Multistep electron transfer systems based on silicon phthalocyanine, [60]fullerene and trinitrofluorenone[†]

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The synthesis and photodynamics in the absence and in the presence of Mg^{2+} ions of a novel TNF-C₆₀-SiPc-C₆₀-TNF pentad are reported. The redox gradient approach allows to obtain a long-lived CS state of 160 ns and 200 µs in the absence and in the presence of Mg^{2+} ions, respectively.

Nowadays much effort is devoted to look for artificial photosynthetic systems,¹ as donor–acceptor dyads,² triads³ or higher order arrays,⁴ presenting similar characteristics to the natural ones. Moreover, bioinspired in the natural photosynthetic structure, the design of multistep electron transfer systems presenting charge shift reactions in a well tuned redox gradient has received particular attention.⁵ The alignment of the units along a electrochemical gradient promotes acceleration of forward electron transfer and deceleration of charge recombination (CR) leading to an efficient long-lived charge separated (CS) state.⁵

Axially substituted silicon phthalocyanines (SiPcs) are very attractive targets to study photophysical processes because they are not able to aggregate due to their special structural features, thus avoiding fluorescence quenching.⁶ High quantum efficiency and low recombination speed made the [C₆₀]fullerene one of the preferred electron acceptor moieties. Photophysical studies of trinitrofluorenone (TNF) derivatives⁸ due to their high electron acceptor capability have been investigated. Different silicon phthalocyanines substituted either with C₆₀⁹ or TNF¹⁰ have been prepared as efficient systems for photoinduced intramolecular electron transfer determining their electron transfer and back electron transfer rate constants. Moreover, C₆₀ has been successfully used as an electron donor linked with an electron acceptor to attain the longest CS lifetime in the presence of Sc^{3+} (23 ms at 298 K) ever reported for electron donor-acceptor linked systems.¹¹

Based in all the previous studies, we report herein the synthesis of a new TNF- C_{60} -SiPc- C_{60} -TNF pentad 1 (as shown

in Scheme 1) and its photodynamics in the absence and in the presence of Mg^{2+} ions. Taking into account the reduction potentials of the C_{60} derivative and the trinitrofluorenone, compound 1 presents a well defined multisequential electron transfer system, with a long distance between the TNF and the Pc unit to avoid CR processes. Moreover the TNF moiety will have the possibility to complex with metal ions decreasing the back electron transfer driving force.¹²

The synthesis of this pentad was carried out through a convergent strategy by reaction of the bishydroxyphthalocyanine **2** with the carboxylic C₆₀-TNF derivative **3** (Scheme 1). The bishydroxyphthalocyanine **2** was prepared by treatment of the dichloro-substituted phthalocyanine with 4-hydroxy benzoic acid. The synthesis of the carboxylic C₆₀ derivative **3** was accomplished by esterification reaction of the hydroxy-trinitrofluorenone **4**¹³ with tertbutylmonomalonate to yield a fluorenone functionalized with a malonate group **5**, which by Bingel reaction forms TNF methanofullerene **6**. Finally, the carboxylic-TNF-C₆₀ derivative **3** was obtained by acid treatment in a very good yield (Scheme 2). (See ESI for analytical and experimental details).†

Semiempirical calculations place the HOMO of the pentad 1 in the phthalocyanine moiety, being the LUMO and LUMO-1



Scheme 1 Synthesis of the TNF- C_{60} -SiPc- C_{60} -TNF pentad 1.

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Scheme 2 Synthesis of TNF-C₆₀ 3.

localized in the trinitrofluorenone and the LUMO-2 and LUMO-3 in the C_{60} moieties (Fig. 1).

A deaerated PhCN solution containing TNF-C₆₀-SiPc-C₆₀-TNF pentad 1 gave rise upon a 355 nm femtosecond laser pulse to transient absorption bands at 880 and 1000 nm due to SiPc^{•+} and $C_{60}^{\bullet-}$ moieties, respectively. At 950 nm the decay of the singlet excited state of SiPc (¹SiPc*) is overlapped with the rise of $C_{60}^{\bullet-}$. This clearly indicates the formation of the CS state. From the rise in absorbance at 880 nm due to SiPc^{•+} in Fig. 2b the rate constant of formation of SiPc^{•+} in the pentad was determined as 1.7×10^9 s⁻¹, that agrees well with the fluorescence quenching rate constant obtained from the decay of the 950 nm due to ¹SiPc* ($1.7 \times 10^9 \text{ s}^{-1}$). This shows that intramolecular electron transfer from ¹SiPc* to C₆₀ occurs in the pentad to produce the charge-separated state, $TNF-C_{60}^{\bullet-}$ - $SiPc^{\bullet +} - C_{60}$ -TNF. The fluorescence from ¹SiPc^{*} is quenched due to the electron transfer to C_{60} in the pentad as compared to that of the SiPc reference compound in PhCN (Fig. S10, ESI).† The lifetime of the CS state in PhCN was determined as 3.6 ns from the decay of absorbance at 880 nm. This photodynamics totally agrees with the previously reported data for C₆₀-SiPc-C₆₀ triad.^{9a}

The transient absorption spectrum obtained upon nanosecond laser pulse excitation (355 nm) of the pentad **1** in deaerated benzonitrile gave rise to the transient absorption bands at 880 and at 550 nm due to SiPc^{•+} unit and 510 nm due to TNF^{•-} moiety (Fig. 3a). These data agree with the radical pairs absorption bands previously reported for the TNF-SiPc-TNF



Fig. 1 Molecular orbitals of pentad 1 calculated by PM3 method.



Fig. 2 (a) Femtosecond transient absorption spectra of TNF-C₆₀-SiPc-C₆₀-TNF pentad 1 in deaerated PhCN at 298 K after laser excitation at 355 nm. (b) Time profile of absorbance at 950 nm. (c) Time profile of absorbance at 880 nm.

triad¹⁰ where a lifetime of the CS state of 22 ps was detected. For the pentad **1**, taking into consideration the decay of the absorption band at 880 nm, a lifetime of 160 ns for the CS state is observed in benzonitrile (Fig. 3b). The quantum yield of the CS state is 23% determined from comparative method using SiPc^{•+} absorbance at 880 nm.¹⁴ Comparison of the lifetime of the CS state (τ_{CR}) of pentad **1** (160 ns) with the τ_{CR} of C₆₀-SiPc-C₆₀ triad (5.0 ns)⁹ indicates an increase of two orders of magnitude of τ_{CR} in a polar solvent through the rational design of a multistep electron transfer system by covalently linking TNF units to the C₆₀.

Upon addition of magnesium perchlorate $[Mg(ClO_4)_2]$ to a PhCN solution of pentad 1, nanosecond laser flash photolysis was recorded with photoexcitation at 355 nm (Fig. 3c). The bands observed at 880 and 550 nm (SiPc^{•+}) and 900 and 510 nm (TNF^{•-}) confirm the formation of the CS state. The decay of the band at 880 nm shows an increase of the lifetime of the CS state till 200 µs (Fig. 3d), the higher value found to



Fig. 3 (a) Nanosecond transient absorption spectra of TNF-C₆₀-SiPc-C₆₀-TNF pentad 1 in deaerated PhCN at 298 K after laser excitation at 355 nm. (b) Time profile of absorbance at 880 nm. (c) Nanosecond transient absorption spectra of TNF-C₆₀-SiPc-C₆₀-TNF pentad 1 in deaerated PhCN at 298 K after laser excitation at 355 nm with Mg(ClO₄)₂ (10 mM). (d) Time profile of absorbance at 880 nm.



Fig. 4 Energy Diagram of Photoinduced Electron Transfer in

TNF-C₆₀-SiPc-C₆₀-TNF pentad 1.

date in Pc-C₆₀ systems in polar solvents. The complexation of the magnesium ion with the fluorenone unit was confirmed by transient absorption spectrum obtained upon addition of magnesium perchlorate to the TNF-SiPc-TNF triad. Photoexcitation of TNF-SiPc-TNF triad at 355 nm results in formation of the CS state where the absorption bands TNF[•]/Mg²⁺ are nearly shifted form those of TNF[•] (Fig. S11).¹⁵

The energy of the CS state $(SiPc^{\bullet^+}-C_{60}-TNF^{\bullet^-}/Mg^{2^+})$ is now lower than the energy of the silicon phthalocyanine triplet excited state $({}^{3}SiPc^{*-}C_{60}-TNF), {}^{9a}$ which decelerates the metal ion-decoupled electron transfer process for charge recombination to the ground state thus increasing the lifetime of the CS state, as shown in Fig. 4, where the CS energy is determined from the redox potentials reported previously.¹⁰

In summary, the synthesis and the photophysical studies of a new TNF-C₆₀-SiPc-C₆₀-TNF pentad 1 have been carried out. We have demonstrated that the redox gradient approach can be also applied to artificial reaction centers with multiple units constructed by Pc, C₆₀ and TNF moieties. The longer $\tau_{\rm CR}$ of pentad 1 (160 ns) in comparison with that of C₆₀-SiPc-C₆₀ (5.0 ns) reflects the role of the multistep system in the deceleration of the charge recombination process of the $SiPc^{\bullet+}-C_{60}-TNF^{\bullet-}$ radical ion pair. The complexation of magnesium ion with the TNF units of the pentad 1 makes the energy of the SiPc^{•+}-C₆₀-TNF^{•-}/Mg²⁺ CS state lower than the ${}^{3}SiPc^{*}-C_{60}$ -TNF excited state, and as a consequence, increasing the τ_{CR} till 200 µs. Thus, the axially substituted silicon phthalocyanine with different acceptor moieties (C₆₀ and TNF) makes it possible to construct the unique pentad that has long wavelength absorption with the redox gradient required for stepwise charge separation to attain the longerlived CS state upon photoexcitation as compared with other multicomponent donor-acceptor ensembles.

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