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Photophysical studies on charge transfer complexes of γ-cyclodextrin–C_{60} with electron-rich amines and sulphur compounds

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Abstract

The formation of donor–acceptor complexes of γ-cyclodextrin–C_{60}–γ-cyclodextrin (CD–C_{60}–CD) with electron-rich amines and sulphur compounds was studied in aqueous solution. The stoichiometry, equilibrium constants and extinction coefficients of the charge transfer complexes were determined by steady state absorption measurements. Picosecond time-resolved studies on CD–C_{60}–CD showed the formation of C_{60} triplets, which were found to decrease with increasing concentration of 1,4-diazabicyclo[2.2.2]octane (DABCO).

Keywords: Photophysical studies; Charge transfer; γ-Cyclodextrin–C_{60}; Amines; Sulphur compounds

1. Introduction

Due to its high electron affinity and the presence of a large number of double bonds, C_{60} takes part in charge transfer reactions in both the ground and excited states [1–5]. Charge transfer complexes are obtained with many electron-rich donors, such as tertiary amines. On the basis of fluorescence measurements Wang [1] reported the formation of charge transfer complexes between fullerenes and diethylaniline. In the presence of the amine, the fluorescence from C_{60} disappeared, with the formation of a new band at 823 nm, which was assigned to the triplet distorted by the charge transfer interaction with amines. Evidence for the existence of a charge transfer complex has been reported by Krusic et al. [6] using electron spin resonance (ESR) spectroscopy at 77 K, where C_{60} anion radicals were detected in the C_{60}–diethylaniline system.

By forming a charge transfer complex with electron-rich donors, the entire symmetry of C_{60} is lost, and such systems are known to induce non-linear optical properties [2]. The reduced forms of C_{60} also play an important role in superconductivity and ferromagnetism [7,8].

Time-resolved methods have contributed significantly to the understanding of the behaviour of charge transfer complexes on photoexcitation [3,4,9]. On the basis of femtosecond studies of the charge transfer complex between dimethylaniline (DMA) and C_{60}, Sension et al. [9] observed $C_{60}{}^{-}$–DMA^{+} ion pair formation in 1–2 ps and reported a charge recombination time of 20–55 ps [9]. Using picosecond spectroscopy, Ghosh et al. [4] reported charge separation, charge recombination and proton transfer reactions of the C_{60}–amine system in benzene.

All of the studies reported so far have been carried out in non-polar solvents because of the very low solubility of C_{60} in polar solvents. Charge transfer complexes are more stable in media with high dielectric constants and hence it is of interest to study their behaviour in such solvents. C_{60} can be solubilized in aqueous medium by the addition of amphiphiles, such as cyclodextrins, surfactants and phospholipids [10–13]. The addition of these compounds to water provides a hydrophobic environment in which non-polar molecules, such as C_{60}, can be housed.

Recently, we have reported the formation of a 1 : 2 complex of C_{60} with γ-cyclodextrin (CD) [14]. This complex exhibits a solubility of the order of 1×10^{-4} mol dm^{-3} in water. The complex was characterized by absorption spectroscopy, X-ray diffraction and thermogravimetry. The photophysical properties of the triplet excited state of the complex were determined by picosecond and nanosecond laser photolysis measurements.

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In this paper, we present the formation of secondary complexes of CD–C_{60}–CD with amines and sulphur compounds. A brief account of the picosecond time-resolved study of such complexes is also reported.

2. Experimental details

C_{60} and CD were obtained from SES Research Chemicals and Sigma Chemicals, USA respectively and were used without further purification. The formation and characterization of the CD–C_{60}–CD complex have been reported elsewhere [14]. The optical absorption spectra of C_{60} and its amine complexes were obtained using a Hitachi-330 spectrophotometer. All other chemicals used were of the highest purity available (better than 99%) and were purified when necessary.

Picosecond laser photolysis experiments were carried out using a pulsed, mode-locked Nd-YAG laser (Continuum USA, model 501-C-10) generating pulses of 35 ps. It was frequency doubled, tripled and quadrupled to give wavelengths of 532, 355 and 266 nm respectively. For these studies, only 355 nm pulses were employed. The transient species were probed by white analysing light (400–900 nm range) produced by focusing the residual fundamental laser at 1064 nm onto an H_2O–D_2O cell (50 : 50). However, due to the small signal-to-noise ratio, the detection below 500 nm was not reliable. The arrival of probe pulses was delayed from 0 to 3800 ps using optical fibres. All other details of this apparatus are given in Ref. [3].

3. Results and discussion

3.1. Steady state measurements

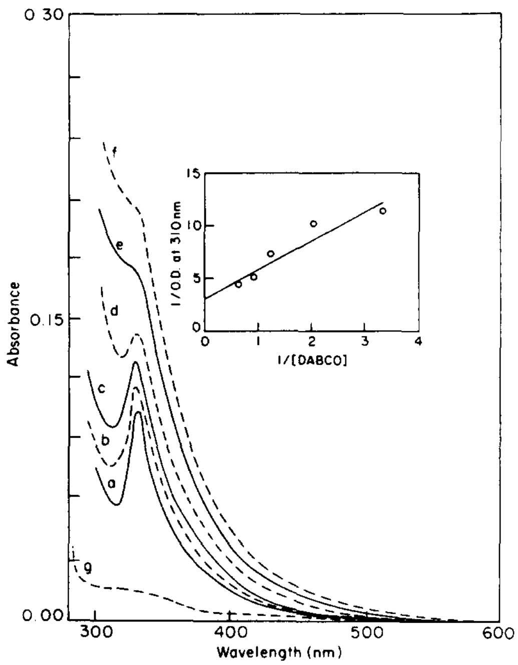

Fig. 1. Optical absorption .spectra of an aqueous solution of CD–C_{60}–CD (9.1×10^{-6} mol dm^{-3}) in the presence of various concentrations of DABCO: 0 (a), 0.3 (b), 0.5 (c), 0.8 (d), 1.05 (e) and 1.55 (f) mol dm^{-3}; (g) optical absorption spectrum of 0.5 mol dm^{-3} DABCO.

An aqueous solution of the inclusion complex of C_{60} with CD (CD–C_{60}–CD) shows characteristic absorption bands of C_{60} at 213, 260 and 330 nm and a shoulder at 410 nm. The ground state extinction coefficient at 330 nm is 11 600 ± 600 dm^3 mol^{-1} cm^{-1}. Fig. 1 shows the optical absorption spectrum of an aqueous solution of the CD–C_{60}–CD complex (9.1×10^{-6} mol dm^{-3}) in the presence of various concentrations of 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.3–1.55 mol dm^{-3}); it can be seen that the optical density due to C_{60} in aqueous solution at 330 nm increases progressively as the DABCO concentration is increased into a broad band with a blue shift of 5 nm. Such an increase in absorbance at 330 nm is not observed in aqueous solution in the absence of the CD–C_{60}–CD complex even at very high concentrations of DABCO. The formation of a new absorption band is not observed and no isosbestic point is obtained. However, the progressive increase in absorbance clearly indicates that some sort of interaction, probably weak charge transfer complex formation, occurs. Assuming an equilibrium to be present, the interaction can be represented as

$$\text{CD–C}_{60}\text{–CD} + \text{DABCO} \rightleftharpoons (\text{CD–C}_{60}\text{–CD:DABCO}) \tag{1}$$

The equilibrium constant for this complex can be determined by a number of methods, such as nuclear magnetic resonance (NMR), fluorescence and optical density measurements. Assuming 1 : 1 complex formation (CD–C_{60}–CD:DABCO), the equilibrium constant (K) and molar extinction coefficient (ϵ) can be determined using the Benesi–Hildebrand equation [15]

$$\frac{1}{\text{OD}} = \frac{1}{[\text{DABCO}]} \times \frac{1}{K\epsilon[\text{CD–C}_{60}\text{–CD}]} + \frac{1}{\epsilon[\text{CD–C}_{60}\text{–CD}]} \tag{2}$$

where OD is the absorbance of the charge transfer complex at an absorption wavelength where the individual donor and acceptor exhibit minimum absorption. For DABCO and CD–C_{60}–CD (Fig. 1), absorption measurements were carried out at 310 nm where the charge transfer complex exhibits large absorption but the uncomplexed forms of DABCO and CD–C_{60}–CD provide little contribution. On the basis of Eq. (2), a linear plot of 1/OD at 310 nm vs. 1/[DABCO] (inset in Fig. 1) confirms 1 : 1 (CD–C_{60}–CD:DABCO) complex formation. Also a plot of 1/OD at 310 nm vs. $1/[\text{DABCO}]^2$ does not show linearity. The intercept gives $1/(\epsilon[\text{CD–C}_{60}\text{–CD}])$ and the intercept divided by the slope gives K. The values for the (CD–C_{60}–CD:DABCO) complex were thus determined to be $\epsilon = 3.68 \times 10^4$ dm^3 mol^{-1} cm^{-1} and $K = 0.899$ dm^3 mol^{-1}. Similar studies on the formation of charge transfer complexes between CD–C_{60}–CD and a number of other amines have also been carried out (Table 1). In each case, increased optical absorption was observed and the data were analysed for 1 : 1 complex formation (CD–C_{60}–CD:amine). From the linear plot, according to Eq. (2), the values of K and ϵ were determined and are listed in Table 1.

Organic sulphur compounds have high electron density at sulphur and can act as electron donors. The optical absorption spectrum of an aqueous solution of CD–C_{60}–CD in the presence of different concentrations of thiodiglycolic acid (TDGA) and 2,2′-thiodiethanol (TDE) also showed an increase in absorption at 400 nm. The data were analysed for 1 : 1 complex formation (CD–C_{60}–CD:sulphide) and the values of K and ϵ are shown in Table 1. 3,3′-Thiodipropanol and 3,3′-thiodipropionate also showed the formation of a charge transfer complex with CD–C_{60}–CD. However, due to the limited solubility of these organic compounds in aqueous solution, the values of K and ϵ could not be calculated.

Although C_{70} is also known to form weak charge transfer complexes with electron donors, investigations could not be carried out in aqueous solution as it was not possible to form a CD–C_{70} complex.

The ΔG values for these complexes, as calculated by the Rehm–Weller equation [17] using the one-electron redox potential values of C_{60}/C_{60}^{-} and DABCO/DABCO^{+}, suggest that the formation of a weak charge transfer complex is possible. Also, the K values are significantly higher in aqueous systems compared with those determined in benzene, indicating solvent stabilization of the donor–acceptor complexes.

3.2. Time-resolved studies

Nanosecond laser flash photolysis of an N_2-saturated aqueous solution of CD–C_{60}–CD showed the characteristic absorption spectrum of the C_{60} triplet ($\lambda_{max} = 740$ nm), similar to that reported by Andersson et al. [10].

Picosecond flash photolysis has contributed significantly to the understanding of the behaviour of charge transfer complexes. Photoexcitation and the subsequent processes of charge transfer complexes can be represented as follows

$$(\text{D, A}) \xrightarrow{h\nu} \underset{\text{CIP}}{(\text{D}^{+}..\text{A}^{-})} \rightleftharpoons$$

$$\underset{\text{SSIP}}{(\text{D}^{+}.....\text{A}^{-})} \Rightarrow \text{D}^{+} + \text{A}^{-} \tag{3a}$$

$$\underset{\text{SSIP}}{(\text{D}^{+}.....\text{A}^{-})} \Rightarrow (\text{D, A}) \text{ or } {}^{1}\text{D}^{*}, {}^{3}\text{D}^{*} \text{ or } {}^{1}\text{A}^{*}, {}^{3}\text{A}^{*} \tag{3b}$$

Photoexcitation of the ground state donor–acceptor complex (D, A) to the Franck–Condon state leads to charge separation to form a contact ion pair (CIP) and a solvent-separated ion pair (SSIP). Deactivation can then occur in two ways: (a) the formation of free ions (Eq. (3a)) and (b) geminate recombination, leading to the ground state complex (D, A) or the donor or acceptor in the excited triplet or singlet state (Eq. (3b)).

Picosecond photolysis of CD–C_{60}–CD leads to the formation of triplet excited states ($\lambda_{max} = 740$ nm) with an intersystem crossing rate of $(6.1 \pm 0.5) \times 10^8$ s^{-1}. This transient exhibits a low absorption cross-section, compared with that in benzene, with an extinction coefficient of 4250 ± 500 dm^3 mol^{-1} cm^{-1} at 740 nm. The triplet

Table 1

Characteristics of the charge transfer complexes of CD–C_{60}–CD with different compounds in aqueous solution (potential (E_{red}) of $C_{60} = -0.40$ V)

Donor	E_{ox} [a] (V)	Monitoring wavelength (nm)	K (dm^3 mol^{-1})	$\epsilon \times 10^{-4}$ (dm^3 mol^{-1} cm^{-1})
DABCO	+0.60	310	0.90	3.68
Triethylamine	+0.69	310	–	1.50
Pyridine	+1.4	400	0.51	0.44
Hexamethylenetetramine	–	400	0.58	1.64
Acrylamide	–	400	0.86	0.51
TDGA	–	400	1.08	1.19
TDE	–	400	1.10	3.81

[a] E_{ox} vs. a saturated calomel electrode (SCE) [16].

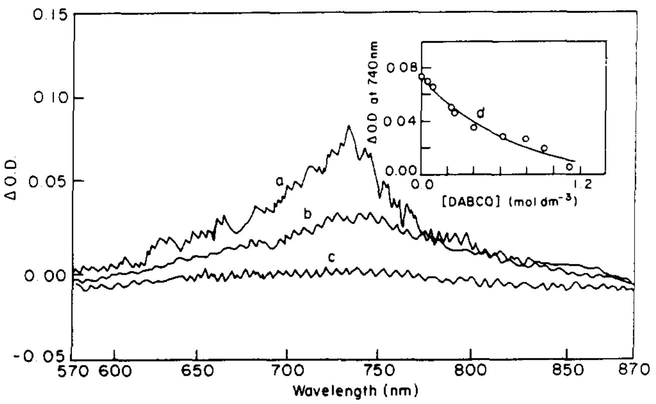

Fig. 2. Transient optical absorption spectra of aqueous solutions of CD–C_{60}–CD (1.0×10^{-4} mol dm^{-3}), obtained 3.8 ns after the pulse, containing DABCO ((a) 0, (b) 0.5 mol dm^{-3}, (c) 1.0 mol dm^{-3}). (d) Dependence of the 740 nm band on DABCO concentration.

lifetime in the absence of O_2 was determined to be 64 ± 5 μs.

Fig. 2 shows the changes in the transient optical absorption spectrum, 3.8 ns after photolysis, of an aqueous solution of CD–C_{60}–CD (1.0×10^{-4} mol dm^{-3}) in the presence of various concentrations of DABCO. In the absence of DABCO, only triplets ($\lambda_{max}=740$ nm) are observed (Fig. 2(a)). As the DABCO concentration is increased, the triplet decreases progressively without the formation of a new band. Finally, at 1 mol dm^{-3} DABCO, the triplet disappears (Fig. 2(c)). Under these conditions, most of the C_{60} would be in the complex form (CD–C_{60}–CD:DABCO). Photoexcitation of this charge transfer complex results in the formation of an SSIP, which may lead to free ions (Eq. (3a)) or geminate recombination yielding excited states of the donor or acceptor or charge transfer in the ground state (Eq. (3b)). Our results did not indicate the formation of free ions. If they are formed, a weak absorption due to the DABCO cation at 465 nm and an initial increase in absorption due to the C_{60} anion at 900 nm should be observed. It was not possible to monitor beyond 900 nm under our experimental conditions. The absence of these two bands suggests that the SSIP must undergo fast recombination (a few picoseconds). Similar studies with CD–C_{60}–CD in the presence of TDE also failed to yield ion pairs of TDE and C_{60}.

Using the equilibrium constant, the concentration of C_{60} present in the free form (CD–C_{60}–CD) was calculated at various concentrations of DABCO. Similarly, the relative triplet yield was calculated by monitoring the absorbance at 740 nm at various concentrations of DABCO. Fig. 3 shows the percentage of C_{60} present in the free form and the C_{60} triplet yield as a function of [DABCO]. While the percentage of C_{60} in the uncomplexed form decreases linearly (Fig. 3(a)) with increasing DABCO concentration, the triplet yield shows an exponential decrease (Fig. 3(b)). From this figure, it can be inferred that, in the initial stage (low concentration of DABCO), the triplet yield follows the same trend as free C_{60}. At higher concentrations of DABCO, where CD–C_{60}–CD is present in the charge transfer complex from (CD–C_{60}–CD:DABCO), photoexcitation leads to fast geminate recombination of the ion pairs. During geminate recombination, while most ion pairs revert to the ground state, some may lead to the formation of the triplet excited state of C_{60}.

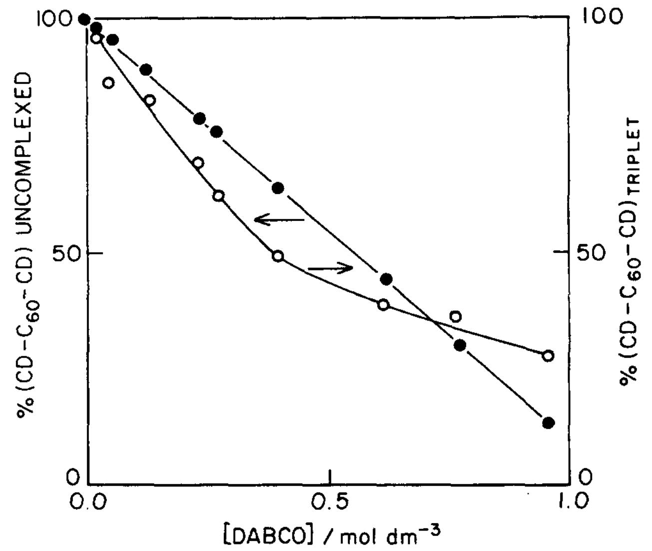

Fig. 3. Variation of free CD–C_{60}–CD (●) and C_{60} triplet (○) as a function of DABCO concentration.

4. Conclusions

CD–C_{60}–CD forms charge transfer complexes with a stoichiometry of 1 : 1 (CD–C_{60}–CD:electron donor) with amines and sulphur compounds. The formation of charge transfer complexes of CD–C_{60}–CD with amines appears to be more favourable in hydrophilic conditions than in hydrocarbon solvents. The transition probabilities are larger for the charge transfer complexes compared with C_{60}. Picosecond studies of the CD–C_{60}–CD:DABCO complex suggest that the triplet yield is reduced in the presence of DABCO and no SSIP is observed.

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