapped with that of the $C_{60}^{\bullet-}$ moiety, making it difficult to identify the position of the radical cation in $C_{60}^{\bullet-}$-(4TV-Fc)$^{\bullet+}$ state. From the lower E_{ox} value of Fc compared to that of 4TV, $C_{60}^{\bullet-}$-4TV-$Fc^{\bullet+}$ is plausible, but from the transient absorption spectra it is difficult to eliminate the possibility of $C_{60}^{\bullet-}$-(4TV-Fc)$^{\bullet+}$. In *o*-DCB and toluene, similar transient absorption spectra are obtained for **13**.

The time profile at 1000 nm in PhCN (inset in Figure 7) seems to decay in two components; thus, the charge-recombination rate constants (k_{CR}) are evaluated to be $1\times10^8\,s^{-1}$ from the initial fast decay and $2\times10^7\,s^{-1}$ from the slow decay. These k_{CR} values correspond to the lifetimes of the charge-separated sates of 10 and 50 ns, respectively. The k_{CR} values in *o*-DCB and in toluene are also evaluated from the time profiles at 1000 nm as summarized in Table 2. It should be mentioned that the k_{CR} value in polar PhCN is lower than those in toluene and *o*-DCB. Thus, the ratio of k_{CS}^{S}/k_{CR} is evaluated to be about 10^3, indicating that **13** is an efficient charge-separation system.

For **12** (C_{60}-2TV-Fc), a transient absorption band, obtained by 532 nm laser light excitation at which the C_{60} moiety is predominantly excited, is observed at 700 nm in toluene (see Supporting Information, Figure S12). The

700 nm band can be attributed to the triplet-state $^3C_{60}*$ moiety. The 1000 nm band, due to $NMPC_{60}^{\bullet -}$, is not observed, from which the lifetime of the charge-separated state is shorter than the laser pulse width (6 ns). In PhCN, no transient absorption appears after ns laser pulse irradiation, suggesting rapid charge recombination. The intensity of the transient absorption band at 700 nm in C_{60}-2TV-Fc is found to be remarkably lower relative to that found for C_{60}-2TV.

Thus, the lifetime of $C_{60}^{\bullet -}$-(4TV-Fc)$^{\bullet +}$ is longer than that of $C_{60}^{\bullet -}$-(2TV-Fc)$^{\bullet +}$ in PhCN and *o*-DCB indicating the importance of the conjugation length on the lifetimes of the radical ion pair.

Intermolecular electron transfer: To evaluate the intermolecular electron transfer, the transient absorption spectra were observed for the mixture of 2TV-Fc (**8**) and pristine C_{60} in PhCN as shown in Figure 8.

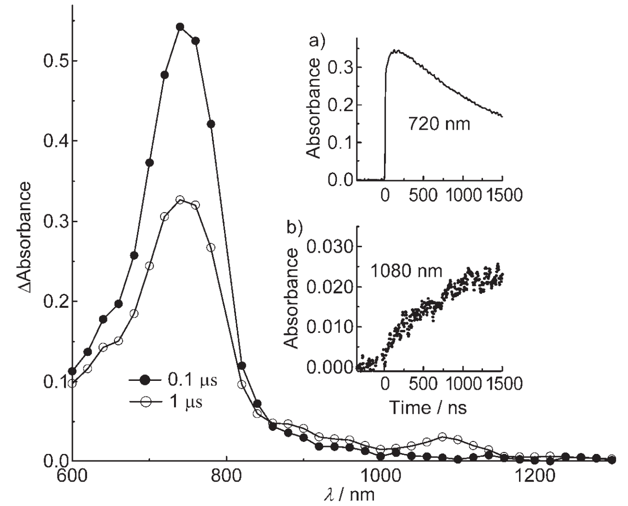


Figure 8. Transient absorption spectra of **8** (2TV-Fc) (0.2 mM) in the presence of C_{60} (0.2 mM) in Ar-saturated PhCN obtained by 532 nm laser light excitation; (insert) time profiles at 720 and 1080 nm.

With the decay of the transient absorption at 720 nm of $^3C_{60}*$, a transient absorption band appeared at 1080 nm is due to $C_{60}^{\bullet -}$. Nondecaying absorption at 700 nm may be (2TV-Fc)$^{\bullet +}$(see Supporting Information, Figure S13) Thus, the occurrence of intermolecular electron transfer via $^3C_{60}*$ to form radical ions, $C_{60}^{\bullet -}$ and (2TV-Fc)$^{\bullet +}$ can be proved. Similarly, for 4TV-Fc, intermolecular electron transfer was confirmed by the transient spectra exhibiting (4TV-Fc)$^{\bullet +}$ and $C_{60}^{\bullet -}$ at 1000 and 1080 nm, respectively (See Supporting Information; Figures S14 and 15).

Energy diagram consideration: The energy diagram in two solvents can be illustrated as shown in Figure 9. The energy level of the $^1C_{60}*$ moiety of triads C_{60}-*n*TV-Fc is evaluated from the fluorescence peaks. The triplet state of the C_{60} moiety is reported in the literature, as evaluated from the weak phosphorescence peak.[28] The radical ion-pair state in the polar solvent can be related to ΔG_{CR} values, which are listed in Table 2. Thus, our findings also indicate that the lifetimes of the radical ion pair for the final charge-separated state in the present systems are comparable to those in some other triad systems such as in C_{60}–oligothiophene–ferrocene triad[29] and in oligoaniline–oligo(*p*-phenylenevinylene)–fullerene triad system.[30]

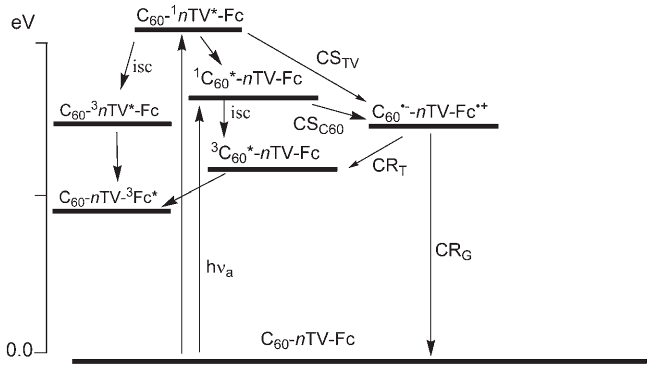


Figure 9. Energy diagram for electron-transfer processes of C_{60}-*n*TV-Fc in PhCN and toluene.

The 355 and 532 nm laser-light excitations pump the triads up to the $^1C_{60}*$ state, from which the charge separation takes place quite efficiently in both polar and nonpolar solvents, as confirmed by the time-resolved fluorescence measurements (Table 2). After charge separation, charge recombination of the ion pair occurs, returning to the ground state. However, in nonpolar solvents, the charge recombination may also take place to the $^3C_{60}*$ state of the triads (CR_T), showing quick decay. In case of **13** in toluene, the charge recombination to the ground state (CR_G) is predominant, showing relatively slow decay.

Conclusion

For C_{60}-*n*TV-Fc, the photoinduced charge-separation processes via the excited singlet state of C_{60} moiety were observed in both nonpolar and polar solvents. A lifetime of 10 ns was evaluated for the radical ion pairs of **13** (C_{60}-4TV-Fc) in toluene at room temperature, whereas a lifetime of the radical ion pair shorter than 6 ns was found for **12** (C_{60}-2TV-Fc). The calculated k_{CS}^{S} and ϕ_{CS}^{S} values were found to be $9.3\times10^{9}\,s^{-1}$ and 0.93 in toluene, respectively, indicating the occurrence of efficient charge separation even in nonpolar solvent within the supramolecular triad **13**. This charge separation was confirmed by the nanosecond transient absorption spectra and time-resolved fluorescence lifetime measurements. The calculated k_{CS}^{S} and ϕ_{CS}^{S} values were also found to be higher in **13** than in **12** or in other C_{60}-*n*TV dyad systems from previous studies. Thus, the present study suggests that the introduction of the Fc donor moiety with the longer chain of TV moiety in C_{60}-*n*TV dyad systems effectively increases the ability and efficiency of the charge-separation processes in supramolecular dyad and triad systems.

Experimental Section

Chemicals: Buckminsterfullerene, C_{60} (+99.95%) was obtained from Mer Corporation. Toluene, PhCN, and *o*-dichlorobenzene (*o*-DCB) were purchased from Aldrich Chemicals. Tetrabutylammonium perchloride ($(n\text{-Bu})_4NClO_4$) used in electrochemical studies was from Fluka Chemicals. All chemicals were used as received.

Electrochemical measurements: Reduction potentials E_{red} and oxidation potentials E_{ox} were measured by cyclic voltammetry with a potentiostat BAS CV50W in a conventional three-electrode cell equipped with Pt-working and counter electrodes with an Ag/AgCl reference electrode at scan rate of $100\,mV\,s^{-1}$.

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.

Time-resolved fluorescence measurements: The time-resolved fluorescence spectra were measured by a single-photon counting method using a streak-scope Hamamatsu Photonics, C4334–01 as a detector, and the laser light second harmonic generation SHG, 410 nm of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950 L2S, fwhm = 1.5 ps) as an excitation source.[21c] Lifetime were evaluated with software provided with the equipment.

Nanosecond transient absorption measurements: Nanosecond transient absorption measurements were carried out by using the SHG (532 nm) of an Nd:YAG laser (Spectra Physics, Quanta-Ray GCR-130, fwhm 6 ns) as the 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).

(*E*)-1,2-Bis[2-(3,4-dihexylthienyl)]ethylene (4): Under an argon atmosphere, $TiCl_4$ (1.40 mL, 12.69 mmol) was slowly added to dry THF (100 mL) at 0 °C. The solution was agitated fro 15 min at this temperature. Then Zn powder (1.66 g, 25.38 mmol) was added portion wise and the mixture was agitated under reflux for one hour. After cooling to 0 °C, a solution of **3** (2.38 g, 8.46 mmol) and dry pyridine (1.20 mL) in dry THF (100 mL) were added. The mixture was refluxed over night. After cooling to room temperature, water was added and the phases were separated. The aqueous phase was extracted with dichloromethane. The organic phase was dried over $MgSO_4$. The resulting oil was purified by column chromatography (silica gel, hexane) to give **4** in 83% yield. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.98$ (s, 2H), 6.73 (s, 2H), 2.54 (t, $J = 7.60$ Hz, 4H), 2.47 (t, $J = 7.60$ Hz, 4H), 1.65–1.55 (m, 8H), 1.70–1.20 (m, 24H), 0.89 ppm (brs, 12H).

(*E*)-1-(5-Formyl-3,4-dihexyl-2-thienyl)-2-(3′,4′-dibutyl-2′-thienyl)ethylene (5): Under an argon atmosphere, $POCl_3$ (0.61 mL, 6.58 mmol) was added to a solution of **4** (2.79 g, 5.27 mmol) and DMF (0.61 mL, 7.90 mmol) in dry DCE (45 mL). The mixture was stirred over night under reflux. After cooling to room temperature, a 1 M solution of sodium acetate was added until the solution became neutral. The mixture was stirred at room temperature for one hour. The phases were separated and the aqueous phase was extracted with dichloromethane. The organic phase was dried over $MgSO_4$. The resulting oil was purified by column chromatography (silica gel, hexane/CH_2Cl_2 1:1) to give **5** in 81% yield.

trans-*Isomerization*: The mixture was dissolve in dry toluene and a catalytic amount of iodine was added. The reaction was heated under reflux for 3 days. The resulting solution was washed with an aqueous $Na_2S_2O_3$ solution (1 M) and water. The organic phase was evaporated and the resulting oil was purified by column chromatography (silica gel, hexane/CH_2Cl_2 1:1). ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.97$ (s, 1H), 7.26 (d, $J = 15.8$ Hz, 1H), 6.95 (d, $J = 15.7$ Hz, 1H), 6.84 (s, 1H), 2.84 (t, $J = 7.0$ Hz, 2H), 2.0 (t, $J = 7.0$ Hz, 4H), 2.48 (t, $J = 7.0$ Hz, 2H), 1.60–1.25 (m, 32H), 0.90 ppm (brs, 12H).

(*E*,*E*,*E*)-1,2-Bis[5-(3′,4′-dihexyl-2′-thienylvinyl)(3,4-dihexyl-2-thienyl)]-ethylene (6): Under an argon atmosphere, $TiCl_4$ (0.67 mL, 6.06 mmol) was slowly added to dry THF (50 mL) at 0 °C. The solution was agitated for 15 min at this temperature. Then Zn powder (792 mg, 12.12 mmol) was added portion wise and the mixture was agitated under reflux for one hour. After cooling to 0 °C, a solution of **5** (2.25 g, 4.04 mmol) and dry pyridine (4 mL) in dry THF (50 mL) were added. The mixture was refluxed over night. After cooling to room temperature, water was added and the phases were separated. The aqueous phase was extracted with dichloromethane. The organic phase was dried over $MgSO_4$. The resulting oil was purified by column chromatography (silica gel, hexane) to give **6** in 70% yield. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.00$ (s, 3H), 6.99 (s, 3H), 6.77 (s, 2H), 2.60–2.46 (m, 16H), 1.66–1.25 (m, 64H), 0.95–0.92 ppm (m, 24H); MALDI-TOF MS: *m*/*z*: 1081.90 $[M+1]^+$.

Synthesis of 7: Under an argon atmosphere, $POCl_3$ (0.33 mL, 3.49 mmol) was added to a solution of **6** (3.02 g, 2.79 mmol), DMF (0.33 mL, 4.19 mmol) in dry DCE (50 mL). The mixture was stirred one night under reflux. After cooling to room temperature, a 1 M solution of sodium acetate was added until the solution became neutral. The mixture was stirred at room temperature for one hour. The phases were separated and the aqueous phase was extracted with dichloromethane. The organic phase was dried over $MgSO_4$. The resulting oil was purified by column chromatography (silica gel, hexane/CH_2Cl_2 1:1) to give **7** in 52% yield (1.60 g, 1.44 mmol) and **7*** in 34% yield.

Data for **7**: ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.97$ (s, 1H), 7.26 (d, $J = 15.3$ Hz, 1H), 6.99 (s, 2H), 6.98 (s, 4H), 6.76 (s, 1H), 2.84 (t, $J = 7.70$ Hz, 2H), 2.88–2.44 (m, 14H), 1.60–1.25 (m, 64H), 0.90 ppm (m, 24H); MALDI-TOF MS: *m*/*z*: 1109.91 $[M+1]^+$.

Data for **7***: ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.97$ (s, 2H), 7.26 (d, J = 15.40 Hz, 2H), 7.01 (s, 2H), 6.94 (d, $J = 15.40$ Hz, 2H), 2.85 (t, $J = 8.0$ Hz, 2H), 2.6 (brs, 12H), 2.47 (t, $J = 8.0$ Hz, 2H), 1.75–1.25 (m, 64H), 0.90 ppm (brs, 24H); MALDI-TOF MS: *m*/*z*: 1137.92 $[M+1]^+$.

Compound 8: Under an argon atmosphere, $TiCl_4$ (204 mg, 1.07 mmol) was slowly added to dry THF (50 mL) at 0 °C. The solution was agitated for 15 min at this temperature then Zn powder (140 mg, 2.14 mmol) was added portion-wise and the mixture agitated under reflux for one hour. After cooling to 0 °C, a solution of **5** (100 mg, 0.18 mmol), ferrocene carboxaldehyde (154 mg, 0.72 mmol) and pyridine (100 μL) in dry THF (50 mL) was added. The mixture was refluxed over night. After cooling to room temperature, water was added and the phases were separated. The aqueous phase was extracted with dichloromethane. The organic phase was dried over $MgSO_4$, evaporated and the resulting solid was purified by column chromatography (Florisil, hexane) to give **8** in quantitative yield. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.98$ (s, 2H), 6.83 (d, $J = 15.8$ Hz, 1H), 6.76 (s, 1H), 6.63 (d, $J = 15.8$ Hz, 1H), 4.45 (t, $J = 1.8$ Hz, 2H), 4.30 (t, $J = 1.8$ Hz, 2H), 4,15 (s, 5H), 2.66–2.46 (m, 8H), 1.70–1.20 (m, 32H), 0.91 ppm (brs, 12H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 143.4$, 141.3, 139.8, 139.7, 137.1, 135.1, 134.0, 126.2, 119.4, 119.3, 118.1, 117.7, 83.6, 69.2, 69.0, 66.6, 31.7, 31.6, 31.6, 31.3, 31.1, 31.0, 29.7, 29.6, 29.4, 29.3, 29.0, 27.0, 22.7, 22.6 ppm; FT-IR (KBr): $\tilde{\nu} = 2917$, 2880, 2676, 1629, 1462, 923, 813, 719 cm^{-1}; MALDI-TOF MS: *m*/*z* (%): 738.2 $[M]^+$.

Compound 9: Under an argon atmosphere, $POCl_3$ (23 mg, 0.15 mmol) was added to a solution of **8** (90 mg, 0.12 mmol), DMF (14 mg, 0.19 mmol) in dry DCE (50 mL). The mixture was stirred one hour under reflux. After cooling to room temperature, a 1 M solution of sodium acetate was added until the solution became neutral. The mixture was stirred at room temperature for one hour. The phases were separated and the aqueous phase was extracted with dichloromethane. The organic phase was dried over $MgSO_4$ and evaporated; the resulting oil was purified by column chromatography (Florisil, hexane/CH_2Cl_2 1:1) to give, in quantitative yield, an *E*/*Z* isomeric mixture of **9** and **9′** in a 5:2 proportion according to ^1H NMR signals. At this stage, further purification by column chromatography (silicagel, CH_2Cl_2/Hexan 1:1) afforded pure **9** in sufficient quantity for analytical purpose, but due to major decomposition of the compounds in these conditions (as well as using neutral or basic alumina instead of silica gel), this technique could not be employed for the purification of **9** in a synthetic scale. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, TMS): $\delta=9.97$ (s, 1H), 7.25 (d, $J=15.4$ Hz, 1H), 6.94 (d, $J=15.4$ Hz, 1H), 6.83 (d, $J=15.8$ Hz, 1H), 6.68 (d, $J=15.8$ Hz, 1H), 4.46 (t, 2H), 4.32 (t, 2H), 4,15 (s, 5H), 2.85 (t, 2H), 2.70–2.40 (m, 6H), 1.70–1.20 (m, 32H), 0.90 ppm (t, 12H); FT-IR (KBr): $\tilde{\nu}=3295$, 2920, 1679, 1595, 1502, 1300, 1272, 1107, 839, 752, 694 cm^{-1}; MALDI-TOF MS: m/z: 1291.06 $[M+H]^+$.

Compound 10: Under an argon atmosphere, TiCl$_4$ (800 mg, 4.22 mmol) was slowly added to dry THF (100 mL) at 0 °C. The solution was agitated for 15 min at this temperature, then Zn powder (551 mg, 8.43 mmol) was added portion-wise and the mixture was agitated under reflux for one hour. After cooling to 0 °C, a solution of **7** (780 mg, 0.70 mmol), ferrocene carboxaldehyde (602 mg, 2.81 mmol) and pyridine (700 µL) in dry THF (100 mL) were added. The mixture was refluxed one night. After cooling to room temperature, water was added and the phases were separated. The aqueous phase was extracted with dichloromethane. The organic phase was dried over MgSO$_4$, evaporated and the resulting solid was purified by column chromatography (silica gel, CH$_2$Cl$_2$/hexane 1:4) to give **10** with a yield of 47 %. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, TMS): $\delta=6.98$ (s, 6H), 6.85, (d, $J=15.8$ Hz, 1H), 6.75 (s, 1H), 6.63, (d, $J=15.8$ Hz, 1H), 4.46 (t, $J=1.8$ Hz, 2H), 4.31 (t, $J=1.8$ Hz, 2H), 4,15 (s, 5H), 2.65–2.50 (m, 12H), 1.70–1.25 (m, 64H), 0.91–0.83 ppm (m, 24H); ^{13}C NMR (50 MHz, CDCl$_3$, 25 °C, TMS): $\delta=143.8$, 142.0, 141.9, 140.5, 140.2, 137.1, 135.9, 135.5, 135.2, 134.4, 126.7, 120.1, 119.8, 119.5, 119.3, 119.1, 118.2, 83.7, 69.5, 66.9, 31.9, 31.8, 31.4, 31.2, 31.1, 29.9, 29.6, 29.5, 29.2, 27.2, 22.8, 14.1 ppm; FT-IR (KBr): $\tilde{\nu}=917$, 2853, 2677, 1635, 1462, 1398, 1039, 923, 811, 723 cm^{-1}; MALDI-TOF MS: m/z: 1291.95 $[M]^+$.

Compound 11: Under an argon atmosphere, POCl$_3$ (41 µL, 0.45 mmol) was added to a solution of **10** (460 mg, 0.36 mmol), DMF (42 µL, 0.53 mmol) in dry DCE (20 mL). The mixture was stirred for 90 min under reflux. After cooling to room temperature a 1 M solution of sodium acetate was added until the solution became neutral. The mixture was stirred at room temperature for one hour. The phases were separated and the aqueous phase was extracted with dichloromethane. The organic phase was dried over MgSO$_4$. The resulting oil was passed through a column chromatography (silica gel, toluene/hexane 1:1) to give **11** in 29 % yield. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, TMS): $\delta=9.98$ (s, 1H), 7.00 (s, 4H), 4.47 (m, 2H), 4.32 (m, 2H), 4.16 (s, 5H), 2.85 (m, 2H), 2.70–2.40 (m, 10H), 1.70–1.20 (m, 64H), 0.93–0.88 ppm (m, 24H); MALDI-TOF MS: m/z: 1319.96 $[M+1]^+$.

Compound 12: A mixture of C$_{60}$ (94 mg, 0.13 mmol), **9** + **9′** (as an *E*/*Z* isomeric mixture; 100 mg, 0.13 mmol), and sarcosine (12 mg, 0.13 mmol) was refluxed under argon in dry toluene (100 mL) during 48 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/toluene 6:4) to give first **12** and a mixture of **12** and **12′**. Despite the use of several columns, **12′** could not be obtained in its pure form but only as a *cis*/*trans* isomeric mixture. Overall cycladdition yield: 24 % (45 mg, 0.03 mmol). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta=7.02$ (d, $J=15.8$ Hz, 1H), 6.92 (d, $J=15.8$ Hz, 1H), 6.78 (d, $J=15.4$ Hz, 1H), 6.59 (d, $J=15.4$ Hz, 1H), 5.34 (s, 1H), 5.01 (d, $J=10.0$ Hz, 1H), 4.44 (brs, 2H), 4.28 (brs, 2H), 4.26 (d, $J=10.0$ Hz, 1H) 4,14 (s, 5H), 2.94 (s, 3H), 2.70–2.40 (m, 8H), 1.70–1.20 (m, 32H), 0.95–0.85 ppm (m, 12H); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, TMS): $\delta=155.8$, 154.0, 153.2, 152.6, 147.3, 146.9, 146.3, 146.2, 146.1, 146.0, 145.9, 145.8, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.1, 144.6, 144.3, 143.1, 142.9, 142.6, 142.5, 142.2, 142.1, 141.9, 141.8, 141.7, 141.6, 141.5, 140.1, 139.7, 139.8, 139.7, 137.2, 136.6, 135.7, 135.6, 135.5, 135.4, 133.7, 130.9, 126.4, 119.9, 118.7, 118.4, 118.0, 79.5, 70.1, 69.2, 69.1, 66.7, 40.5, 31.7, 31.4, 31.1, 30.6, 29.7, 29.4, 29.0, 28.7, 28.3, 27.0, 22.6, 14.2 ppm; FT-IR (KBr): $\tilde{\nu}=2917$, 2851, 2353, 1462, 931, 816, 526 cm^{-1}; MALDI-TOF MS: m/z: 1514.71 $[M+1]^+$.

Compound 13: Under an argon atmosphere, a mixture of C$_{60}$ (74 mg, 0.10 mmol), **11** (136 mg, 0.10 mmol), and sarcosine (9 mg, 0.10 mmol) was refluxed in dry toluene (100 mL) during 48 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/toluene 2:8) to give **13** in 27 % yield (58 mg, 0.028 mmol). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta=6.96$ (brs, 6H), 6.82 (d, $J=15.6$ Hz, 1H), 6.62 (d, $J=15.6$ Hz, 1H), 5.34 (s, 1H), 5.02 (d, $J=9.8$ Hz, 1H), 4.44 (s, 2H), 4.29 (s, 2H), 4.25 (d, $J=9.8$ Hz, 1H), 4,14 (s, 5H), 2.94 (s, 3H), 2.55 (brs, 16H), 1.40–1.30 (m, 64H), 0.95–0.85 ppm (m, 24H); ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, TMS): $\delta=156.2$, 154.3, 153.5, 147.5, 146.6, 146.4, 144.9, 144.4, 143.4, 143.2, 142.4, 142.1, 141.8, 140.4, 140.2, 138.4, 137.1, 136.9, 135.9, 135.6, 135.3, 132.8, 126.6, 119.7, 118.3, 97.4, 83.9, 69.5, 69.3, 66.9, 40.8, 32.0, 31.9, 31.8, 31.4, 29.9, 29.8, 29.5, 29.2, 27.3, 22.9, 22.8, 14.4 ppm; FT-IR (KBr): $\nu=2938$, 2865, 2347, 1463, 924, 815, 523 cm^{-1}; MALDI-TOF MS: m/z: 2067.72 $[M]^+$.

Compound 14: A mixture of C$_{60}$ (129 mg, 0.18 mmol), **5** (100 mg, 0.18 mmol), and sarcosine (16 mg, 0.18 mmol) was refluxed under argon in dry toluene (150 mL) for 48 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/toluene 16:9) to give **14** in 23 % yield (53 mg, 0.04 mmol). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta=7.04$ (d, $J=15.8$ Hz, 1H), 6.93 (d, $J=15.8$ Hz, 1H), 6.73 (s, 1H), 5.33 (s, 1H), 5.02 (d, $J=10.0$ Hz, 1H), 4.26 (d, J = 10.0 Hz, 1H), 2.93 (s, 3H), 2.78 (m, 1H), 2.60 (m, 5H), 2.46 (t, 2H), 1.59–1.22 (m, 32H), 0.94–0.82 ppm (m, 12H).

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