

Photophysical Studies on Covalently-linked Naphthalene and TEMPO Free Radical Systems: Observation of a Charge Transfer State in the Ground State

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Abstract A series of molecules containing a naphthalene chromophore and a stable free radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) covalently linked by a spacer group of different lengths have been synthesized. In *n*-hexane solution, their photophysical behavior was studied and compared with a system of freely moving naphthalene and the free radical TEMPO. The linked molecules showed strong quenching of the singlet and triplet states of the naphthalene moiety, compared to when naphthalene and TEMPO were not linked. The quenching efficiency decreased with increasing the length of the spacer group. In addition, new electronic absorption and emission bands, along with the usual bands of the individual moieties, were also seen. These new bands have been attributed to the formation of electron donor-acceptor charge-transfer complexes in the ground state, arising from the interaction between the two moieties in close proximity. The photophysical dynamics of the linked molecules has been rationalized by assuming the existence of two types of population of the linked molecules: folded and extended. The ground state complex formation is proposed to occur only in the folded conformation of the linked molecules. To our knowledge, this is possibly the first example of a ground state charge-transfer complex formation involving a TEMPO free radical and naphthalene.

Keywords Charge transfer complex · Excited state quenching · Intramolecular quenching · TEMPO · Naphthalene · Ground state charge transfer complex

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Introduction

Quenching of electronically excited states by paramagnetic species such as oxygen has been well studied in scientific literature [1, 2]. It is observed that they can quench both the singlet [3] and the triplet states [4] of organic as well as inorganic compounds. Also well-studied quenchers of excited states are nitroxyls (commonly called nitroxides), which are a class of paramagnetic molecules with a single unpaired electron [5, 6]. For these species too, both singlet and triplet state quenching have been observed. The advent of piperidine-based stable free radicals proved very useful in such studies, as one could now easily control the rate of the quenching process. It was then natural to investigate the quenching mechanism of these nitroxyl radicals.

Based on the studies carried by various research groups [7–10], some general conclusions have been drawn regarding the quenching mechanism. For quenching of triplet states, the electron exchange interaction is the dominant mechanism. There are two variants of the electron exchange induced-quenching, depending on the relative energy of the triplet and the radical [7, 11]. If the triplet energy is higher than that of the radical, the quenching occurs via energy transfer from the triplet to the radical. In contrast, if the triplet energy is lower, the quenching occurs by the enhanced inter-system crossing process.

Fluorescence quenching, on the other hand, cannot be explained by a single mechanism in all cases. Fluorescence quenching of perylene-3,4,9,10-bis (dicarboximide) by TEMPO free radical in tetrahydrofuran takes place by the electron transfer mechanism [12]. Similarly, quenching via resonance energy transfer was proposed to occur in the case of phenanthrene-TEMPO system [13]. However, in majority of systems enhanced internal conversion (S_1 - S_0 EIC) and enhanced inter-system crossing (S_1 - T_1 EISC) have been

observed to be the dominant quenching mechanisms. EISC leads to enhanced triplet quantum yields in the presence of a radical and was convincingly shown for pyrene, perylene, 9, 10-dimethyl anthracene and 9,10-diphenyl anthracene [7, 14]. So far there has been no direct experimental evidence of EIC. While explaining the quenching process of a singlet excited state by a radical, the role of EIC is invoked, only when all other routes of the quenching mechanisms are found to be unsatisfactory [15].

Most of the studies leading to the above body of knowledge were performed in systems where the excited molecule and the quenching radical were separate molecules freely moving in homogeneous solutions, and diffusive encounters between them led to quenching. It is thus conceivable that if the diffusive motion is minimized, by holding the excited molecule and the quencher at a fixed distance, one could get a more detailed insight into the dynamics of the quenching process. With that aim, we covalently linked a naphthalene moiety to a stable radical moiety of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) through a hydrocarbon spacer group of various lengths. Here we present the results of steady-state and time-resolved fluorescence studies on these linked molecules. For some of the systems, we recently reported the sequential quenching of the excited singlet and triplet states of naphthalene by TEMPO, as revealed through the electron spin polarization of the radical at low temperature [16, 17]. The quenching efficiency and the magnitude of the electron spin polarization steadily decrease with increasing the distance between two moieties. While such distance dependence was expected, we present here an unexpected observation of new absorption and fluorescence emission bands in these linked molecules, which are absent when naphthalene and radical molecules are not linked. We proposed the existence of a charge transfer electronic state in the linked molecules to rationalize the observations.

Experimental

The structures and symbolic names of different molecules used in this work are given in Chart 1. The general steps for synthesizing various molecules in our laboratory are given in Scheme 1. The detailed procedures have been described in the Synthesis section later. Starting materials 2-naphthalene methanol, 4-hydroxy-TEMPO, sodium hydride and 1,6-dibromohexane were bought from Sigma-Aldrich (USA) and used as received. The linking group 1,4-dibromobutane was bought from S. D. Fine Chemicals Limited (India). The remaining chemicals were of A. R. grade and bought commercially. Dry dimethylformamide (DMF), purchased from Sigma-Aldrich, was used as a solvent for carrying out all the reactions, except the ones mentioned in the Synthesis section. The column chromatography was done on a standard 60 angstrom silica gel.

Proton nuclear magnetic resonance spectra in CDCl_3 were recorded in a Bruker 500 MHz spectrometer, using TMS as an internal standard. TEMPO-linked molecules do not give any NMR signal because of the presence of the radical. Therefore, their NMR spectra were recorded in the presence of phenyl hydrazine, which reduces the radical to a diamagnetic compound [18]. CD_3OD was used as a solvent in such cases, since in CDCl_3 we observed the formation of a suspension after the addition of phenyl hydrazine. Aromatic protons usually have long T_1 relaxation times (~ 10 – 15 s). So a delay of 60 s between successive acquisitions of the free induction decay signals was kept, which helped to acquire accurate intensities of the proton signals. The GC-MS analysis was performed using a gas chromatograph (Trace GC Ultra, Thermo Electron Corporation, Italy) coupled with an ion trap mass spectrometer (Polaris Q, Thermo Electron Corporation, USA).

The ground state absorption, steady state fluorescence and phosphorescence measurements were done in a UV/Vis spectrophotometer (Lambda 25, Perkin Elmer, USA) and a Jobin-Yvon spectro-fluorimeter (FluoroLog-3, USA), respectively. Fluorescence lifetimes were recorded by a picosecond spectrometer using time-correlated single photon counting technique (TCSPC), built in the laboratory. Nanosecond laser flash photolysis experiments were done, also in a laboratory-built setup. No degassing was done for these measurements, since no effect of dissolved oxygen was observed on the lifetimes of the linked molecules. All these experiments were done in solutions of *n*-hexane.

Synthesis

The method of Williamson ether synthesis was used for synthesizing the linked molecules. For these linked molecules, we wanted that the electronic properties of naphthalene should not change on linking with other moieties. Hence in all the linked molecules, one methylene group was attached to the β carbon atom of naphthalene. This ensured minimum electronic perturbation to the naphthalene moiety when other groups were linked to this methylene group. Nap- CH_2 -O-TEMPO was synthesized in one step by the reaction of 2-bromomethyl naphthalene with 4-hydroxy-TEMPO. Nap- CH_2 -O-(CH_2)₄-O-TEMPO and Nap- CH_2 -O-(CH_2)₆-O-TEMPO were synthesized in two steps. The first step involved reaction of the 2-naphthalene methanol with the linker 1, *n*-dibromoalkanes. In this reaction, we observed decomposition of the starting material 2-naphthalene methanol in basic conditions. It was necessary to circumvent this reaction so as to improve the yield of the required molecule. We achieved this by using 1, *n*-dibromoalkanes itself as the solvent. This method gave reasonable yields of the required molecule. The product of this first step was then reacted with 4-hydroxy-TEMPO,

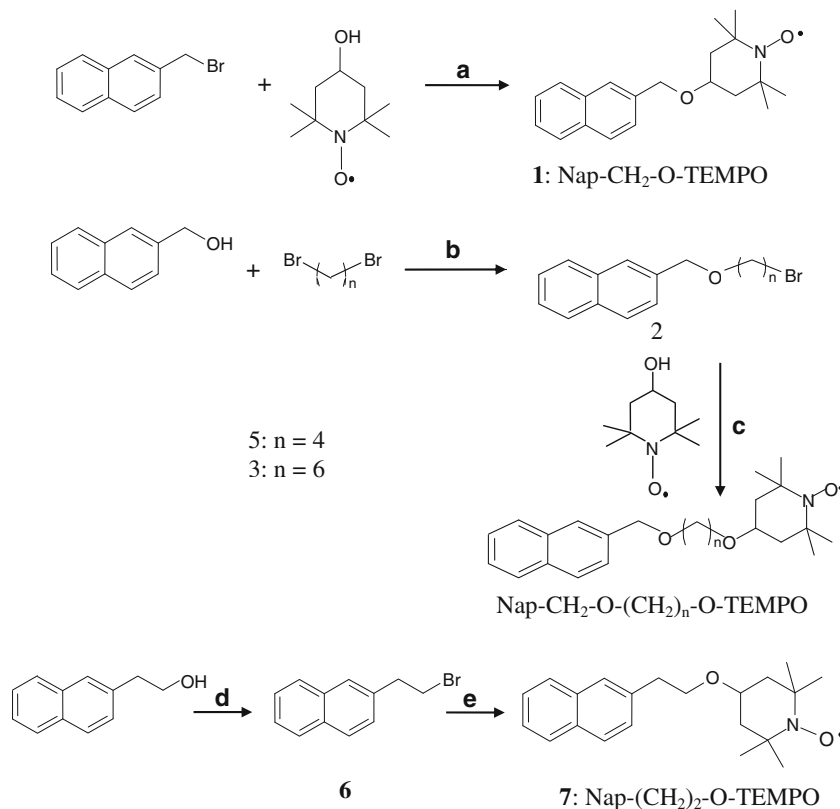
Chart 1 Molecular systems and their symbolic names. The “unlinked system”[†] denotes an equimolar homogeneous mixture of naphthalene and TEMPO

Molecular systems	Symbolic names
	Nap-CH ₂ -O-TEMPO
	Nap-(CH ₂) ₂ -O-TEMPO
	Nap-CH ₂ -O-(CH ₂) ₄ -O-TEMPO
	Nap-CH ₂ -O-(CH ₂) ₆ -O-TEMPO
	Naphthalene and TEMPO, the “unlinked system” [†]

which gave the required linked molecules. For synthesizing Nap-(CH₂)₂-O-TEMPO, 2-naphthalene ethanol was first converted to 2-bromoethyl naphthalene by phosphorus

tribromide. 2-Bromoethyl naphthalene was then reacted with 4-hydroxy-TEMPO in 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid as the solvent to generate Nap-(CH₂)₂-

Scheme 1 **a** NaH, DMF, room temperature; **b** 1,*n*-dibromoalkane, KOH, room temperature, N₂ atm; **c** 4-hydroxy TEMPO, KOH, DMF, room temperature; **d** PBr₃, DMF, room temperature; **e** 4-hydroxy TEMPO, [Bmim][BF₄], 110 °C



O-TEMPO. Details of synthesizing different molecules are given below.

Synthesis of Nap-CH₂-O-TEMPO (1): This molecule was synthesized by following the protocol developed by Dr Amol Deorukhkar in our laboratory. 4-hydroxy TEMPO (1.72 g, 10 mmol) was dissolved in 10 ml of dry THF and cooled to 0 °C. Sodium hydride (0.29 g, 12 mmol) was added gradually with constant stirring. The reaction was stirred for 30 min at low temperature, followed by addition of 2-bromo methyl naphthalene (2.2 g, 10 mmol). The reaction mixture was then warmed to room temperature and stirred until completion (1 day), as monitored by TLC. The reaction mixture was diluted with water (30 ml). The resulting solution was extracted with ethyl acetate (3×50 ml). The combined organic layers were dried with anhydrous sodium sulphate (15 g), filtered, concentrated and purified by column chromatography using 0 to 10 % ethyl acetate/hexane as the eluent to provide an orange solid powder of Nap-CH₂-O-TEMPO (m.p. 82–85 °C). ¹H NMR δ (CD₃OD): 7.85 (m, 4H), 7.48 (br-s, 3H), 4.71 (s, 1H), 3.82 (br-s, 1H), 2.12 (d, 2H), 1.80 (m, 2H), 1.36 (m, 6H), 1.25 (m, 6H).

Synthesis of Nap-CH₂-O-(CH₂)₆-Br (2): To a stirred solution at room temperature of tetrabutylammonium bromide (0.1 g) in 1,6-dibromohexane (15 ml, 64 mmol) and methanol (1.5 ml), 2-naphthalene methanol (2.5 g, 16 mmol) was added. This was followed by addition of sodium hydroxide pellets (1.8 g, 32 mmol). The reaction was stirred for 36 h under nitrogen atmosphere. Then 1,6-dibromohexane was removed by vacuum distillation to yield a white residue. This residue was added to water (30 ml) and extracted with ethyl acetate (3×50 ml). The combined organic layers were dried with anhydrous sodium sulphate (15 g), filtered, concentrated and purified by column chromatography using 0 to 5 % ethyl acetate/hexane as the eluent to provide a white solid powder of Nap-CH₂-O-(CH₂)₆-Br. ¹H NMR δ (CDCl₃): 7.85 (m, 4H), 7.48 (br-s, 3H), 4.67 (s, 2H), 3.52 (t, 2H), 3.40 (t, 2H), 1.87 (m, 2H), 1.66 (m, 2H), 1.44 (m, 4H).

Synthesis of Nap-CH₂-O-(CH₂)₆-O-TEMPO (3): 4-hydroxy TEMPO (0.86 g, 5 mmol) was dissolved in 12 ml acetonitrile. Tetrabutylammonium bromide (0.1 g) was then added followed by the addition of potassium hydroxide (1.4 g, 25 mmol) at room temperature. The resulting mixture was stirred for 1 h and then **2** (1.6 g, 5 mmol) was added. The solution was stirred under nitrogen atmosphere for 1 day. The reaction mixture was then diluted with water (30 ml) and extracted with ethyl acetate (3×50 ml). The combined organic layers were dried with anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography using 0 to 10 % ethyl acetate/hexane as the eluent to yield an orange

solid powder of Nap-CH₂-O-(CH₂)₆-O-TEMPO. ¹H NMR δ (CD₃OD): 7.80 (m, 4H), 7.47 (br-s, 3H), 4.66 (s, 2H), 3.56 (s, 1H), 3.51 (t, 2H), 3.41 (t, 2H), 1.93 (d, 2H), 1.66 (m, 2H), 1.57 (m, 2H), 1.50 (m, 2H), 1.40 (m, 4H), 1.23 (m, 6H), 1.18 (m, 6H).

Synthesis of Nap-CH₂-O-(CH₂)₄-Br (4): To a stirred solution of tetrabutylammonium bromide (0.1 g) in 1,4-dibromobutane (20 ml, 170 mmol) and water (4 ml), a solution of 2-naphthalene methanol (1.58 g, 10 mmol) in DMSO (4 ml) was added at room temperature. This was followed by the addition of sodium hydroxide pellets (1.7 g, 30 mmol). The reaction was stirred for 24 h under nitrogen atmosphere. 1.7 g of sodium hydroxide and 0.8 g tetrabutylammonium bromide was added again and the reaction was continued for further 24 h until 2-naphthalene methanol reacted completely, which was monitored by TLC. 1,4-Dibromobutane was then removed by vacuum distillation to yield a white residue. This residue was added to water (30 ml) and extracted with ethyl acetate (3×50 ml). The combined organic layers were dried with anhydrous sodium sulphate (15 g), filtered, concentrated and purified by column chromatography using 0 to 5 % ethyl acetate/hexane as the eluent to yield a white solid powder of Nap-CH₂-O-(CH₂)₄-Br. ¹H NMR δ (CDCl₃): 7.86 (m, 4H), 7.51 (br-s, 3H), 4.70 (s, 2H), 3.58 (t, 2H), 3.48 (t, 2H), 2.03 (p, 2H), 1.82 (p, 2H).

Synthesis of Nap-CH₂-O-(CH₂)₄-O-TEMPO (5): 4-hydroxy TEMPO (1.7 g, 10 mmol) was dissolved in 25 ml acetonitrile and cooled to 0 °C. Potassium *tert*-butoxide (2 g, 18 mmol) was added to it over a period of 10 min. The reaction mixture was stirred for further one hour and then **4** was added. The solution was warmed to room temperature and was stirred under nitrogen atmosphere for 1 day. The reaction mixture was then diluted with water (30 ml) and extracted with ethyl acetate (3×50 ml). The combined organic layers were dried with anhydrous sodium sulphate (15 g), filtered, concentrated and purified by column chromatography using 0 to 10 % ethyl acetate/hexane as the eluent to yield an oily orange liquid. ¹H NMR δ (CD₃OD): 7.82 (m, 4H), 7.48 (br-s, 3H), 4.71 (s, 2H), 3.59 (s, 1H), 3.54 (t, 2H), 3.45 (t, 2H), 1.94 (d, 2H), 1.69 (m, 4H), 1.52 (m, 2H), 1.24 (m, 6H), 1.18 (m, 6H).

Synthesis of Nap-(CH₂)₂-Br (6): Phosphorus tribromide (1.93 ml, 20 mmol) was added dropwise to a stirred solution of 2-naphthalene ethanol (3.44 g, 20 mmol) in DMF at 0 °C. The solution was warmed to room temperature and was stirred under nitrogen atmosphere for 3 h. The reaction mixture was then diluted with water (30 ml) and extracted with ethyl acetate (3×50 ml). The organic layer was evaporated in vacuum to give a white solid (yield≈35 %, m.p. 64–67). ¹H NMR δ (CDCl₃): 7.85

(m, 3H), 7.7 (s, 1H), 7.5 (p, 2H), 7.37 (d, 1H), 3.69 (t, 2H), 3.36 (t, 2H).

Synthesis of Nap-(CH₂)₂-O-TEMPO (7): 4-Hydroxy TEMPO (4.3 g, 25 mmol) and **6** (235 mg, 1 mmol) were added to a reaction vessel containing 2 ml 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid ([Bmim] [BF₄]). The resulting mixture was then heated at 110 °C for 3 days. The solution was then cooled to room temperature and diluted with water (30 ml) and extracted with ethyl acetate (3×50 ml). The combined organic layers were dried with anhydrous sodium sulphate (15 g), filtered, concentrated and purified by column chromatography using 0 to 10 % ethyl acetate/hexane as the eluent to yield an orange solid (<1 %). ¹H NMR δ (CD₃OD): 7.78 (m, 4H), 7.44 (m, 3H), 3.73 (t, 2H), 3.58 (m, 1H), 3.03 (t, 2H), 1.93 (br-d, 2H), 1.52 (t, 2H), 1.23 (m, 6H), 1.13 (m, 6H).

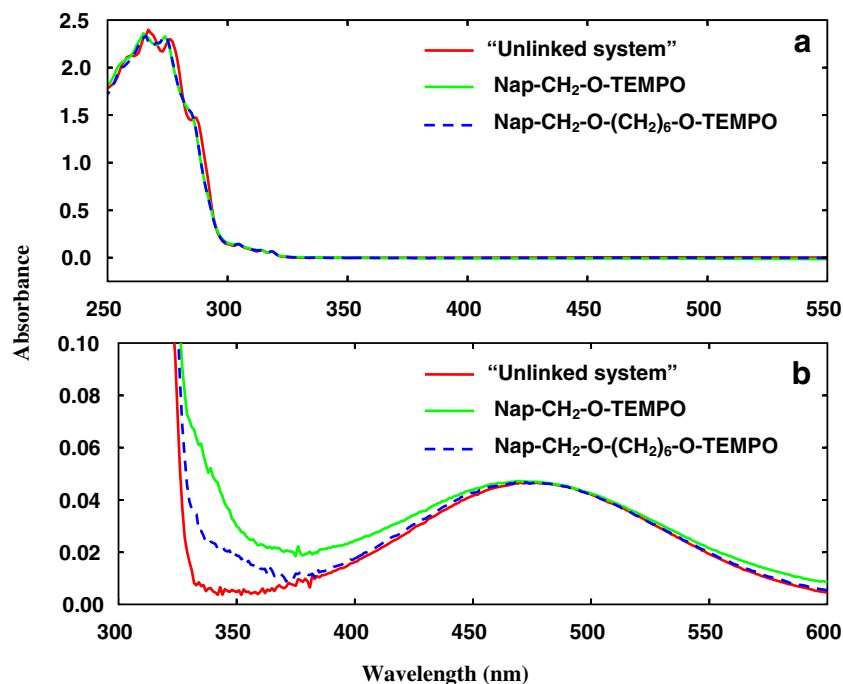
Results and Discussion

In the following discussion, the phrase “unlinked system” will be used to mean an equimolar mixture of naphthalene and TEMPO, without being linked, present in homogeneous solution of *n*-hexane.

UV–Vis Absorption Spectroscopic Measurements

Figure 1a shows the UV-Visible absorption spectra of 1.0 mM solution of two linked molecules along with the spectrum of

Fig. 1 UV-visible absorption spectra of the linked molecules and the “unlinked system” in *n*-hexane. **a** conc. 1.0 mM; **b** conc. 10.0 mM. Higher concentration in **b** was used to record the weak absorption band in the 350–600 nm region



the “unlinked system” of the same concentration in *n*-hexane. The spectrum of separate chromophores is also shown. Strong bands corresponding to naphthalene were seen in the region of 250–300 nm. A weak absorption band centered at 480 nm corresponding to TEMPO’s D₀ → D₁ transition was also present, but not seen there, because of its low molar absorptivity. This band, however, could be readily seen when the concentration was increased (Fig. 1b). The absorption spectra of the linked molecules were broadly a superposition of the corresponding spectrum of naphthalene and TEMPO. This indicates the absence of any strong electronic coupling between naphthalene and TEMPO in the linked molecules. However, when the spectrum was expanded vertically (Fig. 1b), we could see a difference in the spectrum of linked and “unlinked” molecules in the region of 350 nm. The linked molecules showed the presence of an extra band at around 350 nm.

Steady-State and Time-Resolved Fluorescence Measurements

Figure 2a shows the fluorescence emission spectra of Nap-CH₂-O-(CH₂)₆-O-TEMPO, the “unlinked system” and naphthalene in *n*-hexane solution at the room temperature of 21 °C. The 325-nm band, which corresponds to the emission from the S₁ state of naphthalene, was present in both Nap-CH₂-O-(CH₂)₆-O-TEMPO and the “unlinked system.” We attributed this emission band in the region of 325–375 nm to arise from a locally excited (LE) state of naphthalene in the linked molecules. The reduced intensity in the linked systems indicates quenching of naphthalene fluorescence by TEMPO. Similar quenching was seen in all the linked molecules, with

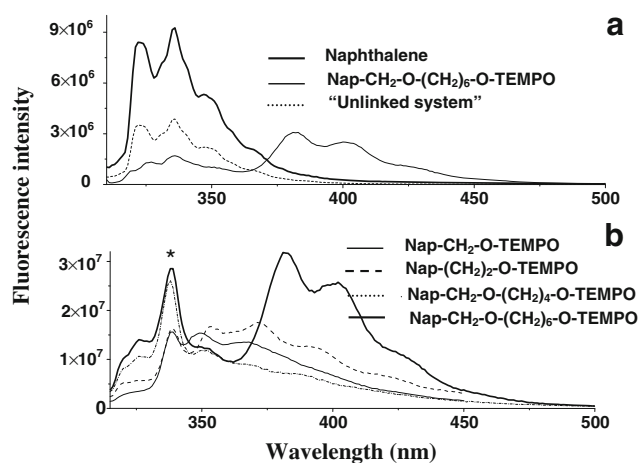


Fig. 2 Fluorescence emission spectra of 0.1 mM solution of (a) naphthalene and linked molecules in *n*-hexane, (excitation wavelength $\lambda_{EX}=295$ nm); **b** Nap-CH₂-O-TEMPO, Nap-(CH₂)₂-O-TEMPO, Nap-CH₂-O-(CH₂)₄-O-TEMPO and Nap-CH₂-O-(CH₂)₆-O-TEMPO in *n*-hexane, ($\lambda_{EX}=308$ nm). The sharp peak at 335 nm (starred) in **b** is the Raman peak due to the solvent

the maximum quenching observed for Nap-CH₂-O-TEMPO molecule. The quenching efficiency went down in the order Nap-(CH₂)₂-O-TEMPO, Nap-CH₂-O-(CH₂)₄-O-TEMPO and Nap-CH₂-O-(CH₂)₆-O-TEMPO, as could be seen from the intensity in the 325–375 nm region (Fig. 2b). Thus, the quenching efficiency decreased with increasing the length of the spacer group. Figure 2a also shows that decrease in intensity in the linked molecules was much more than in the “unlinked system” of naphthalene and TEMPO of the same concentration. Since absorbance of naphthalene at the excitation wavelength was kept same for both the linked and the “unlinked molecules,” more intensity reduction in the linked molecules showed that the quenching in the linked molecules was dominantly an intra-molecular phenomenon (This was also reflected in the lifetime studies. See Table 1).

In addition to the LE emission band around 325–375 nm region, discussed above, Nap-CH₂-O-(CH₂)₆-O-TEMPO

showed a prominent emission band around 400 nm, with vibrational structures similar to the other band. Other linked molecules also showed such an extra band, at slightly different wavelengths (Fig. 2b). Such an extra emission band was not present in the “unlinked system” consisting of an equimolar concentration of naphthalene and TEMPO, where only the band around 325–375 nm could be seen. The extra band could not be detected in the “unlinked system” even when the concentrations of naphthalene and TEMPO were increased to 100 mM. We, therefore, concluded that the origin of the extra emission band was due to specific interactions involving the naphthalene and the radical moieties in the linked systems. In order to understand the origin of this band, we investigated the excitation spectra of these systems.

Figure 3a and b, respectively, shows the excitation spectra of Nap-CH₂-O-(CH₂)₆-O-TEMPO and the naphthalene in *n*-hexane at room temperature. Here, the emission was monitored at 335 nm corresponding to the LE state of naphthalene. Both the spectra were nearly identical and matched with the absorption spectrum of naphthalene. Other linked molecules also showed similar behavior. When the emission was monitored at 401 nm corresponding to the extra band mentioned above, the excitation spectrum was, however, very different from the absorption spectrum of naphthalene (Fig. 3c). This excitation spectrum showed a band with a hump in the 320–370 nm region, bearing no resemblance to the absorption spectrum of naphthalene. Nor did it resemble the absorption spectrum of TEMPO. Close inspection of the absorption spectrum of linked molecules showed that this band of the excitation spectra was very similar to the extra absorption band around 350 nm, shown by these linked molecules (Fig. 1b). We now discuss the various possibilities for the origin of this extra band.

First we considered the possibility of the existence of an impurity, giving rise to the extra band. As the linked molecules were synthesized in our laboratory from the starting materials that were obtained from commercial sources, there was some possibility of small impurities remaining in the final products

Table 1 Fluorescence lifetimes of various molecules, measured by time-resolved fluorescence experiments in *n*-hexane solvent at 21 °C

Molecule	Lifetimes/ns (relative contribution)
Naphthalene ^a	7.58±0.02 (0.94), 0.8±0.1 (0.06)
Naphthalene + TEMPO (“unlinked system”) ^b	6.5±0.1 (0.8), 0.8±0.1 (0.2)
Nap-CH ₂ -O-TEMPO ^c	0.12±0.01 (0.80), 0.9±0.3 (0.09), 4.2±0.3 (0.11)
Nap-(CH ₂) ₂ -O-TEMPO ^d	0.35±0.01 (0.69), 1.38±0.3 (0.26), 5.4±0.4 (0.05)
Nap-CH ₂ -O-(CH ₂) ₄ -O-TEMPO ^e	0.43±0.01 (0.75), 1.61±0.01 (0.13), 5.48±0.06 (0.12)
Nap-CH ₂ -O-(CH ₂) ₆ -O-TEMPO ^f	0.76±0.01 (0.98), 4.0±0.1 (0.02)

^{a,b} Excitation at 304 nm, emission observed at 335 nm

^{c,e} Excitation at 304 nm, emission observed at 355 nm

^d Excitation at 295 nm, emission observed at 355 nm

^f Excitation at 290 nm, emission observed at 335 nm

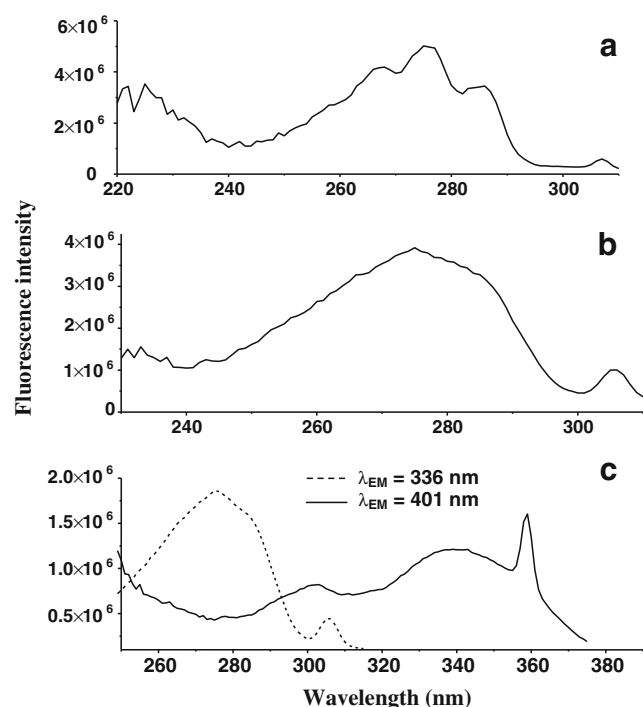
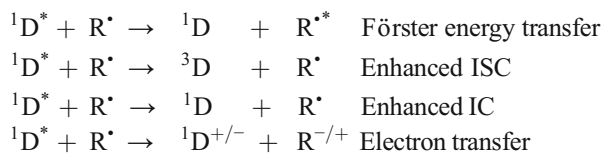


Fig. 3 Fluorescence excitation spectra of 0.1 mM solution in *n*-hexane of (a) naphthalene (emission wavelength $\lambda_{EM}=335$ nm); (b) Nap-CH₂-O-(CH₂)₆-O-TEMPO in *n*-hexane, $\lambda_{EM}=335$ nm; (c) Nap-CH₂-O-(CH₂)₆-O-TEMPO in *n*-hexane, ($\lambda_{EM}=401$ nm). The dotted curve in C shows the same spectrum of b for comparison. The sharp peak at about 360 nm in c is the Raman peak due to the solvent

of the linked molecules. We ruled out this possibility based on the following points. (1) The band was present even after purifying the products through HPLC. (2) For a particular linked molecule, the relative intensity of the extra band and the LE band remained the same for different, independently synthesized batches. (3) NMR and ESI-MS spectroscopic techniques also did not give any indication of impurities.

Next we considered whether the band was related to the quenching of fluorescence of naphthalene of the linked molecules. The following pathways are considered to be responsible for quenching of a singlet excited state ($^1D^*$) by a free radical (R^\bullet).

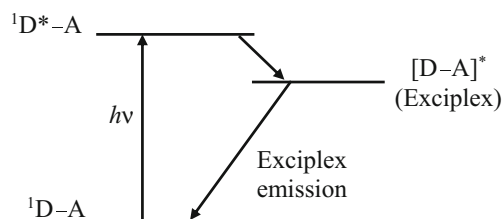


For the linked molecules, D is the naphthalene moiety and R^\bullet is the TEMPO moiety. For the naphthalene-TEMPO system, Green et al. [8] have shown that the Förster energy transfer and the electron transfer pathway do not operate. The authors could not distinguish between the enhanced ISC and enhanced IC and hence concluded that the true mechanism can be either of them or both. One way to distinguish between

the two mechanisms is by time-resolved EPR spectroscopy to detect enhancement of electron spin population of the radical, when it participates in the quenching of an excited state. Enhanced ISC can generate spin polarization in the radical via radical triplet pair mechanism [16, 19, 20]. Enhanced IC cannot generate any spin polarization on the radical. We will consider if any of these mechanisms, if they are occurring, could explain the extra emission band around 400 nm.

Enhanced ISC can explain the extra band if this band is associated with the phosphorescence of naphthalene. We ruled out this possibility, as the emission band did not match with the phosphorescence spectrum of naphthalene recorded at 77 K. Moreover, at room temperature naphthalene is known to be non-phosphorescent. Similarly, enhanced IC is a non-radiative process and hence cannot be associated with any emission band. In Förster energy transfer, the excitation energy of the donor is transferred to the acceptor via dipole-dipole interaction. The spectral overlap between the fluorescence emission of naphthalene and the absorption spectrum of TEMPO is poor [8]. In addition, TEMPO is non-fluorescent. Hence, the Förster energy transfer process could not explain the origin of the extra emission band. This leaves us with the electron transfer mechanism. Electron transfer mechanism could explain the emission band if it was associated with the emission during charge recombination process. This mechanism too, however, has been shown to be inoperative for the naphthalene-TEMPO system based on the absence of any correlation with the redox potentials and reaction rate [8]. We too did not observe any evidence of charged species in nanosecond laser flash photolysis studies (data not shown). So, none of the mechanisms listed above could explain the observed extra band around 350–410 nm in the fluorescence spectrum of the linked molecules.

Fluorescence quenching of naphthalene by typical amines has been shown to occur via charge transfer exciplex formation [21]. This mechanism is shown in Scheme 2. Typically, the exciplex decay is associated with a red shifted emission (relative to the LE band). An exciplex is formed if the two interacting species satisfy exergonic electron transfer requirement ($\Delta G_{ET} < 0$) and are spatially sufficiently close, so that the orbitals involved in the charge transfer can interact appreciably. Since in the present system the extra emission band is red shifted relative to LE band and naphthalene-TEMPO system



Scheme 2 Photophysical scheme of naphthalene-TEMPO linked molecules showing exciplex formation

has negative ΔG_{ET} [8], we examined whether the extra emission band could be associated with the exciplex emission.

In the exciplex, appreciable charge transfer takes place with the result that the exciplex emission wavelength depends strongly on the polarity of the solvent. With the increase of polarity, the exciplex band shows a red shift due to stabilization of the exciplex. Figure 4 shows the fluorescence spectrum of Nap-CH₂-O-(CH₂)₆-O-TEMPO in hexane ($\epsilon=1.88$) and acetonitrile ($\epsilon=35.9$). The extra emission band showed a red shift of 13 nm when the solvent was changed from hexane to acetonitrile. The LE band, on the other hand, did not show any significant shift. This shows that the extra band has a polar character and hence could be assigned to an exciplex emission. The exciplex formation, as shown in Scheme 2, takes place in the excited state of naphthalene. Thus the excitation spectrum of the extra band (Fig. 5b) should correlate with the absorption spectrum of naphthalene, as is observed in case of naphthalene-triethylamine exciplex, which obeys Scheme 2. As shown in Fig. 3b, the excitation spectrum of the extra band, however, did not match with the absorption spectrum of naphthalene. This is inconsistent with Scheme 2. To further check the validity of this scheme, we did the lifetime studies. According to Scheme 2, the exciplex rise time should match with the decay of naphthalene's LE state. Figure 6 shows the time profile of LE band and the extra emission band of Nap-CH₂-O-(CH₂)₆-O-TEMPO recorded using the TCSPC technique (instrument response time ≈ 120 ps). The LE band had a decay time of 0.75 ns. The extra band was seen to rise much faster, with a rise time limited by the instrument response function. Thus, we concluded that Scheme 2 could not be applied to the current system.

So the features of the extra emission band observed in naphthalene-TEMPO linked system are the following: (1) This band was influenced by the polarity of the solvent. (2) This band was seen only in the linked system. (3) The excitation spectrum of this band matched with an absorption band of linked molecules, but not with the absorption spectrum of separate chromophores. (4) The rise time of the extra emission

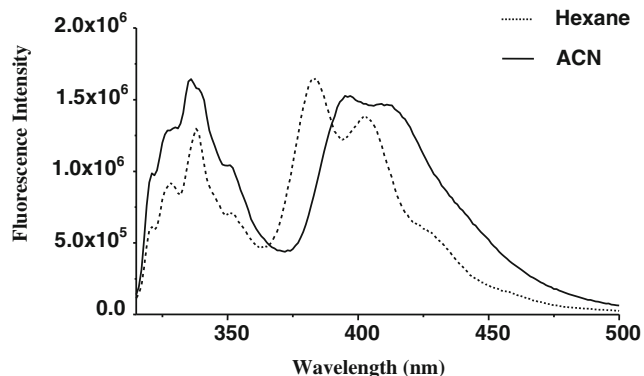


Fig. 4 Fluorescence emission spectra of 0.1 mM solution of Nap-CH₂-O-(CH₂)₆-O-TEMPO in *n*-hexane (dotted line) and acetonitrile (solid line); $\lambda_{EX}=308$ nm

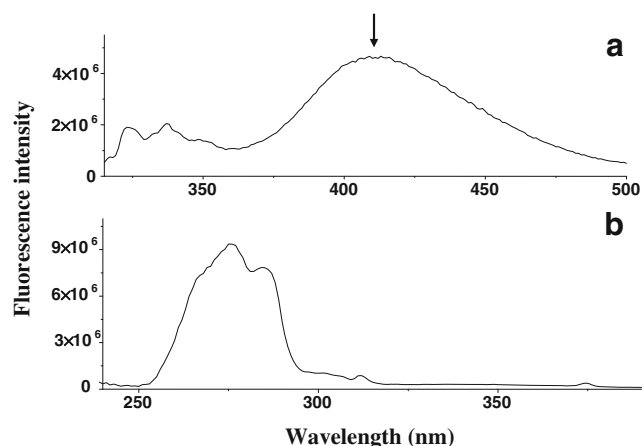


Fig. 5 **a** Fluorescence emission spectra of a solution containing 0.1 mM naphthalene and 100 mM triethylamine in *n*-hexane, Excitation wavelength, λ_{EX} : 290 nm. The broad band around 420 nm corresponds to exciplex emission. **b** Fluorescence excitation spectra of the same solution Emission wavelength fixed at λ_{EM} : 420 nm (marked with an arrow in a.)

band was much faster than the decay of the LE band. Based on these features, we argued if the existence of electron donor-acceptor (EDA) complexes in the ground state of the linked molecules could explain the observed spectral features.

In contrast to exciplex states, which exist only in the excited state, molecules with strong electron donating or accepting tendencies are known to form EDA complexes in the ground state. The formation of EDA complexes is revealed in the absorption spectrum with the appearance of a new absorption band, called a charge transfer band. The extra absorption around the 350 nm region in the linked molecules too (Fig. 1b) could be assigned to a charge transfer band. When excited within this band, the observed emission around 400 nm could be attributed to the emission from the charge transfer state in the linked molecules. The charge transfer state, being formed directly from the ground state molecules, had a much faster rise time which was reflected in the lifetime measurements (Fig. 6).

Table 1 shows the fluorescence lifetimes of the locally excited S₁ state of the linked molecules as well as the “unlinked system.” We observed that none of the systems gave a single

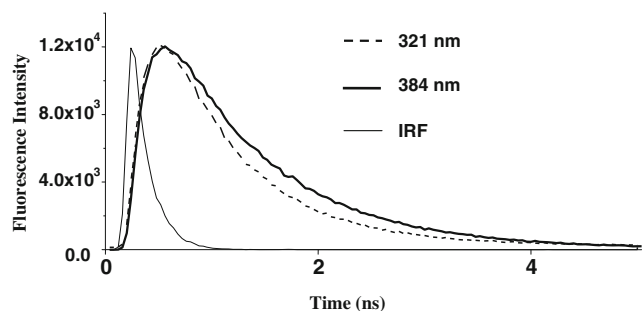


Fig. 6 Fluorescence decay profiles of Nap-CH₂-O-(CH₂)₆-O-TEMPO in *n*-hexane at 21 °C at 321 nm (dashed line) and 384 nm (thick solid line). The instrument response function (IRF) is also shown (thin solid line)

exponential lifetime, including pure naphthalene. However, only one of the components has a dominant contribution. So we considered only this major component for our analysis. In case of naphthalene, the minor component with a lifetime around 1.0 ns was found to disappear when the solution was made free of dissolved oxygen by saturating it with nitrogen gas. Under that condition, a single lifetime of about 100 ns was observed. So this minor component was attributed to the quenching of the excited state by dissolved oxygen. The third component in linked molecules with a lifetime of about 5 ns was attributed to a charge transfer band, as described later. For Nap-CH₂-O-TEMPO with its spacer group of the shortest length, the CT band almost overlapped with the LE band of naphthalene. Hence its contribution in the LE band (the amplitude of the third component) was more than that of the linked molecules with longer spacer groups. In the latter molecules, the appreciable red shifts of the CT band decreased its contribution. From the behavior of the dominant component, we inferred that the fluorescence was efficiently quenched in all the linked molecules, as shown by their reduced lifetimes, compared to that of naphthalene. The quenching efficiency decreased steadily with increasing the linker length. This result is difficult to reconcile with observation that the molecule with the longest spacer group showed the most intense emission from the proposed charge-transfer state. One way to rationalize this observation would be to assume that only a small fraction of molecules was in a folded conformation giving the EDA complex, while the remaining major fraction were in the extended conformation.

In order to address the appropriate conformation necessary for the formation of the EDA complex, we consider the dependence of energy of charge transfer emission band of linked molecules on the length of the spacer group. According to the charge transfer theory of complex formation [22], the energy of a charge transfer state (E_{CT}) in a non-polar solvent is given by

$$E_{CT} = E_{D/D^+}^0 - E_{A/A^-}^0 - E_{coulombic}$$

$$E_{coulombic} = \frac{e^2}{4\pi\epsilon r}$$

Here E_{D/D^+}^0 and E_{A/A^-}^0 are, respectively, the standard oxidation potential of the donor and the standard reduction potential of the acceptor in the solvent under consideration. $E_{coulombic}$ represents the coulombic interaction between two charged particles separated by distance r in a medium of dielectric constant ϵ . Of all the terms, only $E_{coulombic}$ depends on the distance between the naphthalene and the TEMPO moieties. For a series of molecules with identical donor and acceptor moieties, the relative energy difference between the CT state and the LE state depends on the coulombic term [23]. So if the molecules form EDA complexes in the extended conformation, then the stabilization of the charge transfer state

should decrease with increasing linker length. Thus a blue shift should be observed for the extra emission band with increase in the linker length. However, the linked molecules showed a red shift with increase in the linker length. Thus the EDA complexes do not form in the extended conformation. A folded conformation, on the other hand, will facilitate the interaction between the interacting orbitals of naphthalene and TEMPO in forming the EDA complex. The steric strain in forming the folded complexes should decrease on decreasing the length of the spacer group. This should help in the donor and acceptor moieties to approach each other closely, thereby lowering the energy of the CT state. Thus, the red shift in the CT band, seen with the increase of the length of the spacer, indicated that the EDA complexes possibly formed in the folded conformation.

Observation of CT complexes involving TEMPO radical and its derivatives has been reported in the literature [24]. In those complexes, the acceptor molecule is 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄) or 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone (DDQ). These molecules are much stronger electron acceptors (standard reduction potential: +0.57 V (TCNQF₄) and +0.47 V (DDQ), with respect to SCE [24]) than naphthalene (standard reduction potential: -2.49 V, with respect to SCE [25]). As a result, their CT complexes with TEMPO radicals can be isolated as solid compounds. In contrast, the CT complex of naphthalene with TEMPO radical could be seen only in the linked molecules because of their close proximity afforded by the covalent linkage of the two moieties.

From Fig. 1b, the intensity of charge transfer absorption band is seen to be very small compared to absorption bands of naphthalene and TEMPO. Though we do not have any estimate of their molar absorptivity, but by comparing the intensities of the CT bands in other systems, which form strong EDA complexes such as naphthalene-dicyanovinyl complex [26], with the intensity observed here, we concluded that the population of ground state EDA complexes was small. This, in turn, means that the population of folded conformation is small compared to extended conformation. This is expected since the extended conformation is the thermodynamically favored form in the non-polar solvent *n*-hexane.

Finally, we would like to comment on the possible fluorescence quenching mechanism in the naphthalene-TEMPO system. The present studies showed that for the molecules in extended conformation, direct absorption to the charge transfer state is not possible. Further, the CT state is not populated even from the locally excited state of naphthalene (Scheme 2). Thus the dominant quenching mechanism cannot be exciplex formation or the electron transfer. As found by Green et al. [8], the quenching mechanism must be enhanced IC or enhanced ISC or combination of both. There is no confirmatory test for enhanced IC and it is invoked only when other mechanisms do not seem to play any role [12]. So to conclude that

enhanced IC is the sole mechanism for naphthalene-TEMPO system, it is necessary to check whether enhanced ISC occurs or not. The earlier attempts to prove enhanced ISC were to look for enhanced triplet yield in optical experiments. However, such experiments might prove to be inclusive when the radical can quench both singlet and triplet states efficiently. This is particularly the case for naphthalene-TEMPO system [8], and the evidence for enhanced ISC came from the time-resolved EPR studies.

The relative contributions of EISC and EIC are not known in these systems. EISC pathway leads to electron spin polarization in TEMPO radical via RTPM [11, 16]. For chromophore-radical pair with a negative J , the doublet-quartet energy separation, singlet quenching leads to absorptive spin polarization and triplet quenching leads to emissive polarization of TEMPO radical. TREPR studies in our laboratory showed that electron spin polarization is generated in the TEMPO moiety during the quenching of excited naphthalene in several linked systems [16, 17]. These results show that EISC is a dominant quenching process.

Based on the above results, our proposal for the photophysical dynamics of the linked molecules is shown in Scheme 3. The linked molecules exist in folded and extended conformations, which are in dynamic equilibrium. The extended molecules on photoexcitation populate the locally excited state (S_1 state) of the naphthalene moiety. The S_1 state then decays rapidly within 1 ns to populate the triplet state of the naphthalene moiety via EISC. The CT state cannot be populated either by direct excitation or from the S_1 state. Thus, the photophysical behavior of linked molecules in extended conformation is the same as that of the “unlinked system” of

naphthalene and TEMPO. The folded molecules on the other hand form ground state EDA complexes. On photoexcitation, they can populate either the S_1 state or the CT state depending on whether the excitation energy falls in the LE band (energy= $h\nu_1$) or the CT absorption band (energy= $h\nu_2$). The LE state should follow the dynamics similar to that of the extended molecules, while the CT state can either populate the triplet state or can decay back to the ground state.

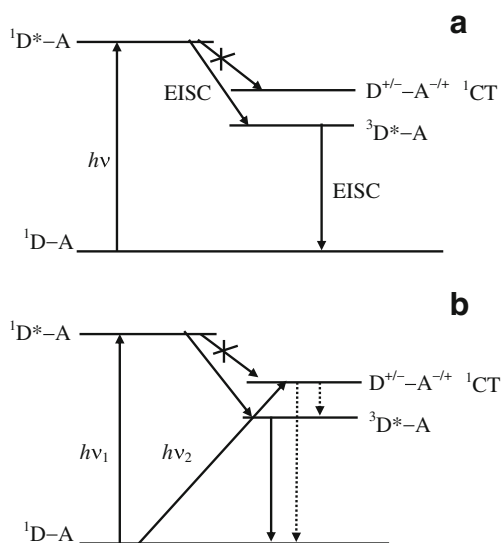
Summary and Conclusions

In the present work, photophysical studies on covalently-linked naphthalene and TEMPO moieties, separated by a spacer group of different lengths, have been described. The presence of the free radical showed efficient quenching of the excited singlet state of naphthalene. New electronic absorption and emission bands, in addition to the usual bands of the individual moieties, are seen. We attributed these new bands to the electron donor-acceptor complexes in the ground state, for a small fraction of the population of the molecules. The complex formation in the ground state occurs between naphthalene and TEMPO when the two moieties are sufficiently close. The photophysical dynamics of the linked molecules shows an additional pathway compared to its counterpart where the two molecules are not linked together. This pathway is the direct excitation to the charge transfer state on photoexcitation, followed by an emission from this state. To our knowledge, this is possibly the first example of ground state charge-transfer complex formation involving the TEMPO free radical and naphthalene.

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Scheme 3 Energy level diagram along with the photophysical scheme of naphthalene-TEMPO linked molecules in **a** extended and **b** folded conformations. The dotted arrows show additional pathways present in the folded molecules. D and A denote the naphthalene and the TEMPO moieties, respectively

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