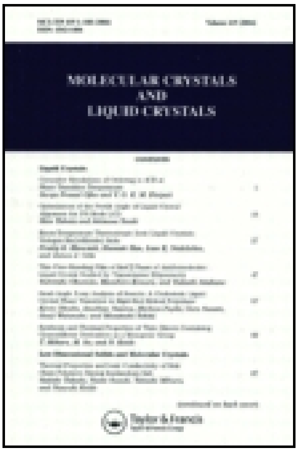

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Preparation of Charge Transfer Complexes Based on 1,2-Dicyano C 60

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Preparation of Charge Transfer Complexes Based on 1,2-Dicyano C_{60}

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New nine solid charge transfer (CT) complexes have been prepared based on 1,2-dicyano C_{60}, $C_{60}(CN)_2$ and characterized spectroscopically. IR spectra of the complexes can be fully assigned by the superposition of those of the neutral component molecules, indicating the neutral ground state of the complexes. The neutral electronic feature of the complexes is also supported substantially by CT absorption bands observed in solid UV-Vis spectra. Since the absorption band shifts negatively by *ca.* 1×10^3 cm^{-1} relative to corresponding C_{60}-based one, it is then evident that $C_{60}(CN)_2$ is a stronger electron acceptor than parent C_{60}, consistent with the expectation from cyclic voltammetry.

Keywords C_{60} derivative; 1,2-Dicyano C_{60}; TTF donor;
Charge transfer (CT) complex; CT band; Ionicity diagram

INTRODUCTION

For further extensive application of spherical fullerene skeleton to the electron-accepting source, the relatively weak electron accepting ability of the fullerene molecule [1] is necessary to be improved. Toward such a functionalization, C_{60} derivatives attached by electronegative atoms such as chlorine or bromine seem to satisfy the above requirement. However, the chlorinated or brominated C_{60} is produced by a sequence of 1,4-additions (Figure 1a) rather than 1,2-additions (Figure 1b) due to the steric hindrance [2], and therefore is electronically unstable mainly caused by the presence of double bonds in pentagon rings (Figure 1a) [2,3]. In this sense, 1,2-added dicyano C_{60}, $C_{60}(CN)_2$ might be a suitable candidate for the electron acceptor because of the electrochemical stability as expected from the addition pattern (Figure 1b) and the positive shift of 140 mV relative to parent C_{60} for the first redox potential ($E^1_{1/2}$(A); –0.25 V for $C_{60}(CN)_2$ and –0.39 V for C_{60}) [4]. Although this molecule was firstly synthesized by Keshavarz-K *et al.* in 1995 [5], the charge transfer (CT) complexes based on that have been scarcely reported, and only recently, an ionic CT complex with

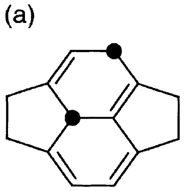

FIGURE 1 Addition patterns at (a) 1,4- and (b) 1,2-positions on C_{60} skeleton.

cobaltocene (Cp_2Co, $E^1_{1/2}(D) = -0.94$ V) was prepared by Suo *et al.* in 1998 [6]. In the present work, nine kinds of $C_{60}(CN)_2$-based CT complexes have been newly prepared with TTF (tetrathiafulvalene) analogues, TDAP (1,3,6,8-tetrakis(dimethylamino)pyrene) or ferrocene (Cp_2Fe), and characterized spectroscopically.

EXPERIMENTAL

1,2-$C_{60}(CN)_2$ was synthesized according to the literature procedure [5]. CT complexes with TMTTF (tetramethyl-TTF), OMTTF (octamethylene-TTF), BEDO-TTF (bisethylenedioxy-TTF, BO), EOET-TTF (ethylenedioxy-ethylenedithio-TTF, EOET), TTC_1-TTF (tetrakis-(methylthio)-TTF), BEDT-TTF (bisethylenedithio-TTF, ET), DBTTF (dibenzo-TTF), TDAP or Cp_2Fe were prepared by the direct mixing in benzene under open air. The attempts to obtain single crystals enough to refine the crystal structures were unsuccessful. UV-Vis spectra were measured in KBr pellets on Shimadzu UV-3100 spectrophotometer (2600–240 nm). FT-IR spectra were taken in KBr pellets with a Perkin-Elmer 1000 Series spectrophotometer (400–7800 cm^{-1}).

RESULTS AND DISCUSSION

Solid products prepared (Table 1) were extremely stable toward atmosphere, in similar to neutral C_{60} complexes. In addition, IR spectra for the complexes were fully assigned by the superposition of those of the neutral component molecules, indicating neutral ground state with little degree of CT ($\gamma \sim 0$). For the CN stretching mode of the $C_{60}(CN)_2$ molecule, the frequency was kept at 2241 cm^{-1} by cocrystallization.

TABLE 1 First redox potentials ($E^1_{1/2}$(D)) of counter donors in CH_3CN, and appearances and CT absorption bands in KBr ($h\nu_{CT}$) for $C_{60}(CN)_2$-based CT complexes

	donor	$E^1_{1/2}$(D) (V vs. SCE)	complex		$h\nu_{CT}$ (10^3 cm^{-1})
1	TDAP	0.018	black	block	9.2
2	TMTTF	0.285	black	powder	9.7
3	OMTTF	0.292	dark brown	powder	9.8
4	Cp_2Fe	0.427	black	block	12.0
5	BO	0.430	dark brown	plate	10.7
6	EOET	0.465	dark brown	plate	11.3
7	TTC_1-TTF	0.520	dark brown	block	11.6
8	ET	0.520	dark brown	plate	11.9
9	DBTTF	0.625	dark brown	plate	~14

Figure 2 shows the electronic absorption spectra for the complexes and pristine $C_{60}(CN)_2$ in KBr disk in the order of electron donating ability from the top. For pristine $C_{60}(CN)_2$, two distinct bands which can be safely assigned to the π-π* intramolecular transitions, have been observed at 30.7 and 38.2×10^3 cm^{-1}, and remain in the product as shown in the figure. In the products, a new absorption band appears at 10–14×10^3 cm^{-1} and can be ascribed to the CT one, which is generally related to the transition from $D^{+\gamma}A^{-\gamma}$ to $D^{+(1-\gamma)}A^{-(1-\gamma)}$ when the component molecules stack alternately [7,8].

For judging whether these products have neutral or ionic ground state, the CT absorption energy values ($h\nu_{CT}$) were plotted (closed circles) as a function of $\Delta E_{1/2}$ (= $E^1_{1/2}(D) - E^1_{1/2}(A)$), and compared with those of C_{60}-based complexes (open circles) [1] as shown in Figure 3. It is clear that all complexes locate substantially along the right-hand line, indicating the neutral CT transition from donor to acceptor molecules [8] as expected from the IR spectra in this work. The $h\nu_{CT}$ value of $C_{60}(CN)_2$-based complex shifts negatively by *ca.* 1×10^3 cm^{-1} relative to corresponding C_{60}-based one, indicating the stronger electron-accepting

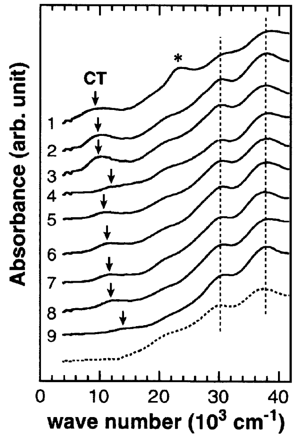

FIGURE 2 UV-Vis spectra of $C_{60}(CN)_2$-based CT complexes (1–9, the numbers correspond to those listed in Table 1) and pristine $C_{60}(CN)_2$ (dotted line). The asterisk indicates the absorption characteristic of TDAP molecule, and the vertical arrows indicate the CT absorption bands. For the vertical dotted

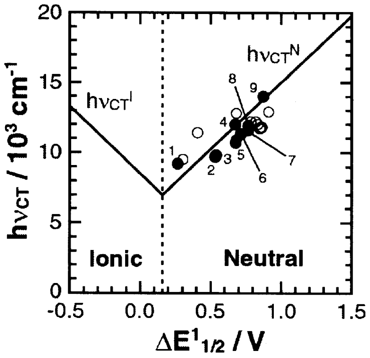

FIGURE 3 Dependence of CT absorption energies of C_{60} (open circles) and $C_{60}(CN)_2$ (closed circles, the numbers correspond to those listed in Table 1) complexes in KBr ($h\nu_{CT}$) on $\Delta E^1{}_{1/2}$ (= $E^1{}_{1/2}(D) - E^1{}_{1/2}(A)$). For assignment of the V-shaped line, see ref. 8.

ability of $C_{60}(CN)_2$ than that of parent C_{60}. This feature is essentially consistent with the expectation from cyclic voltammetry. Although the combination with $(Me_5Cp)_2Fe$ and $C_{60}(CN)_2$ ($\Delta E_{1/2}$ = 0.16 V) would be located in the vicinity of the neutral–ionic (N–I) boundary (represented by the vertical dotted line in Figure 3) and so expected to afford a partial CT complex possibly accompanied by a metallic behavior [9,10], no substantial solid complex has not been precipitated so far.

Acknowledgments

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