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Close Proximity Dibenzo[*a*,*c*]phenazine–Fullerene Dyad: Synthesis and Photoinduced Singlet Energy Transfer

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A dibenzo[*a*,*c*]phenazine–fullerene (DBPZ-C_{60}) dyad in which two chromophores are linked in close proximity to each other has been synthesized and studied in detail by optical spectroscopy to explore a new energy donor–acceptor system. The dyad was prepared by Prato reaction between 11-formyldibenzo[*a*,*c*]phenazine and fullerene. 3,5-Di-*tert*-butylbenzyl group was introduced onto the fulleropyrrolidine unit to achieve adequate solubility of the dyad. A thorough study of the photophysical properties of the dyad and relevant reference compounds, performed by means of steady state and time resolved spectroscopic measurements, has revealed the presence of highly efficient (ca. 98 %) and extremely fast ($k_{en} = 5 \times 10^{11}\ s^{-1}$) intramolecular photoinduced singlet–singlet energy-transfer process from singlet excited state of the DBPZ moiety to fullerene. In both polar and nonpolar environment transduction of singlet excited state energy governs the excited state deactivation, but the efficiency and rate of energy transfer were found to be higher in nonpolar solvents in comparison to polar. The DBPZ singlet excited state decays within 2 and 4.7 ps in toluene and benzonitrile, respectively, via singlet–singlet energy transfer to produce a fullerene singlet excited state which decays with a life time of 1.5 ns to give a very long-lived fullerene triplet state as final populated excited state.

Introduction

Many intensive efforts have been carried out over the past few decades to construct photosynthetic models which can mimic natural photosynthesis involving photoinduced electron and energy transfer as fundamental processes.[1] Fullerene (C_{60}) has emerged as one of the most promising energy and electron acceptor due to its fascinating physical and chemical properties such as easy functionalization,[2] excellent electron accumulation ability[3] and ability to act as an energy trap.[4] Therefore a wide range of fullerene-based molecular dyads and more complex systems that absorb visible light and undergo directional electron and/or energy transfer have been synthesized and investigated extensively during the past two decades to attain a better understanding of mechanisms that convert sunlight into chemical energy.[5] These systems have also been used to construct devices of future interest like organic solar cells.[6] Therefore a better knowledge of electronic interactions of fullerene with various molecules that can function as efficient electron and/or energy donors is essential; not only to enhance our understanding of natural systems but also for the development of the new molecular photovoltaic devices.

Besides many favorable properties, the low molar absorption coefficient of fullerene in the visible region limits its utility as promising *n*-type material in many applications like bulk heterojunction type polymer/fullerene solar cells.[7] The attachment of a molecule which can efficiently and rapidly transfer harvested light energy to fullerene without diminishing its electron-acceptor ability may provide a reasonable solution to this problem. Moreover, in order to perform the specific role of harvesting and transferring of light energy to fullerene, the light-harvesting molecule must have high enough oxidation potential to prevent any electron transfer to fullerene. At the same time it is also important that the molecule has higher first reduction potential than fullerene so that only the fullerene moiety could act as unambiguous electron acceptor when the system is incorporated in a bulk heterojunction device with the electron-donor material.

A literature survey shows that a large number of fullerene-donor systems have been reported in which photoinduced energy and electron-transfer processes either compete with each other or take place selectively depending on the polarity of the media.[8] However, there are very few examples which exhibit exclusive transfer of energy from the light-harvesting antenna to the fullerene unit in both polar and nonpolar environment.[9] In our quest for finding new light-harvesting C_{60}-based systems in which the light-harvesting antenna not only satisfies the electrochemical

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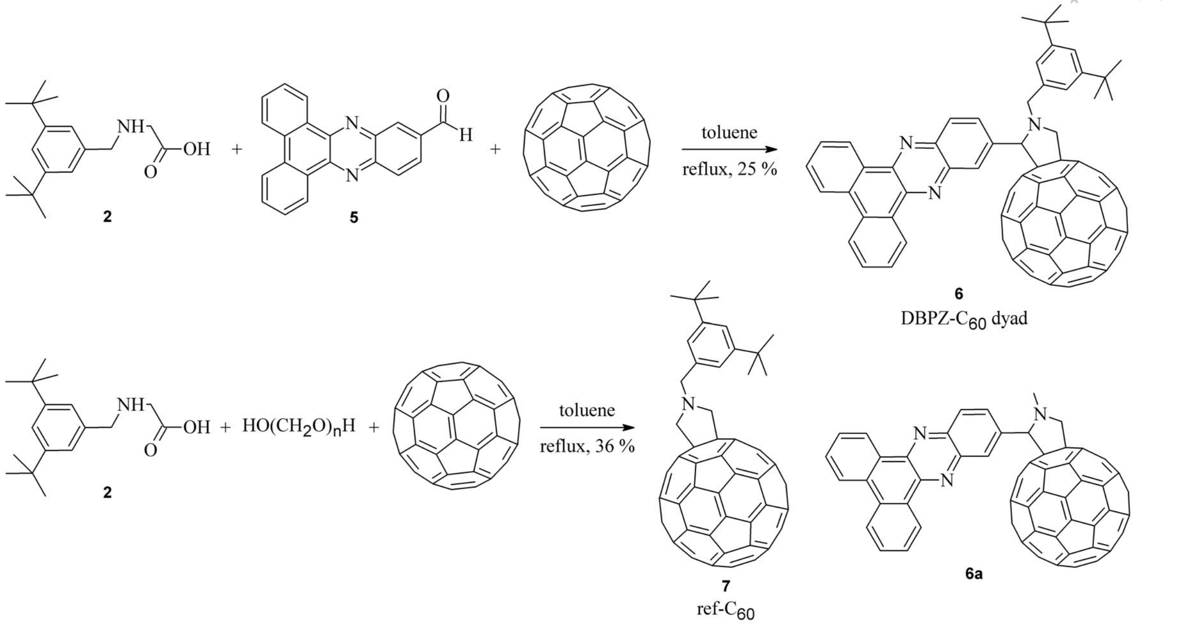


Scheme 1. Synthesis of DBPZ-C_{60} dyad **6** and ref-C_{60} (**7**).

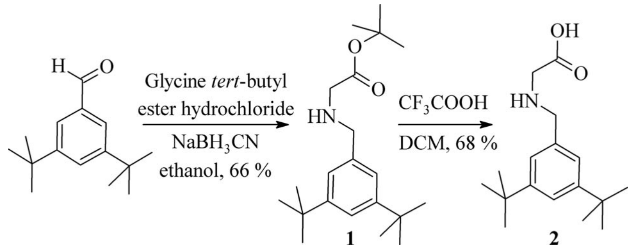
requirements but also performs efficient and fast transfer of energy to the fullerene, we have designed a novel energy donor–acceptor system involving dibenzo[*a*,*c*]phenazine as energy donor. The rationale behind the selection of DBPZ as energy donor is based on its interesting spectroscopic and electrochemical properties which came into light very recently.[10] In addition, this compound has some synthetic importance too, as its corresponding phenazine derivative, namely dipyrido[*a*,*c*]phenazine, can also be synthesized and functionalized following the same synthetic procedure and may be utilized for the supramolecular attachment with various metals.[11]

In this paper we describe the results of an exploratory study on the synthesis and on the electrochemical and photophysical properties of a novel close proximity DBPZ-C_{60} dyad along with parallel studies on relevant model compounds. The electrochemical and photophysical properties of these compounds have been undertaken thoroughly by means of differential pulse voltammetry, steady state UV/Vis absorption, steady state and time resolved fluorescence, flash photolysis and pump-probe measurements to shed some light on the photoinduced processes taking place between the two covalently linked moieties.

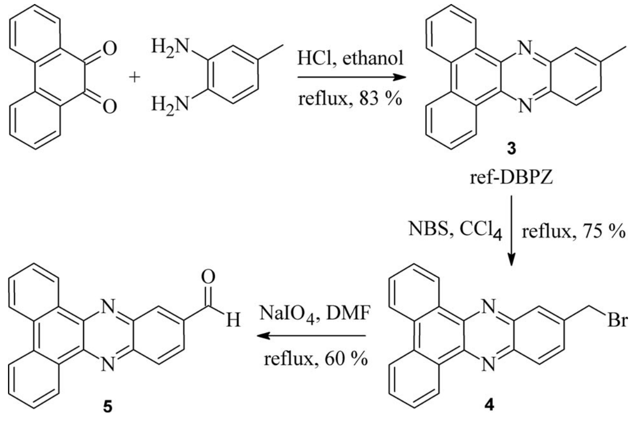
Results and Discussion

Synthesis and Characterization

The syntheses of the dyad and reference compounds are summarized in Schemes 1, 2, and 3. 1,3-Dipolar cycloaddition reaction between 11-formyldibenzo[*a*,*c*]phenazine (**5**) and fullerene in the presence of *N*-(3,5-di-*tert*-butylbenzyl)glycine (**2**) led to the target DBPZ-C_{60} dyad **6**.[12] Introduction of 3,5-di-*tert*-butylbenzyl group on the pyrrolidine ring was necessary to enhance the solubility of the dyad in various organic solvents such as toluene, chloroform, dichloromethane, THF and benzonitrile, which was essential for the characterization and detailed spectroscopic and electrochemical studies of the dyad. Previously we had also synthesized the dyad **6a** using sarcosine (*N*-methylglycine) in place of *N*-(3,5-di-*tert*-butylbenzyl)glycine, but the resulting dyad had very low solubility in common organic solvents. The poor solubility led to the low yield (17%) of the reac-



Scheme 2. Synthesis of *N*-(3,5-di-*tert*-butylbenzyl)glycine (**2**).



Scheme 3. Synthesis of 11-formyldibenzo[*a*,*c*]phenazine (**5**).

tion and also caused trouble during purification and characterization of the dyad. To the best of our knowledge, this is the first time when *N*-(3,5-di-*tert*-butylbenzyl)glycine was synthesized and successfully employed in the Prato reaction. Earlier longer alkyl chains (e.g. dodecyl, octadecyl) were used to increase the solubility of fulleropyrrolidine derivatives.[13] A similar procedure was applied to synthesize ref-C_{60} (**7**) by using paraformaldehyde instead of 11-formyldibenzo[*a*,*c*]phenazine.

N-(3,5-Di-*tert*-butylbenzyl)glycine *tert*-butyl ester (**1**) was synthesized in good yield (66%) by the reaction of 3,5-di-*tert*-butylbenzaldehyde with glycine *tert*-butyl ester hydrochloride and sodium cyanoborohydride in ethanol at room temperature. Subsequently *N*-(3,5-di-*tert*-butylbenzyl)glycine (**2**) was synthesized in 68% yield by deprotection of carboxylic group by the treatment with TFA in dichloromethane.[14]

11-Formyldibenzo[*a,c*]phenazine (**5**) was synthesized in three steps. First, 9,10-phenanthrenequinone and 3,4-diaminotoluene were condensed in ethanol (in presence of concentrated aqueous HCl) to give 11-methyldibenzo[*a*,*c*]phenazine (**3**). By using ethanol/HCl combination, we managed to improve the yield up to 83.2% which is far better than 64% obtained earlier by condensing the reactants in toluene.[10b] 11-Bromomethyldibenzo[*a*,*c*]phenazine (**4**) was obtained in 75% yield by benzylic bromination of 11-methyldibenzo[*a*,*c*]phenazine (**3**) with *N*-bromosuccinimide.[15] We always obtained around 10% of dibrominated compound and some unreacted starting material which were difficult to separate by chromatography because of their almost same mobility. So we separated them out from the desired product **4** on the basis of their higher solubility in toluene. Oxidation of 11-bromomethyldibenzo[*a,c*]phenazine (**4**) by $NaIO_4$/DMF yielded **5** in good yield (60%).[16] All the synthesized compounds were unambiguously characterized by spectroscopic analysis including ^1H NMR and ESI-TOF mass spectra (see Exp. Section).

Since dibenzo[*a*,*c*]phenazine can be easily replaced by dipyrido[*a*,*c*]phenazine in the dyad following exactly the same synthetic procedure, this synthetic work openes access to a novel fullerene-containing ligand. The ability of resulting dyad to coordinate with various transition metals may be utilized for the synthesis of fullerene-containing supramolecular systems.[17,11] This will be the focus area of our future research.

^{1}H NMR Spectra

The ^1H NMR spectrum (Figure 1) of the dyad displays some characteristic features supporting the assumption of the close proximity of the two acting moieties in the dyad. Large downfield shifts were observed for the H^9, H^{10} and H^{12} protons of the DBPZ moiety of the dyad with respect to the corresponding protons in ref-DBPZ. The H^{12} proton is the one which is most affected by the presence of the fullerene unit. In addition to the large downfield shift, its sharp singlet appears as broad signal in the dyad. The doublet of H^1 and H^8 protons also turned into doublet of triplet. These changes are attributed to the deshielding effect resulting from C_{60} π-electrons. The methyne proton (H^{17}) of the pyrrolidine ring also exhibits a downfield shift with respect to the corresponding methyne proton of very similar fulleropyrrolidine derivative *N*-benzyl-2-(meth-

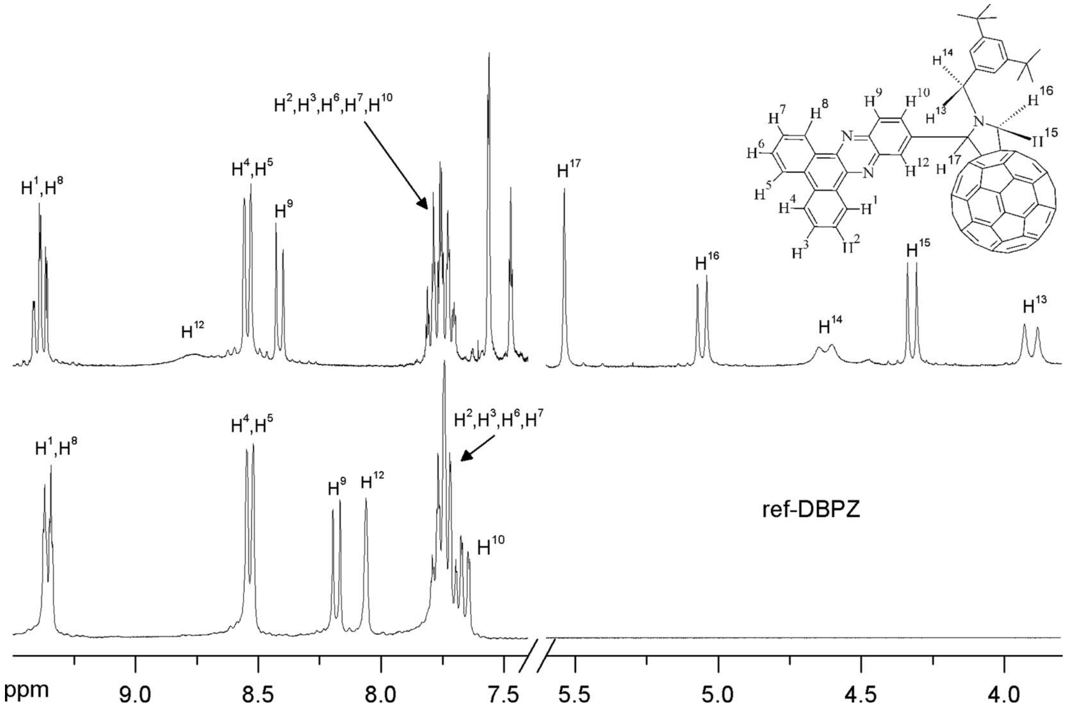


Figure 1. ^1H NMR spectra of the dyad and ref-DBPZ in $CDCl_3$.

oxycarbonyl)pyrrolidine–C_{60} (reported earlier[12]) because of the deshielding effect of DBPZ moiety. All these changes may be taken as indication of the close proximity of the two moieties and ground state interaction between them.[18]

Electrochemistry

The electrochemical properties of the DBPZ-C_{60} dyad and relevant reference compounds were investigated by differential pulse voltammetry in benzonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. The differential pulse voltammogram of dyad is shown in Figure 2 and the obtained redox potentials are shown in Table 1.

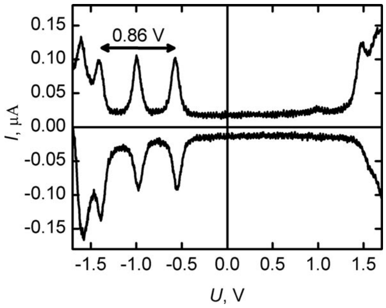


Figure 2. Differential pulse voltammogram of the dyad in PhCN, vs. Ag/AgCl reference electrode. In measurement with ferrocene in the solution, the oxidation peak of ferrocene was observed at 0.46 V.

Table 1. Redox potential values (voltage measured vs. Ag/AgCl) of DBPZ-C_{60} dyad and reference compounds obtained by DPV.

	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}	E_1^{ox}
dyad	–0.55	–0.98	–1.41	–1.59	+1.47
ref-C_{60}	–0.58	–0.99	–1.57		+1.44
ref-DBPZ	–1.41				n.o.[a]

[a] Not observed.

The dyad shows four one-electron reduction processes, which occur at –0.55, –0.98, –1.41 and –1.59 V vs. Ag/AgCl. Comparison with the reduction potentials of ref-C_{60} (–0.58, –0.99 and –1.57 V) and ref-DBPZ (–1.41 V) reveals that the first, second and fourth reduction process corresponds to the mono-, di-, and tri-anion of fullerene and the third one to the DBPZ reduction. The only oxidation potential for the dyad was observed at 1.47 V and corresponds to the oxidation of the fullerene moiety. The influence of the DBPZ moiety on the fullerene in the dyad is clearly visible by the shift in the oxidation and first reduction potential of the fullerene moiety in the positive direction by 30 mV, compared to that of ref-C_{60}.

The dyad has two noticeable features; firstly, the DBPZ moiety of the dyad does not display an oxidation potential (not observed earlier also[10b]) in the scanning range of the measurement, i.e. 1.7 to +1.7 V, which reflects its incapability to donate electrons to the fullerene moiety. Secondly, the DBPZ moiety has a much higher first reduction potential than fullerene. The large difference in the first reduction potentials of two electroactive chromophores [$\Delta E = E_1^{red}(C_{60}) - E_1^{red}(\mathrm{DBPZ}) = 86$ mV] ensures that the two moieties will perform their well-defined roles, i.e. DBPZ will act as light-harvesting antenna whereas fullerene will accept the electrons when this dyad is mixed with *p*-type materials in bulk-heterojunction-based solar cells.

Steady-State Absorption Studies

The absorption spectra of the dyad and the model compounds, ref-DBPZ and ref-C_{60} in toluene are shown in Figure 3. ref-DBPZ strongly absorbs at wavelengths lower than 420 nm and exhibits two absorption maxima at 375 and 396 nm corresponding to n–π* and π–π* transitions, respectively. In the dyad these absorption bands appear at 380 and 403 nm and are shifted to longer wavelengths by 5 and 7 nm, respectively, indicating the substantial ground-state electronic interactions between DBPZ and fullerene moieties.

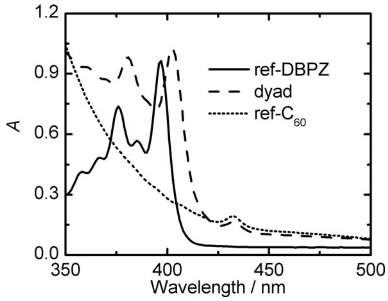


Figure 3. Steady-state absorption spectra of the dyad, ref-DBPZ and ref-C_{60} in toluene. The concentrations were maintained at 41 μM.

Although, an additional 1–2 nm red shift was observed in the absorption maxima of DBPZ moiety of the dyad and of ref-DBPZ in more polar solvents including chloroform and benzonitrile, but the extent of ground state interaction between the two moieties found to be almost same as in toluene. These results are in accordance with the NMR and DPV studies which also indicate for the ground state interaction between the two moieties of the dyad. A sharp band at 432 nm, characteristic of the fulleropyrrolidine provides a way for the selective excitation of the fullerene moiety of the dyad since DBPZ moiety has no absorption at wavelengths higher than 420 nm. Similarly at the wavelength 403 nm, where the DBPZ moiety absorbs strongly, fullerene has a low absorption ($\varepsilon \approx 4 \times 10^3$ M^{-1} cm^{-1}).

Steady-State Emission Studies

The fluorescence emission spectra of the dyad and ref-DBPZ in toluene obtained with excitation at 378 nm are shown in Figure 4. Optical densities of both solutions were identical at the excitation wavelength; ref-DBPZ shows an emission maximum at 422 nm. In the case of the dyad, emission of DBPZ moiety is efficiently quenched (98%) in toluene.

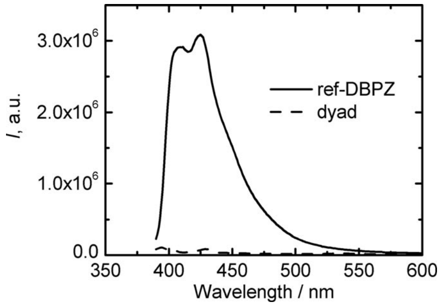


Figure 4. Steady-state fluorescence spectra of the dyad and the ref-DBPZ compound in toluene at the excitation wavelength (λ = 378 nm).

The same experiments were carried out in chloroform and also in benzonitrile. The dyad showed efficient quenching (97%) of DBPZ emission with respect to ref-DBPZ in moderately polar chloroform, but in polar benzonitrile relatively less efficient quenching (89%) was observed. The decrease in the fluorescence quantum yield of DBPZ moiety in the dyad in comparison to ref-DBPZ also resemble with the quenching ratios (Table 2).

There could be two possible mechanisms for the observed efficient quenching of the DBPZ emission; electron and/or energy transfer to the fullerene unit. The involvement of the electron transfer process, however, can be ruled out on electrochemical grounds. Therefore we presume that quenching of the DBPZ singlet excited state is solely due to singlet–singlet energy transfer to fullerene, whose first excited singlet state lies at lower energy. To verify the energy transfer in the dyad, emission spectra of equimolar solutions of dyad and ref-C_{60} were measured with irradiation (λ = 403 nm) where the DBPZ moiety of the dyad absorbs predominately (the dyad has a four times higher absorbance than ref-C_{60}). We observed an almost four times enhancement of the fullerene emission in the dyad with respect to the ref-C_{60} (Figure 5). The observed sensitized emission of fullerene moiety of the dyad confirms singlet–singlet energy transfer from DBPZ to fullerene. Nearly the same results were obtained in more polar solvents like chloroform and benzonitrile.

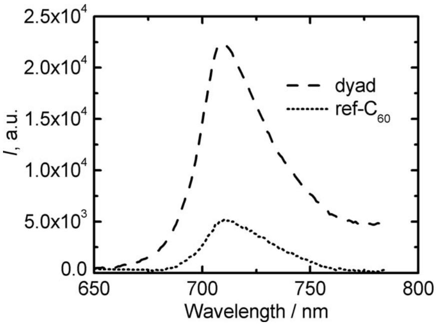


Figure 5. Sensitized emission of fullerene moiety of the dyad with respect to ref-C_{60} obtained from excitation of equimolar toluene solutions at 403 nm.

Time-Resolved Fluorescence Studies

Time-resolved fluorescence studies were carried out by time correlated single photon counting (TCSPC) method. For TCSPC measurements the solutions of dyad and reference compounds in toluene and benzonitrile were excited at 404 nm and emission time profiles of DBPZ and fullerene moieties were collected at 450 and 704 nm, respectively. For the DBPZ moiety of the dyad, the singlet-state life time of 12 ps was observed, whereas, for the reference compound, ref-DBPZ, life time of 97 ps was observed. It must be noted that lifetime of ca. 12 ps obtained is only an upper limit of the actual lifetime due to the time resolution limitation of the instrument i.e. 60 ps. On the other hand, singlet-state life time of the fullerene moiety of the dyad (1.46 ns) was found to be almost same as that for ref-C_{60} (1.50 ns), see Figure 6.

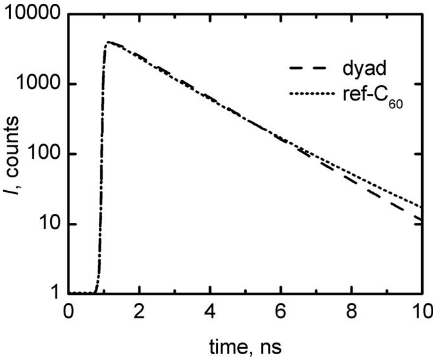


Figure 6. Fluorescence decay time profiles for fullerene moiety of the dyad and ref-C_{60} at 704 nm, in toluene, λ_{ex} = 404 nm.

Table 2. Selected photophysical data of dyad, ref-DBPZ and ref-C_{60}.

Compound	Solvent	Quenching	DBPZ Φ_{fl}[a]	τ [ps][b]	Fulleropyrrolidine τ [ns][b]	k_{en}[c]
Dyad	toluene	98%	4×10^{-4}	12	1.46	5.0×10^{11} s^{-1}
	PhCN	89%	8×10^{-4}	21	1.50	2.1×10^{11} s^{-1}
ref-DBPZ	toluene		7.3×10^{-3}	97		
	PhCN		1.3×10^{-2}	105		
ref-C_{60}	toluene				1.50	
	PhCN				1.47	

[a] Fluorescence quantum yields were determined using anthracene as a standard (Φ_{fl} = 0.27 in ethanol). [b] Fluorescence singlet life times measured by TCSPC. [c] Rates of singlet–singlet energy transfer; calculated from the lifetimes data obtained from picosecond transient absorption experiments at room temperature.

In benzonitrile similar results were obtained, the ref-DBPZ and ref-C_{60} had singlet life times of 105 ps and 1.47 ns, respectively. In the dyad, singlet life times of DBPZ and fullerene moieties were found to be 21 ps and 1.50 ns, respectively. Thus, the singlet state of DBPZ moiety is strongly quenched, whereas singlet state of the fullerene moiety remains unaffected.

Microsecond Transient Absorption Studies

In both steady-state and time-resolved emission measurements, carried out in polar and nonpolar environment, quenching of the DBPZ excited singlet state was observed, whereas, no quenching was observed for the fullerene moiety. In order to investigate, the fate of excited singlet states of DBPZ and fullerene moieties, transient absorption studies were carried out in the microsecond time scale. Nitrogen-purged equimolar toluene solutions of dyad, ref-DBPZ and ref-C_{60} were excited at 401 nm, where DBPZ moiety absorbs strongly, but the fullerene absorption is moderate. Thus at that excitation wavelength the absorbances of the dyad and ref-DBPZ solutions were identical, whereas absorbance of ref-C_{60} solution was one third of these. The transient absorption spectra of the three compounds are shown in Figure 7.

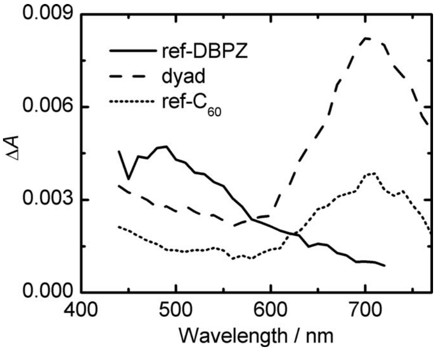


Figure 7. Transient absorption spectra of the dyad, ref-DBPZ and ref-C_{60} in toluene obtained with the excitation at 401 nm. The concentrations of the solutions were maintained at 41 μM.

The ref-DBPZ has an absorption band at 480 nm which is attributed to its triplet excited state. It has no absorption at wavelengths higher than 600 nm. The dyad and ref-C_{60} show absorption bands at 700 nm, which is the characteristic band of the fullerene triplet state.[19] The life times of the triplet transients of dyad, ref-C_{60} and ref-DBPZ were found to be 37, 31 and 81 μs, respectively. The dyad has a triplet-transient life time close to the ref-C_{60} and exhibits a diminished absorption below 600 nm. These observations clearly suggest that there is significant decrease in the triplet-state absorption of DBPZ moiety of the dyad which is also in accordance with the fact that DBPZ singlet state is quenched by singlet–singlet energy transfer to fullerene, and essentially no DBPZ triplet state is therefore formed by intersystem crossing. The sensitized triplet-state absorption observed for the fullerene moiety of the dyad indicates that the harvested light energy by the DBPZ antenna is transferred to the fullerene singlet excited state, which undergoes intersystem crossing to give the fullerene triplet as the final populated state in high yield. The triplet character of this species is verified by its ability to sensitize singlet-oxygen formation.

Similar experiments were also carried out in benzonitrile and the life times of the triplet transients of dyad, ref-C_{60} and ref-DBPZ were found to be 43, 38 and 67 μs, respectively. The dyad has, also in benzonitrile, the triplet transient life time close to the model compound, ref-C_{60}, and amount of the absorption below 600 nm is lesser than ref-DBPZ indicating that the negligible amount of DBPZ triplet contributes to the transient absorption of the dyad. In addition, in both toluene and benzonitrile, no triplet–triplet energy transfer was observed between fullerene triplet state and DBPZ triplet state.

Picosecond Transient Absorption Studies

The transient pump-probe method was used to shed light on the nature of the short living products and to investigate the formation of charge separation state. For these measurements the dyad, ref-C_{60} and ref-DBPZ were excited at wavelength 404 nm at which DBPZ moiety of the dyad has maximum absorption. The decay component spectra of dyad in toluene are shown in Figure 8.

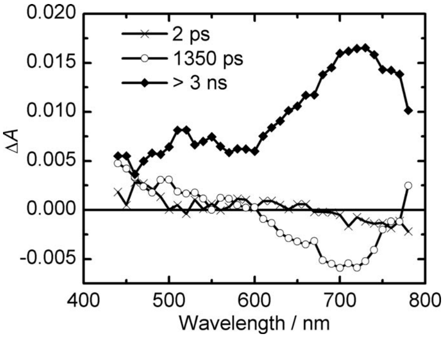


Figure 8. Decay component spectra of the dyad in toluene (λ_{ex} = 404 nm).

The very long living component, with a life time >> 3 ns and a positive amplitude at 700 nm, clearly corresponds to the triplet state of the fullerene which was also observed in flash photolysis measurements. The short living component, with a life time of roughly 1350 ps and a negative amplitude at 700 nm, corresponds the decay of the singlet excited state of fullerene. The fastest component with a life time of 2 ps can be attributed to the energy transfer from the singlet excited state of DBPZ moiety to the singlet excited state of fullerene. In benzonitrile the life time of the component corresponding to the singlet–singlet energy transfer was found to be 4.7 ps, which clearly indicates that the rate of energy transfer is lower in benzonitrile than in toluene.

As far as charge separation is concerned, no spectral evidences for the fullerene radical anion (which should exhibit characteristic transient absorption band around

1000 nm[8d]), DBPZ radical cation or CS state were found either in toluene or in benzonitrile. These results confirm that the energy transfer from the DBPZ moiety to the fullerene unit is the only photoinduced process taking place in the dyad in both polar and nonpolar environment.

Conclusions

We have designed, synthesized and investigated a novel energy donor-acceptor system in which two chromophores, namely dibenzo[*a*,*c*]phenazine and fullerene, are linked at close proximity. In both polar and nonpolar media, the harvested light energy by the DBPZ antenna is transferred very efficiently to the fullerene unit on a picosecond time scale. Subsequently the fullerene singlet excited state decays on a nanosecond time scale to give the fullerene triplet state as final populated excited state. We presume that such a high rate of singlet–singlet energy transfer is a consequence of the close proximity of the two acting moieties. The main evidence in support of the energy transfer hypothesis comes from the steady state emission studies in which sensitized emission of the fullerene moiety was observed upon exciting DBPZ moiety of the dyad and further confirmed by the TCSPC measurement which does not show any quenching of the fullerene singlet-state life time (Figure 9).

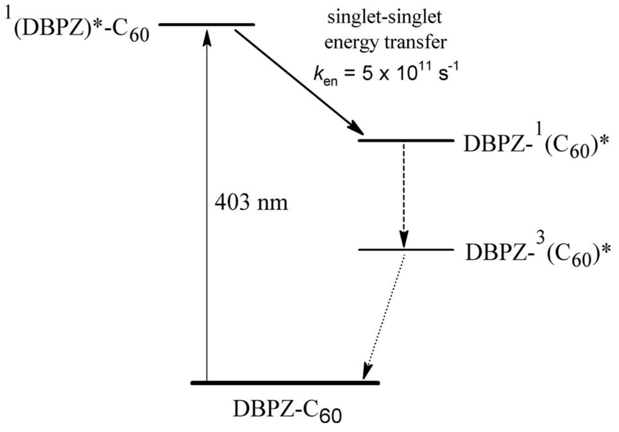


Figure 9. Energy-level diagram showing the processes that take place in DBPZ-C_{60} dyad upon excitation of DBPZ moiety in toluene at room temperature.

It has to be emphasized that no spectral evidences for the electron transfer were found, neither in polar nor in nonpolar solvents. Due to the combination of the efficient and fast energy transfer and favorable electrochemical properties, the synthesized dyad could be a good candidate for future photovoltaic applications with well-defined roles of both acting chromophores; DBPZ acting as a light-harvesting antenna and fullerene acting as an electron acceptor in the photoactive layer.

Experimental Section

General Remarks: All reagents for syntheses were purchased from Sigma–Aldrich Co. and used as received. 3,5-Di-*tert*-butylbenzaldehyde was synthesized according to the literature procedure.[20] The solvents were of HPLC grade and purchased from VWR and used without further purification. The sorbents for column chromatography (Silica 60, Silica 100), TLC plates (silica gel 60 F_{254} on aluminium sheets) were purchased from Merck.

The proton NMR spectra were recorded with Varian Mercury 300 MHz spectrometer in $CDCl_3$ at room temperature. All chemical shifts are quoted relative to TMS (δ = 0.0 ppm); δ values are given in ppm and J values in Hz. Melting points were measured on Stuart SMP 10 apparatus. Mass spectra were measured with Waters LCT Premier XE ESI-TOF benchtop mass spectrometer. Differential pulse voltammetry was performed with Faraday MP, Obbligato Objectives Inc., in a three-electrode single-compartment cell consisting of a platinum-in-glass working electrode, Ag/AgCl as reference electrode, and a graphite rod as counter electrode. During the measurements, the values of pulse height, pulse width and step voltage were set to 20 mV, 20 ms, and 2.5 mV, respectively. Benzonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate was used as solvent. The measurements were done under a continuous flow of nitrogen. A Fc/Fc$^+$ couple was used as an internal standard. The measurements were carried out in both directions: towards the positive and negative potential. The reduction and oxidation potentials were calculated as an average of the two scans.

If not otherwise indicated, all the spectroscopic measurements were carried out at room temperature. The absorption spectra were recorded with Shimadzu UV-2501PC spectrophotometer and the fluorescence spectra using a Fluorolog-3 (SPEX Inc.) fluorimeter. The emission spectra were corrected using a correction function supplied by the manufacturer. Fluorescence quantum yields were determined relative to anthracene in ethanol (Φ = 0.27).[21]

Fluorescence decays of the samples on nanosecond and sub-nanosecond time scales were measured using a time-correlated single photon counting (TCSPC) system (PicoQuant GmbH) consisting of PicoHarp 300 controller and PDL 800-B driver. The samples were excited with the pulsed diode laser head LDH-P-C-405B at 404 nm and fluorescence decays were measured at the wavelength of emission maximum. The signals were detected with a micro channel plate photomultiplier tube (Hamamatsu R2809U). The time resolution of the TCSPC measurements was about 60–70 ps (FWHM of the instrument response function).

The flash-photolysis method was used to study time-resolved absorption on the microsecond time-scale. The instrument has been described elsewhere.[22] The samples were deoxygenated by nitrogen bubbling for 20 min before measurements. Pump-probe technique for time-resolved absorption was used to detect the fast processes with a time resolution shorter than 0.2 ps. The instrument and the used data analysis procedure have been described earlier.[5c,23]

***N*-(3,5-Di-*tert*-butylbenzyl)glycine *tert*-Butyl Ester (1):** To a solution of 3,5-di-*tert*-butylbenzaldehyde (100 mg, 0.46 mmol) in ethanol (15 mL), glycine *tert*-butyl ester hydrochloride (155 mg, 0.92 mmol) and sodium cyanoborohydride (500 mg, 7.95 mmol) were added and suspension was stirred at room temperature for 3 d. Then the solvent was evaporated under reduced pressure and the residue dissolved in diethyl ether (100 mL) and washed with water (3 × 100 mL). The organic layer was collected, dried with sodium sulfate and the solvents evaporated. The crude product was purified by column chromatography using $CHCl_3$ as eluent to yield the desired product (100 mg, 65.7%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 18 H, Ph*t*Bu), 1.50 (s, 9 H, CO-O*t*Bu), 1.94 (s, 1 H, N-H), 3.35 (s, 2 H, CH_2COO*t*Bu), 3.79 (s, 2

H, PhCH_2), 7.18 (d, J = 1.8 Hz, 2 H, phenyl-H), 7.34 (t, J = 1.9 Hz, 1 H, phenyl-H) ppm. MS (ESI-TOF): m/z = 356.2555 $[M + Na]^+$.

***N*-(3,5-Di-*tert*-butylbenzyl)glycine (2):** Ester **1** (100 mg) was dissolved in dichloromethane (2 mL) and subsequently 2,2,2-trifluoroacetic acid (2 mL) was added. The reaction mixture was stirred for 4 h at room temperature. Then dichloromethane and TFA were removed under reduced pressure. The residue was dissolved in chloroform (50 mL) and washed with water (3 × 50 mL). The organic layer was collected, dried with sodium sulfate and evaporated to yield a solid residue. The crude product was washed with hexane and dried to yield the product (57 mg, 68 %) as a white solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 18 H, *t*Bu), 3.61 (s, 2 H, CH_2COOH), 4.15 (s, 2 H, PhCH_2), 6.20 (br. s, 1 H, N-H), 7.21 (d, J = 1.7 Hz, 2 H, phenyl-H), 7.44 (t, J = 1.7 Hz, 1 H, phenyl-H) ppm. MS (ESI-TOF): m/z = 300.1938 $[M + Na]^+$.

11-Methyldibenzo[*a*,*c*]phenazine (3): 9,10-Phenanthrenequinone (2.00 g, 9.60 mmol) and 3,4-diaminotoluene (1.17 g, 9.60 mmol) were placed into a round-bottomed flask (500 mL) equipped with a reflux condenser. Subsequently ethanol (200 mL) and concentrated aqueous HCl (10 mL) were added and reaction mixture was heated to reflux. After a short period of time the product began to precipitate from the solution. The progress of the reaction was monitored by TLC and after 4 h the reaction mixture was allowed to cool to room temperature; the precipitate was filtered off and washed thoroughly with ethanol. The crude product was recrystallized from $CHCl_3$/ethanol and dried to afford the product (2.35 g, 83.2 % yield) as yellow needles; m.p. 222 °C (ref.[24] 220–221 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.66 (s, 3 H, CH_3), 7.66 (dd, J = 1.8, J = 8.7 Hz, 1 H, H^{10}), 7.85–7.69 (m, 4 H, H^2, H^3, H^6, H^7), 8.06 (s, 1 H, H^{12}), 8.18 (d, J = 8.7 Hz, 1 H, H^9), 8.53 (d, J = 8.0 Hz, 2 H, H^4, H^5), 9.36 (d, J = 7.5 Hz, 2 H, H^1, H^8) ppm. MS (ESI-TOF): m/z = 295.1241 $[M + H]^+$. UV/Vis ($CHCl_3$): λ_{max}/nm (ε/$L\,mol^{-1}\,cm^{-1}$) = 396 (22500), 376 (17000). Fluorescence ($CHCl_3$): λ_{max} = 408 nm.

11-(Bromomethyl)dibenzo[*a*,*c*]phenazine (4): A mixture of **3** (1.08 g, 3.68 mmol), NBS (0.79 g, 4.42 mmol) and benzoyl peroxide (50 mg) in CCl_4 (300 mL) was refluxed for 48 h. The reaction mixture was cooled, kept overnight at room temperature and the precipitate of succinimide and unreacted NBS was filtered off. The filtrate was evaporated under reduced pressure and the solid residue was dissolved in chloroform. The solution was washed with water, dried with sodium sulfate and the solvents evaporated. The crude product was dissolved in 30 mL of toluene (slight heating was required) and kept overnight at room temperature to get the precipitate of **4** (1.03 g, 75 %) as a yellow solid; m.p. 228 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.79 (s, 2 H, CH_2), 7.90–7.68 (m, 5 H, H^2, H^3, H^6, H^7, H^{10}), 8.34–8.28 (m, 2 H, H^9, H^{12}), 8.55 (d, J = 8.1 Hz, 2 H, H^4, H^5), 9.38 (d, J = 6.8 Hz, 2 H, H^1, H^8) ppm. MS (ESI-TOF): m/z = 373.0365 $[M + H]^+$. UV/Vis ($CHCl_3$): λ_{max}/nm (ε/$L\,mol^{-1}\,cm^{-1}$) = 396 (20200), 376 (16800). Fluorescence ($CHCl_3$): λ_{max} = 427 nm.

11-Formyldibenzo[*a*,*c*]phenazine (5): Compound **4** (428 mg, 1.15 mmol) and sodium periodate (270 mg, 1.26 mmol) were dissolved in DMF (110 mL) and heated to reflux for 4 h. The reaction mixture was allowed to cool at room temperature and concentrated under reduced pressure. The crude product was chromatographed on silica gel using toluene as eluent to afford **5** (211 mg, 60 %). Bright yellow solid; m.p. 221–222 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.70 (m, 4 H, H^2, H^3, H^6, H^7), 8.29 (dd, J = 1.7, J = 8.9 Hz, 1 H, H^{10}), 8.37 (d, J = 8.8 Hz, 1 H, H^9), 8.56 (d, J = 7.8 Hz, 2 H, H4, H5), 8.75 (d, J = 1.8 Hz, 1 H, H^{12}), 9.37 (dt, J = 1.7, J = 6.9 Hz, 2 H, H^1, H^8), 10.32 (s, 1 H, CHO) ppm. MS (ESI-TOF): m/z = 309.0334 $[M + H]^+$. UV/Vis ($CHCl_3$): λ_{max}/nm (ε/$L\,mol^{-1}\,cm^{-1}$) = 406 (16600), 385 (16500). Fluorescence ($CHCl_3$): λ_{max} = 468 nm.

Dibenzo[*a*,*c*]phenazine–Fullerene Dyad (6): To a solution of fullerene (35 mg, 0.048 mmol) in toluene (100 mL), **5** (75 mg, 0.24 mmol) and **2** (26 mg, 0.093 mmol) were added. The reaction mixture was refluxed for 48 h under argon atmosphere, allowed to cool down and evaporated under reduced pressure. The crude product was purified by column chromatography eluting with 2:1 hexane/chloroform to afford the dyad (15 mg, 25 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.43 (s, 18 H, *t*Bu), 3.90 (d, J = 13.5 Hz, 1 H, H^{13}), 4.32 (d, J = 9.6 Hz, 1 H, H^{15}), 4.63 (d, J = 13.5 Hz, 1 H, H^{14}), 5.05 (d, J = 9.6 Hz, 1 H, H^{16}), 5.54 (s, 1 H, H^{17}), 7.47 (t, J = 1.8 Hz, 1 H, phenyl-H), 7.56 (d, J = 1.8 Hz, 2 H, phenyl-H), 7.83–7.68 (m, 5 H, H^2, H^3, H^6, H^7, H^{10}), 8.41 (d, J = 8.7 Hz, 1 H, H^9), 8.54 (d, J = 8.1 Hz, 2 H, H^4, H^5), 8.76 (br. s, 1 H, H^{12}), 9.39 (dt, J = 1.8, J = 7.7 Hz, 2 H, H^1, H^8) ppm. MS (ESI-TOF): m/z = 1245.3136 $[M + H]^+$.

ref-C_{60} (7): To a solution of fullerene (26.4 mg, 0.037 mmol) in toluene (70 mL), paraformaldehyde (5.5 mg, 0.18 mmol) and **2** (20.5 mg, 0.073 mmol) were added. The reaction mixture was refluxed for 18 h under argon atmosphere and then allowed to cool down. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography eluting with 2:1 hexane/chloroform to afford **7** (12.8 mg, 36 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.40 (s, 18 H, *t*Bu), 4.34 (s, 2 H, PhCH_2), 4.47 (s, 4 H, pyrrolidine-H), 7.44 (t, J = 1.9 Hz, 1 H, phenyl-H), 7.58 (d, J = 1.8 Hz, 2 H, phenyl-H) ppm. MS (ESI-TOF): m/z = 966.2309 $[M + H]^+$.

Supporting Information (see also the footnote on the first page of this article): ^1H NMR spectra of all synthesized compounds.

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