Fullerenes

Versatile Bisethynyl[60]fulleropyrrolidine Scaffolds for Mimicking Artificial Light-Harvesting Photoreaction Centers

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Abstract: Fullerene-based tetrads, triads, and dyads are presented in which [60]fulleropyrrolidine synthons are linked to an oligo(*p*-phenyleneethynylene) antenna at the nitrogen atom and to electron-donor phenothiazine (PTZ) and/or ferrocene (Fc) moieties at the α carbon of the pyrrolidine cycle through an acetylene spacer. Cyclic voltammetry and UV/ Vis absorption spectra evidence negligible ground-state electronic interactions among the subunits. By contrast, strong excited-state interactions are detected upon selective

Introduction

In natural photosynthesis, sunlight is converted into chemical energy by a complex sequence of reactions initiated by a cascade of energy- and electron-transfer processes.^[1,2] Initially, sunlight is absorbed by light-harvesting pigments, that is, the antenna moieties, which funnel the excitation energy to the so-called reaction center through a sequence of energy-transfer steps.^[3] At the reaction center, the energy is utilized to trigger an electron-transfer reaction that constitutes the primary step of energy harvesting.^[3] Understanding these fundamental processes has prompted chemists to engineer artificial chemical assemblies that mimic them and might provide the basis for artificial solar-energy conversion devices.^[4,5]

In this context, C_{60} and its derivatives are optimal components to be incorporated into artificial reaction centers

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light irradiation of the antenna (UV) or of the fullerene scaffold (Vis). When only PTZ is present as electron donor, photoinduced electron transfer to the fullerene unit is unambiguously detected in benzonitrile, but this is not the case when Fc is part of the multicomponent system. These results suggest that Fc is a formidable energy transfer quencher and caution should be used in choosing it as electron donor to promote efficient charge separation in multicomponent arrays.

because of the exceptional electron-accepting properties, the low-lying level of their excited states, their small reorganization energy, and their remarkable stability under light irradiation.^[6,7] In particular, their use in donor–acceptor systems for photovoltaic devices has impressively expanded.^[8,9] To this end, a variety of [60]fullerene derivatives linked to electron-donating units such as, among others, porphyrins,^[10–14] tetrathiafulvalenes (TTFs),^[15] ferrocene,^[16] phthalocyanines,^[17] oligophenylene-vinylenes,^[18] and transition-metal complexes^[19–21] have been prepared. The mechanisms of photoinduced electron and energy transfer have been elucidated by means of time-resolved spectroscopic methods, thus showing a strong intramolecular quenching of the excited singlet and triplet states of C_{60} through the formation of charge-separated (CS) radical ion pairs.

One of the main challenges in this field of research is the rational assembly of different molecular components in a spatially organized fashion to enable stepwise light harvesting and conversion of light into chemical energy.^[22] In this context, we have now designed and synthesized a novel fullerene scaffold that features geometrical constraints that afford a hierarchical and spatial organization of the chromophores (Figure 1). In particular, by exploiting the 1,3-dipolar cycloaddition on $C_{60'}^{[23]}$ we have prepared tetrads that bear a chromophoric antenna (an oligo(p-phenyleneethynylene) derivative, OPE) directly attached the nitrogen atom of [60]fulleropyrrolidine and two photoactive electron-donor moieties (i.e., ferrocene (Fc) and phenothiazine (PTZ)) rigidly attached to the α carbon of the same pyrrolidine ring (Figure 1) through an acetylene spacer. A full account of the electrochemical and photophysical properties of conjugates 1-4 along with those of the corresponding reference compounds 7-10 (Figure 2) is reported, which shows the occurrence of a charge-separated state that lives for 250 ns

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Figure 1. Chromophore hierarchical organization of the fullerene-based photoreaction centers proposed in this work (ε_{T} = energy transfer, e_{-T}^{-} = electron transfer, $E_{DG1/2}$ represents the electron donor groups).

for molecule **4**. Notably, for the derivatives that contain the ferrocenyl moiety, the spectroscopic fingerprints of the electronic excited states of the individual components are completely quenched in both toluene (PhMe) and in benzonitrile (PhCN), thus suggesting ultrafast quenching by energy transfer to the Fc units. could be the precursors of choice to form tetrads. Nevertheless, only a limited number of reports describe the 1,3-dipolar cycloaddition of azomethine ylides using ketones,^[37–47] and in most cases with modest yields (<40%). This has prompted us to further investigate the feasibility of the 1,3-dipolar cycloaddition of azomethine ylides generated from the thermal condensation of α -amino acids and various ketones.

1,3-Dipolar cycloaddition of azomethine ylides generated in situ using ketones

Effects of the hydrocarbon substituents: As a starting point we studied the 1,3-dipolar cycloaddition of azomethine ylides generated by the condensation reaction of three different symmetric ketones (Table 1): an aliphatic (11),^[43] an aromatic (12), and an ethynyl silylated derivative (13 and 14)^[48,49], with sarcosine (15) or other (16 and 17) amino acids under reflux conditions in PhMe or *o*-dichlorobenzene (ODCB).

By using undecan-6-one (11), the corresponding [60]fulleropyrrolidine 18a was obtained in modest yields (Table 1, entry a) after 16 h under reflux conditions in ODCB. Surprisingly, when using benzophenone (12), no conversion of the initial ketone was observed (Table 1, entry b). However, when using

Results and Discussion

Synthesis

Among the synthetic methods to functionalize C_{60} ^[24-27] the 1,3-dipolar cycloaddition of azomethine ylides^[23, 28, 29] to yield [60]fulleropyrrolidines that are formed across the 6-6 junction of the fullerene core is certainly one of the most attractive route for preparing covalent conjugates for materials science. This because [60]fulleropyrrolidines are known to be very stable under both oxidative and reductive conditions, and the retrocycloaddition reaction^[30, 31] is essentially observed under harsh conditions (heating to reflux in o-dichlorobenzene (ODCB) in the presence of a strong dipolarophile and a Lewis acid such as Cu(OTf)₂). Although azomethine ylides are unstable and must be prepared in situ, several methods have been developed for their synthesis, such as proton abstraction from imine derivatives of α -amino acids, thermolysis or photolysis of aziridines, and dehydrohalogenation and decarboxylation of immonium salts derived from thermal condensation of α amino acids and aldehydes or ketones. In particular, depending on the chemical nature of the carbonyl (aldehyde or ketone) and amino acid derivatives, different functional groups can be introduced on the three different positions of the pyrrolidine ring, and a large variety of [60]fullerene dyads and triads can be synthesized a priori.^[7, 11, 17, 32-36] By taking advantage of the versatile 1,3-dipolar cycloaddition of azomethine ylides to C_{60} , we found that ketones



Figure 2. Chemical structures of the targeted [60]fulleropyrrolidine-based chromophores (Hex $=-C_{6}H_{\rm 13}$).

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Table 1. 3-Dipolar cycloaddition of azomethine ylides to C_{60} generated in situ through thermal decarboxylationof immonium salts derived from the condensation of ketones 11–14 and amino acids 15–17.



tetramethylsilane (TMS)- or triisopropylsilyl (TIPS)-protected ketones **13** and **14**, the corresponding [60]fulleropyrrolidines, **18b** and **18c**, were obtained with high yields (61 and 72%, respectively; Table 1, entries c and d). Notably, under reflux conditions in ODCB, TMS-protected ketone **13** led to lower yields (42%), probably due to thermal decomposition. Interestingly, when sarcosine was replaced by more soluble amino acids (i.e., derivatives **16** and **17**), an unprecedentedly high yield of 92% was obtained with *tert*-butyloxycarbonyl (Boc)-protected amino acid **17** (Table 1).

Electronic effects: We then investigated the formation and reactivity of azomethine ylides using ketones that bore different electron-donating (ED) or electron-withdrawing (EW) groups (**19–21**; Scheme 1 and Table 2). 1,5-Bis(phenyl)penta-

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1,4-diyn-3-one (19) and 1,5-bis[p-N,N-di(n-hexyl)anilino]penta-1,4diyn-3-one (20) were prepared according to the reported procedures,^[50, 51] whereas 1,5-bistrifluormethylpenta-1,4-diyn-3-one (21) was synthesized by following the route displayed in Scheme 2. Starting from commercially available prop-2-yn-1ol, Sonogashira-type cross-coupling with 1-bromo-4-(trifluoromethyl)benzene (22) followed by oxidation of alcohol intermediate 25 with BaMnO₄ gave 3-[4-(trifluoromethyl)phenyl]prop-2ynal (26) in very good yields (Scheme 1). Addition of Li-ethynylide analogue of derivative 23 to aldehyde 26 gave, after oxida-

0 0 20 N(nHex)₂ F₂C 21 (nHex)₂N BaMnO₄ (2 eq.) 88% CH₂Cl₂, RT, 16h 1) TMS-acetylene (1.2 eq.) Cul (0.01 eq.) 1) *n*BuLi (1 eq.) THE. -40 to 0°C, 15 min. 2) **26** (1 eq.) [PdCl₂(PPh₃)₂] (0.02 eq.) ОН (iPr)₂NH/DMF (4/1) -40°C to RT. 2h 3) aq. NH₄Cl μW, 90°C, 25 min. 47% 2) K₂CO₃ (0.1 eq.) MeOH, RT, 2H 24 F₂C CF₂ 23 98x75% B 22 Prop-2-yn-1-ol (1.2 eq.) Cul (0.01 eq [PdCl₂(PPh₃)₂] (0.02 eq.) OH BaMnO₄ (2 eq.) F₂(F₂C (iPr)2NH/DMF (4/1) CH2Cl2, RT, 24h μΨ, 90°C, 15 min. 25 26 71% 94%

Scheme 1. Synthesis of CF_3 -terminating ketone 21. Ketones 19–20 were prepared by following the protocols described in the literature.^[50,51]

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tion, the desired ketone (**21**; Scheme 1).

Whereas from ketone 19 and sarcosine 15, the corresponding addition product 18f was obtained with good yield (48%) after 48 h under reflux conditions in PhMe (Table 2, entry a), no product formation was detected when the reaction was performed in ODCB (Table 2, entry b) despite the full conversion of the ketone. Notably, when electron-rich ketone 20 was employed, no conversion of the latter was observed in PhMe (Table 2, entry c), whereas [60]pyrrolidinofullerene 18 a was isolated with modest yield when ODCB was used as a solvent (Table 2, entry d). Finally, when using electron-deficient

ketone **21**, the corresponding addition product **18h** was obtained with good yields (59%) after 48 h (Table 2, entry e). Again, no product was observed under reflux conditions in ODCB (Table 2, entry f).

Synthesis of the chromophoric dyad, triads, and tetrads

The synthesis of the dyad (2), triads (3–5), and tetrads (1 and 6) shown in Figure 2 are reported in Scheme 2 and in the Supporting Information. The same synthetic strategy as that described in the previous sections has been used for all chromophores, therefore in this section we describe only the preparative route for tetrad 1. The reader can find all the detailed experimental conditions in the Supporting Information (all known intermediates have been synthesized following







Scheme 2. Synthetic route toward tetrad 1 (Hex = $-C_6H_{13}$). For the other chromophoric systems, see the Supporting Information.

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the literature protocols).^[23,48–58] By exploiting the ketone strategy, molecule **1** could be obtained by 1,3-dipolar cycloaddition

to C_{60} of the azomethine ylide generated by the condensation of OPE-bearing amino acid **37** with ketone **42** (Scheme 2).

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The synthesis of amino acid 37 started with the regioselective iodination of 27 using ICI in MeOH to give 1-bromo-4-iodoaryl derivative 28 in good yield. The latter was then coupled with trimethylsilylacetylene (TMSA) under Sonogashira-type cross-coupling conditions to yield bromoaryl 29, which was subsequently subjected to a second cross-coupling reaction with 2-ethynylaryl 30 (prepared according to reported procedures;^[59-61] see the Supporting Information) to yield, after deprotection of the TMS protecting group, bisphenylethynyl derivative 32 in 63% over three steps. Molecule 32 was then coupled with another equivalent of 1-bromo-4-iodoaryl derivative 28 to give bromo-terminating OPE derivative 33. A final cross-coupling reaction between 33 and 4-pentyn-1-ol gave alcohol 34, which was converted into aldehyde 35 under Swern oxidation conditions. Reductive amination of the latter gave, after saponification, targeted OPE-bearing amino acid 37.

The synthesis of ketone **42** started with the synthesis of iodophenyl-phenothiazine **38**, which was prepared by following the protocols reported in the literature,^[54,55] except for the Pd-catalyzed cross-coupling reaction, which was performed under microwave conditions (see the Supporting Information). Molecule **38** was coupled to TMSA (**39**) and converted into aldehyde **40** by successive deprotection (**10**) and lithiation exchange reaction with *n*BuLi followed by addition of DMF. Subsequent addition of Li-ethynylferrocene to a solution of aldehyde **40** gave alcohol **41**, which, after oxidation with BaMnO₄, was transformed into targeted ketone **42** with an overall yield of 76% over two steps.

In situ condensation of an equimolar mixture of α -amino acid **37** and ketone **42** followed by thermal decarboxylation in the presence of two equivalents of C₆₀ in PhMe under reflux conditions for five days gave, after purification, the expected tetrad **1** in a yield of 21% (Scheme 2).

Electrochemical studies

Cyclic voltammetry: The voltammograms of reference molecular subunits 7-10 and of the multichromophoric systems 1-4 in CH_2CI_2 with 0.1 mol L⁻¹ nBu_4NCIO_4 (TBAP) are depicted in Figure 3. Within the electrochemical stability window of the solvent, fulleropyrrolidine reference 7 exhibits three reversible reduction waves at -0.62, -1.02, and -1.53 V, which are in good agreement with the literature data.^[62,63] Notably, the reduction behavior of the fullerene moiety is virtually unaffected over the whole series of multicomponent systems (Table 3). Molecular reference compounds 8, 9, and 10 do not exhibit any detectable reduction processes. However, reference ferrocene 9 and phenothiazine 10 show a quasi-reversible oxidation wave at 0.63 and 0.78 V, respectively. These potentials are little or not affected in the two triads but get closer in the tetrad, in which the wave of ferrocene 9 slightly shifts anodically (0.66 V) and overlaps that of phenothiazine 10, which in turn moves to less positive potentials (0.72 V). This behavior likely reflects a non-negligible electronic interaction between the two geminal electron donors linked at the 2-position of the pyrrolidine ring and therefore in close proximity.

Reference OPE **8** exhibits an irreversible oxidation process with two partially overlapping waves; the half-wave potential related to the first shoulder is at 1.17 V ($E_{1/2}$, Table 3). The oxidation behavior of fullerene derivatives **2**, **3**, and **4** relative to fulleropyrrolidine reference **8** is significantly different, with a new irreversible peak appearing at about 1.07 V (marked with an asterisk in Figure 3). The related process is likely the



Figure 3. Voltammograms of reference molecular subunits **7–10** and of multicomponent systems **1–4** obtained in CH_2Cl_2 with 0.1 mol L⁻¹ nBu_4NCIO_4 (TBAP) as supporting electrolyte. Scan rate: 0.2 Vs⁻¹.

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Table 3. Standard redox potentials in CH_2Cl_2 with 0.1 mol L^{-1} TBAP versus SCE (-0.47 V versus Fc/Fc⁺). Working electrode: Pt, counter electrode: Pt. Scan rate: 0.1 Vs⁻¹. $E^{\circ} = E_{pa} - \Delta E_{pp}/2$, in which E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively; $\Delta E_{pp} = E_{pa} - E_{pc}$. For the irreversible process, the half-wave potential has been reported as the best approximation of E° .

	$E^{\rm o}_{\rm red3}$ [V]	$E^{\rm o}_{\rm red2}$ [V]	$E_{\rm red1}^{\rm o}$ [V]	E_{ox1}^{o} [V]	E_{ox1}^{o} [V]	E _{1/2} (ox3) [V]
9	-	-	-	0.63	-	-
10	-	-	-	-	0.78	-
8	-	-	-	-	-	1.17(irr)
7	-1.53	-1.02	-0.62	-	-	-
2	-1.55	-1.01	-0.62	-	-	1.02
3	-1.52	-1.00	-0.62	0.61	-	1.06
4	-1.53	-1.00	-0.62	-	0.78	1.06
1	-1.53	-1.01	-0.63	0.66	0.72	1.15

result of an interaction between the OPE antenna and the fullerene moiety. Notably, the peak at +1.07 V is not detected in the tetrad, in which the two previously accumulated charges could anodically shift the related process toward potentials close to that of the reference OPE module **8**.

Spectroelectrochemistry of 10: A 0.5 mmol L^{-1} solution of reference phenothiazine **10** in PhCN with 0.1 mol L^{-1} TBAP exhibits an electronic absorption spectrum with maximum at 314 nm (Figure 4, black dashed line). By increasing the poten-



Figure 4. Spectroelectrochemistry of reference phenothiazine **10** in PhCN with 0.1 mol L⁻¹ TBAP as supporting electrolyte. The black profile is obtained at open circuit voltage (OCV), whereas the other traces are the spectra recorded at increasing potentials under steady-state currents (Fc/Fc⁺ = 0.08 V versus Ag/Ag⁺). Inset: Voltammogram of **10** at 0.1 Vs⁻¹ on Pt grid in the spectroelectrochemical cell. The potentials at which the spectra have been recorded are marked on the oxidation wave.

tial up to the half-wave oxidation value (0.35 V versus Ag/Ag⁺; Figure 4, inset) the absorption peak of **10** decreased by about 10% and two envelopes of absorption bands appeared in the ranges 400–600 and 650–900 nm, which are attributable to the PTZ radical cation. The extinction coefficient of this species at the absorption maximum (520 nm) was estimated to be $1.7 \times$ 10^4 cm⁻¹ mol⁻¹, assuming that the 9% absorption decrease centered at 314 nm and 0.35 V leads to the formation of a corresponding amount of the radical cation of **10**.^[64] This value is comparable to that reported for phenothiazine derivatives such as promazine and chlorophenazine.^[65]

Photophysical studies

absorption Ground-state and luminescence properties: The absorption spectra of the reference molecules N-methylfulleropyrrolidine (7), OPE antenna module 8, and of the multicomponent systems 2 and 4 in toluene (PhMe) solutions are depicted in Figure 5. Owing to the negligible absorption of the ferrocene moiety (see below), the spectra of reference dyad 1 and triad 3 are virtually identical to those of fulleropyrrolidine derivatives 2 and 4, respectively, and are not reported in Figure 5. The absorption spectra of the reference electron-donor modules 10 and 9 in PhMe are characterized by moderate to low extinction coefficients, which is in line with the literature data^[66] (Figure S1 in the Sup-





Figure 5. Absorption spectra in PhMe solution: 7 (black), 8 (gray), 2 (dashed line), and 4 (dotted line). The inset shows the enlarged spectra in the region from 430 to 700 nm.

porting Information). Molecule 10 weakly absorbs in the UV spectral window with a maximum at 325 nm ($\varepsilon = 6 \times$ $10^3 \,\mathrm{m^{-1} \, cm^{-1}}$). In agreement with the literature reports, ferrocene **9** exhibits a faint band at $\lambda_{max} = 450 \text{ nm}$ ($\varepsilon = 10^2 \text{ M}^{-1} \text{ cm}^{-1}$; Figure S1 in the Supporting Information), which arises from spin-allowed d-d electronic transitions.[66] The reference antenna unit 8 exhibits a strong absorption band with a maximum at 385 nm ($\varepsilon = 4.6 \times 10^4 \,\mathrm{m^{-1} \, cm^{-1}}$), in line with similar OPEs.^[67] The substantial intensity difference of the absorption spectrum of 8 with respect to electron donors 9 and 10 allows for the selective excitation of the antenna moiety in the multicomponent systems. Reference N-methylfulleropyrrolidine (7) exhibits broad absorption across the UV and visible regions, which is also in accordance with the literature reports.^[7] The absorption spectra of dyad 2, triads 3 and 4, as well as tetrad 1 are essentially the sum of the spectra of their molecular fragments, thus indicating negligible intramolecular interactions in the ground state.

Reference phenothiazine donor **10** is weakly luminescent $(\lambda_{max} = 450 \text{ nm}, \Phi_{em} = 1\% \text{ in PhMe};$ Figure S2 in the Supporting Information). As expected, reference ferrocenyl **9** deactivates nonradiatively from its lowest-lying triplet level and does not exhibit any luminescence.^[68] Reference OPE **8** shows a strong fluorescence band with $\lambda_{max} = 420 \text{ nm}$ ($\Phi_{em} = 64\%$ in PhMe and

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42% in PhCN, with a τ of 1.1 ns in both solvents), which is attributable to the deactivation from the lowest-lying singlet excited state (Figure S2 in the Supporting Information). Similar quantum efficiencies and spectral features were reported earlier for analogous oligo(*p*-phenyleneethynylene) compounds.^[67] Fullerene derivative **7** exhibits a weak fluorescence band typical of fulleropyrrolidines with $\lambda_{max} = 710$ nm, $\tau = 1.4$ ns, $\Phi_{em} \approx 0.04\%$ in PhMe and PhCN (Figure S2 in the Supporting Information). These values are in accordance with the literature data.^[7]

The strong luminescence of the OPE fragment is dramatically quenched when attached to the fullerene chromophore. In PhMe, the fluorescence quantum yield of *N*-OPE fulleropyrrolidine **2** (λ_{exc} =385 nm) drops from 64 to 0.14%, whereas in PhCN it drops from 42 to 0.49% (Table 4), thus indicating

Table 4. Fluorescence quantum yields (Φ) and related excited-state lifetimes (τ).									
	OPE moiety			C_{60} moiety				r [pc] ^[d]	
	PhMe	PhCN	PhMe	PhMe	PhCN	PhMe	PhCN	PhMe	PhCN
8	64	43	1.1	-	-	-	-	-	-
7	-	-	-	0.04	0.04	1.4	1.3	1.4	1.4
2	0.14	0.49	pprox 0.025	0.04	0.03	1.4	1.4	1.4	1.4
4	0.20	0.42	pprox 0.025	0.03	0.01	1.5	0.7	1.6	0.8
3	0.17	0.49	pprox 0.025	< 0.01	< 0.01	_ ^[e]	_ ^[e]	_ ^[e]	_ ^[e]
1	0.18	0.48	pprox 0.025	< 0.001	< 0.001	_ ^[e]	_ ^[e]	_ ^[e]	_ ^[e]
[a] λ_{exc} = 385 nm. [b] λ_{exc} = 373 nm. [c] λ_{exc} = 500 nm. [d] λ_{exc} = 465 nm. [e] Too weak to be detected.									

strong excited-state intramolecular interactions between the fullerene and OPE moieties. Although the quenched lifetime of the antenna is at the limit of the resolution of our instrumentation, lifetime values of about 25 ps were determined in both PhMe and PhCN upon deconvolution of the decay profile of the laser excitation source, which set a lower limit for the rates of the quenching processes at about $4 \times 10^{10} \text{ s}^{-1}$.

Upon selective excitation of the OPE fragment, efficient sensitization of the *N*-methylfulleropyrrolidine was observed for dyad **2** in both PhMe and PhCN (Figure 6), thus indicating the expected antenna behavior. In PhMe, when excited at λ_{exc} =385 nm, the luminescence quantum yield (0.04%) and singlet lifetime (1.4 ns) of the fullerene core of **2** is exactly the same as that of reference **7**.^[69] These same values were obtained by the direct excitation of the fullerene moiety of **2** at 500 nm, thus confirming the quantitative energy transfer from the OPE moiety to the carbon sphere (Table 4).

In PhCN, upon excitation of the antenna, the luminescence of the fulleropyrrolidine moiety in **2** is about 40% lower ($\Phi_{\rm em}$ =0.03%) than (i) the reference **7** in the same solvent or (ii) **2** in PhMe, which can indicate the presence of a quenching process for the OPE unit in the more polar solvent. However, the singlet lifetime value of the fulleropyrrolidine moiety was determined to be 1.4 ns, regardless of the excitation wavelength. This suggests that the lower $\Phi_{\rm em}$ in PhCN of the fulleropyroles.



Figure 6. Emission spectra of the fulleropyrrolidine moiety upon its selective excitation at λ_{ex} = 500 nm in PhMe (left) and in PhCN (right) in **2** (black line), **4** (gray line), **3** (dotted line), and **1** (dashed line).

opyrrolidine moiety in dyad **2** upon excitation of the antenna is not due to quenching by photoinduced electron transfer but rather to a less efficient energy transfer in polar solvent, which was also previously observed in similar cases.^[70]

Photophysical properties of triad 4 in PhMe are similar to those of dyad 2. Similar quenching of luminescence and lifetime of the antenna moiety is observed as well as slightly less efficient sensitization of the fullerene fluorescence. For derivative 4 in PhCN, upon excitation of the OPE moiety, the sensitized emission from the singlet excited state of the fulleropyrrolidine unit is around 75% lower than that of reference molecules 7 and 2. Likewise, direct excitation of the fulleropyrrolidine moiety results in approximately 60% decreased emission (Figure 6). This trend was confirmed by measurements of the lifetime of the fulleropyrrolidine singlet excited state of 4, which was revealed to be reduced to about 750 ps for both direct (λ_{exc} = 465 nm) and sensitized excitation (λ_{exc} = 373 nm) in PhCN, thus indicating the presence of another quenching pathway, presumably electron transfer. In molecules 3 and 1 (Figure 6), the observed quenching of the fullerene singlet emission is virtually complete (\geq 95%), regardless of the solvent and excitation wavelength. However, the steady-state and time-resolved data on the quenching of the antenna moiety in 3 and 1 are essentially the same as molecules 2 and 4 (Table 4), which suggests the occurrence of an identical antenna→fulleropyrrolidine energy-transfer process (see above).

In the absence of excited-state deactivation processes, the lowest singlet level of the fullerene derivatives $({}^{1}C_{60}^{*})$ undergoes extensive intersystem crossing to yield the corresponding triplet $({}^{3}C_{60}^{*}).^{[71,72]}$ This species can be conveniently monitored in an indirect way by recording the emission of sensitized singlet oxygen in the near-infrared (NIR) region,^[20,73] which originates according to the following reaction scheme [Eq. (1)]:^[7]

$$C_{60} \xrightarrow{h\nu_{UV/VIs}} {}^{1}C_{60} \xrightarrow{*} \xrightarrow{isc} {}^{3}C_{60} \xrightarrow{*} \xrightarrow{O_{2}} C_{60} + {}^{1}O_{2} \xrightarrow{*} \rightarrow C_{60} + O_{2} + heat + h\nu_{1270 nm}$$
(1)

These measurements are reported in Figure 7 and provide a clear picture of the presence of the fullerene triplet in all of

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Figure 7. Sensitized singlet O₂ luminescence spectra in PhMe (left) and in PhCN (right) upon selective excitation of the fullerene moiety at $\lambda_{ex} = 500$ nm for **2** (black), **4** (gray line), **3** (dotted line), and **1** (dashed line).

our multicomponent arrays. Quantitative production of ${}^{3}C_{60}^{*}$ was determined only for dyad **2** in both solvents and for triad **4** in PhMe when compared to reference **7** under identical experimental conditions. These findings, along with the observed quenching of the OPE antenna by fluorescence measurements (see above), further confirm the light-harvesting character of this moiety to funnel the excitation energy to the lowest available excited state (${}^{3}C_{60}^{*}$), thus validating our molecular design approach.

On the contrary, triad **4** exhibits virtually no traces of ${}^{3}C_{60}^{*}$ in PhCN. This suggests that, in addition to the OPE \rightarrow fulleropyrrolidine energy transfer, the presence of a phenothiazine donor unit in a polar medium promotes an additional excited-state quenching process, presumably an electron transfer. This hypothesis is supported by electrochemical data, from which it is possible to place the energy of the charge-separated state that corresponds to the oxidation of the phenothiazine moiety and the reduction of the $C_{\rm 60}$ moiety in ${\bf 4}$ (Table 3) at 1.40 eV in CH₂Cl₂.^[74] This value sets an upper limit on the energy of the charge-separated (CS) state, which is expected to be even lower-lying in PhCN.^[7] The energy of the CS level clearly shows that an electron-transfer process is thermodynamically possible upon excitation of both the higher-lying antenna and fullerene singlet levels, placed at about 3.2 (estimated from the maximum of the fluorescence band, 385 nm) and 1.72 eV,^[7] respectively.

Finally, all architectures that incorporate a ferrocenyl moiety do not exhibit any measurable population of ${}^{3}C_{60}^{*}$, regardless of the solvent polarity. This behavior might also in principle indicate the occurrence of a photoinduced electron transfer, since the ferrocenyl unit exhibits an even lower oxidation potential than that of phenothiazine.

Transient absorption spectroscopy: To prove photoinduced electron transfer through the observation of radical cationic and anionic species, transient absorption spectra were recorded in O_2 -free PhCN. Formation of charge-separated states for the systems bearing the ferrocenyl unit (**3**, **1**) in both solvents was never evidenced. No fullerene radical anion bands in the NIR spectral region (900–1600 nm) were found down to a time

resolution of 30 ps. However, ferrocene is known to have no detectable fingerprints to be exploited for tracing photoinduced electron transfer and this further hampers unequivocal rationalization.^[63] In principle, the strong quenching of the fullerene excited states in all of the systems containing a ferrocenyl moiety can be attributed to the 1) ferrocenyl—fulleropyrrolidine electron transfer with ultrafast charge separation and slower charge recombination,^[75] or 2) fulleropyrrolidine \rightarrow ferrocenyl singlet to triplet Dexter energy transfer, as was determined for porphyrin–ferrocenyl dyads, for instance.^[76] In PhMe, the latter mechanism is likely to be operative as recently discussed for ferrocenyl–fullerene dyads^[63] and in line with bimolecular quenching studies that involve pristine C₆₀ and a number of ferrocenyl derivatives.^[68]

The transient absorption spectrum of triad **4** in degassed PhCN is radically different from those obtained for reference molecules **10** and **7** (Figures S3 and S4 in the Supporting Information), which exhibit maxima at 450 ($\tau = 4 \mu s$) and 690 ($\tau = 16.5 \mu s$) nm, respectively. Triad **4** shows a characteristic feature at 510 nm that can be attributed to the radical cation of the ED phenothiazine moiety (Figure 8), in accord with the absorption profiles obtained through spectroelectrochemical measurements for reference compound **10** (Figure 4). Moreover, in the NIR region, the radical anion of the fullerene moiety was detected at around 1000 nm,^[77] thereby confirming the occurrence of photoinduced electron transfer. Notably, the kinetics determined at 1000 nm are identical to that monitored at



Figure 8. Top: Transient absorption spectrum of **4** in O₂-free PhCN. Bottom: Absorbance decays of the radical cation (520 nm) and radical (at 1000) anion species; λ_{exc} =355 nm, 1 mJ per pulse.

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510 nm within the experimental error. Therefore, triad **4**, which entails an antenna and a charge-separation module, undergoes photoinduced electron transfer with a charge-separated state that lives (250 ± 10) ns.

Conclusion

We have designed and synthesized a family of modular multicomponent systems (one dyad, one tetrad, two triads) that entail a fulleropyrrolidine scaffold to which were connected 1) at the nitrogen atom an OPE fragment that absorbs in the UV/Vis region up to 450 nm, and 2) at the α -carbon atom of the pyrrolidine cycle through acetylene spacers a phenothiazine and/or ferrocene electron donors that exhibit weak absorption relative to the other subunits. The syntheses of the triads and tetrads were accomplished by means of 1,3-dipolar cycloaddition of azomethine ylides generated in situ by the condensation reaction of an OPE-bearing amino acid and 1,5disubstituted penta-1,4-diyn-3-one ketones. Yields as high as 90% were achieved when TMS- or TIPS-protected ketones were employed.

In addition to acting as a structural scaffold, the fullerenebased moiety further serves as a selective light-absorbing unit above 450 nm as well as an electron acceptor. The final target, namely, modular multicomponent arrays capable of undergoing selective excitation on a given unit while maintaining specific electronic properties of each component, was achieved. In fact, electrochemical data indicate small to negligible ground-state electronic interactions among individual components while, across the whole series, absorption profiles are essentially the sum of the spectra of each chromophore.

Photochemical studies on the model dyad 2 show that the OPE unit invariably undergoes ultrafast energy transfer to the fullerene acceptor with a rate constant of $4 \times 10^{10} \text{ s}^{-1}$ both in nonpolar (PhMe) and in polar solvents (PhCN). This validates its antenna role under any conditions. The occurrence of photoinduced electron transfer with a relatively long-lived chargeseparated state (250 ns) is unambiguously demonstrated only in one case, namely, the triad 4 in polar PhCN. In the two systems that contain ferrocene (3 and 1), compelling evidence of electron transfer was not found, in line with previous findings on systems that contained ferrocenyl and fullerene moieties.^[63] The present results confirm that caution must be used in choosing ferrocene units as electron donors to promote efficient charge separation in multicomponent arrays, also on account of their optical elusiveness as a triplet or a radical cation.^[78] Indeed, ferrocenes might be formidable energytransfer quenchers^[68] as most likely happens in the present case.

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Keywords: energy transfer • fullerenes • light harvesting • spectroelectrochemistry • synthetic methods

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FULL PAPER

A fuller(ene) picture: Fullerene-based arrays are reported in which [60]fulleropyrrolidine synthons are linked to an oligo(*p*-phenyleneethynylene) antenna and to phenothiazine (PTZ) and/or ferrocene (Fc) electron donors. When only PTZ is present photoinduced electron transfer occurs, whereas energy transfer is observed whenever Fc is inserted into the multicomponent array. (see figure; ε_T = energy transfer, e^-_T = electron transfer, E_{DG1/2} represents the electron donor groups).



Fullerenes

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Versatile Bisethynyl[60]fulleropyrrolidine Scaffolds for Mimicking Artificial Light-Harvesting Photoreaction Centers