

New charge transfer complexes from dicyanodihydrofullerene and metallocene

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Novel charge transfer complexes based on $M\text{Cp}_2$ ($M = \text{Co}$ or Ni) and dicyanodihydrofullerene $[\text{C}_{60}(\text{CN})_2]$ have been prepared and the charge transfer in them investigated by UV-NIR, EPR and other spectra. The dicyanodihydrofullerene was reduced to the monoanion in the compound $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$, which showed a characteristic NIR band at 1016 nm.

The discovery of the organic soft ferromagnetic material $\text{TDAE} \cdot \text{C}_{60}^{1-}$ [TDAE = tetrakis(dimethylamino)ethylene] has provoked great interest in synthesis of new charge transfer complexes with excellent physical properties based on C_{60}^{2-} and research on the chemistry of fullerene anions.³ The main approaches to synthesize new charge transfer complexes based on fullerenes lie in enhancing the donating capability of the donors on the one hand, and modifying fullerenes with various electron-withdrawing groups on the other hand. However, most reports so far have concentrated on the former and relatively few examples⁴ of charge transfer complexes based on functionalized buckminsterfullerenes have been reported. Li *et al.*^{4a,4b} and Xiao^{4c} have reported charge transfer complexes based on C_{60}Br_n ($n = 2, 6$ or 24) and TTF as well as its derivatives, in which $(\text{TTF})_3\text{C}_{60}\text{Br}_2$ shows ferromagnetism.^{4b} Although a few examples have been reported in which an acceptor unit or electronegative atoms are linked to C_{60} ,⁵ few of them show more electronegativity than the parent fullerene. Dicyanodihydrofullerene $[\text{C}_{60}(\text{CN})_2]$ ^{5b} is a new acceptor with higher electron affinity, whose first reduction potential is -935 mV vs. Fc/Fc^+ , 120 mV more positive than the first reduction potential of C_{60} . Here we report a novel family of charge transfer complexes based on $\text{C}_{60}(\text{CN})_2$ and $M\text{Cp}_2$ ($M = \text{Co}$ or Ni , $\text{Cp} = \text{cyclopentadienyl}$).

Experimental

General

The complexes $\text{C}_{60}(\text{CN})_2$ and $M\text{Cp}_2$ ($M = \text{Co}$ or Ni) were synthesized according to refs. 5(b) and 6, respectively; FeCp_2 (No. 1 Chemicals Factory, Shanghai) is chemically pure and was recrystallized before use, and CS_2 and dimethylformamide (DMF) (No. 4 Chemicals Factory, Shanghai) are analytically pure and were carefully purified and degassed before use. All the experiments were performed in an inert atmosphere.

The UV-NIR spectra were recorded on a Shimadzu UV-3100 spectrometer, IR spectra on a Bruker IFS66VFT-IR spectrometer, EPR spectra on a Bruker ER 200-D-SRC 10/12 spectrometer and mass spectra on a Finnigan mat APISSQ-710 mass spectrometer. Electrochemical data were measured on a EG&G potentiostat/galvanostat model 273 electrochemical analyzer. The one-compartment electrochemical cell was airtight with high-vacuum glass stopcocks connecting it to the Schlenk system. The working electrode consisted of a platinum

microdisc, and the counter electrode consisted of a platinum wire. The quasi-reference electrode was a silver wire and ferrocene was used as internal reference.

Syntheses

$\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$. To a blue CS_2 solution (10 ml) of CoCp_2 (12 mg, 0.065 mmol), a brownish red CS_2 solution (70 ml) of $\text{C}_{60}(\text{CN})_2$ (50 mg, 0.065 mmol) was added or *vice versa* in an inert atmosphere dry-box, which afforded instantaneous deposition of some brown-black solids. The nearly colorless solution was decanted and the air-sensitive solids were then washed with CS_2 in the Schlenk system, dried in vacuum and sealed for further characterization [Found: C, 84.68; H, 1.68; N, 2.82. $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$ requires C, 84.47; H, 0.97; N, 2.69%]. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (CoCp_2^+) 3102w, 1412vs, 1008s, 875.3w, 856.9s, 459.2s; $[\text{C}_{60}(\text{CN})_2^-]$ 2233w, 1446s, 1191w, 1064w, 1049w, 550.8w, 524.6s; (CS_2) 1509vs and 2170w. $\delta_{\text{H}}[500 \text{ MHz}, (\text{CD}_3)_2\text{SO}]$ 5.76 (10 H, s, $2\text{C}_5\text{H}_5$). $\delta_{\text{C}}[500 \text{ MHz}, (\text{CD}_3)_2\text{SO}]$ 84.9 (s, $2\text{C}_5\text{H}_5$) and 147.8 [br s, $\text{C}_{60}(\text{CN})_2$]. m/z 189.0 (CoCp_2), 242.1 [$\text{CoCp}_2 + (\text{CH})_4 + \text{H}$] and 798.2 [$\text{C}_{60}(\text{CN})_3$]. $\lambda_{\text{max}}/\text{nm}$ (DMF) 1016 nm.

$(\text{NiCp}_2)_m \cdot \text{C}_{60}(\text{CN})_2 \cdot (\text{CS}_2)_x$. To a CS_2 solution of NiCp_2 (12 mg, 0.065 mmol), a CS_2 solution of $\text{C}_{60}(\text{CN})_2$ (50 mg, 0.065 mmol) was added and maintained for 2 h with vigorous stirring. The solution didn't show any obvious change, but after careful evaporation some deep brown crystalline solids were obtained, which showed some features different to either NiCp_2 or $\text{C}_{60}(\text{CN})_2$. $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (NiCp_2) 2966w, 2919w, 1425w, 1260w, 1005s, 773.7vs; $[\text{C}_{60}(\text{CN})_2]$ 2239w, 1433s, 1185w, 1032s, 551.6s, 526.3vs, 486.2s; (CS_2) 1511vs, 2330w and 2188w. m/z 291.2 [$\text{NiCp}_2 + \text{Ni} + (\text{CH}_3)_3$], 188.0 (NiCp_2), 772.2 [$\text{C}_{60}(\text{CN})_2$] and 788.3 [$\text{C}_{60}(\text{CN})_2\text{O}$].

Results and discussion

Solubility

The complex $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$ was easy to dissolve in strong polar solvents, *e.g.* DMF, dimethyl sulfoxide (DMSO), and moderately soluble in tetrahydrofuran (THF) and *o*-dichlorobenzene (ODCB). On the contrary, $(\text{NiCp}_2)_m \cdot \text{C}_{60}(\text{CN})_2 \cdot (\text{CS}_2)_x$ showed poor solubility in DMF but was soluble in CS_2 and toluene.

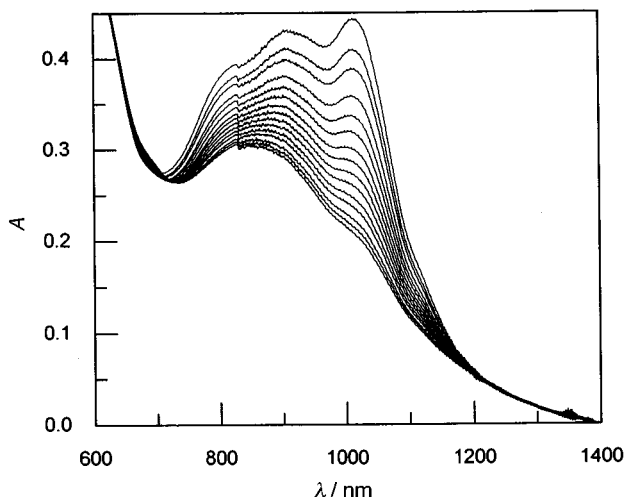


Fig. 1 Decrease of the 1016 nm peak of a DMF solution of $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$.

UV-NIR, EPR and FTIR spectra

For the charge transfer complex from CoCp_2 and $\text{C}_{60}(\text{CN})_2$, elemental analysis data gave a chemical formula of $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$ though the observed %H was not in good agreement with the required value. All the data from ^1H , ^{13}C NMR, and FTIR and EPR spectra showed that CoCp_2 was in the form of cobaltocenium.⁷ So, in order to maintain the electronic neutrality of the compound, $\text{C}_{60}(\text{CN})_2$ must be in the form of $\text{C}_{60}(\text{CN})_2^-$ monoanion. This is reasonable when considering the analogue of $\text{CoCp}_2 \cdot \text{C}_{60} \cdot \text{PhCN}$.⁸

Compared with the electronic absorption spectra of both CoCp_2 and $\text{C}_{60}(\text{CN})_2$, the brown-black DMF solution of $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$ showed a new peak at 1016 nm, which gradually decreased and finally disappeared completely when the solution was exposed to air (Fig. 1). As is well known, a band of 1075 nm is characteristic of C_{60}^- monoanion in THF,⁹ and we suggest the band of 1016 nm is characteristic of $\text{C}_{60}(\text{CN})_2^-$ monoanion in DMF. The hypsochromic shift of the near IR band of $\text{C}_{60}(\text{CN})_2^-$ indicated an enhanced HOMO-LUMO energy gap compared with C_{60}^- , as confirmed by the AM1 calculation results mentioned later. A similar phenomenon was observed by Belik *et al.*¹⁰ for the anions of the monoadduct of 1,2-dimethoxy-*o*-xylylene and C_{60} .

The EPR spectrum of $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$ showed a very strong sharp peak at ambient temperature ($g = 1.9998$, $\Delta B_{\text{pp}} = 2.1$ and 3.0 G for powder and solution sample, respectively). This peak was due to $\text{C}_{60}(\text{CN})_2^-$ monoanion radical and the narrow width resulted from lower symmetry (C_{2v}) and slower rotation rates of substituted fullerene than for C_{60}^- anion.^{9a} Previously Monton *et al.*¹¹ reported that alkylfullerene radicals, in which the unpaired electron was mainly localized on the carbon atoms of the surface adjacent to the point of substitution, had g values between 2.0023 and 2.0025, almost equal to that of the free electron (2.00232). However, the g value of $\text{C}_{60}(\text{CN})_2^-$ was slightly lower and nearly identical with that of C_{60}^- , which implied that the contributions of spin-orbital coupling to the depressed g values, compared with the free electron, were similar for both $\text{C}_{60}(\text{CN})_2^-$ and C_{60}^- , and the distribution of unpaired electron density of $\text{C}_{60}(\text{CN})_2^-$ might be different to that of alkylfullerene radicals. Unlike $\text{CoCp}_2^+ \cdot \text{C}_{60}^-$, for which the EPR peak width of C_{60}^- monoanion radical changed considerably with time and temperature,⁸ the peak width of $\text{C}_{60}(\text{CN})_2^-$ anion radical in $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$ changed slightly with temperature (Fig. 2) and remained unchanged for at least half a year. This fact may be partially due to the charge transfer in $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$, which is more complete and faster than in $\text{CoCp}_2 \cdot \text{C}_{60} \cdot \text{PhCN}$, so there is no intermediate ion

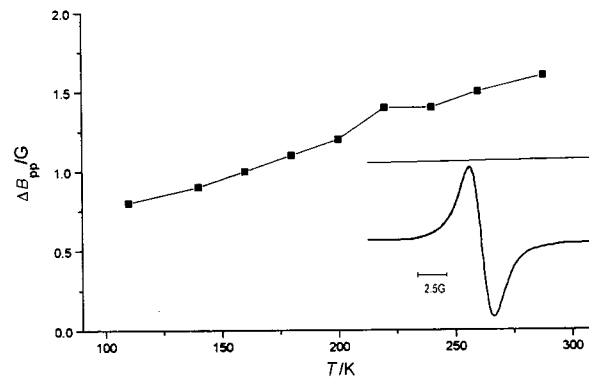


Fig. 2 Thermal behaviour of the g value of $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$.

pair for the former,^{8b} and partially due to the spin relaxation rate of $\text{C}_{60}(\text{CN})_2^-$, which is relatively unchanged and slow in the measured temperature range.

The complex $(\text{NiCp}_2)_m \cdot \text{C}_{60}(\text{CN})_2 \cdot (\text{CS}_2)_x$ also showed a weak EPR signal ($g_1 = 2.0332$, $g_2 = 2.1258$) different to that of NiCp_2 . Although the reasons for so large a shift are still uncertain, the charge transfer from NiCp_2 to $\text{C}_{60}(\text{CN})_2$ might play a role. Furthermore, in the absorption spectra of $(\text{NiCp}_2)_m \cdot \text{C}_{60}(\text{CN})_2 \cdot (\text{CS}_2)_x$ the characteristic band of $\text{C}_{60}(\text{CN})_2^-$ monoanion at 1016 nm was absent. This means that the charge transfer amount in this complex is too small to be detected by NIR spectroscopy.

We also attempted to obtain a charge transfer complex from FeCp_2 and $\text{C}_{60}(\text{CN})_2$ but the resulting solid only showed a very weak EPR signal ($g = 2.0016$, $\Delta B_{\text{pp}} = 2.3$ G). Furthermore, like pristine C_{60} , $\text{C}_{60}(\text{CN})_2$ also showed a signal in air ($g = 2.0014$, $\Delta B_{\text{pp}} = 2.5$ G), which could be eliminated by heating at 100 °C under vacuum for 6 h. So we suggest that the observed EPR signal for the system of FeCp_2 and $\text{C}_{60}(\text{CN})_2$ is really due not to the intermolecular charge transfer, but to oxygen contaminated $\text{C}_{60}(\text{CN})_2$. Also, the characteristic 1016 nm peak was not found for the $\text{FeCp}_2 \cdot \text{C}_{60}(\text{CN})_2$ system.

The FTIR spectrum of C_{60} shows splitting and shifts upon accepting an electron,¹² and this is due to the fact that the electron density is mainly located in the equatorial zone and, thus, the decrease of the I_h symmetry (Jahn-Teller effect), as suggested by Dresselhaus and co-workers.¹³ A similar blue-shift was also observed in the FTIR spectrum of $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$, say, 1430.4, 1461.7 and 1185.3 cm^{-1} , corresponding to vibration of the skeleton of $\text{C}_{60}(\text{CN})_2$, shifted to 1446.3, 1475.1 and 1190.8 cm^{-1} , respectively. Furthermore, the 1030.7 cm^{-1} peak of neutral $\text{C}_{60}(\text{CN})_2$ shifted and split into two peaks for $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$, 1063.8 and 1049.1 cm^{-1} . Although a previous report^{6a} pointed out 1049.1 cm^{-1} as a band of CoCp_2^+ cation in $\text{CoCp}_2^+ \text{Br}_3^-$, a splitting of 1030.7 cm^{-1} was also observed in a complex without CoCp_2 , $\text{TDAE} \cdot \text{C}_{60}(\text{CN})_2$,¹⁴ so we assign this splitting to the $\text{C}_{60}(\text{CN})_2^-$ anion. However, the 2238.8 cm^{-1} band corresponding to the vibration of cyano-groups shifted to 2232.6 cm^{-1} , which was consistent with the red-shift in $\text{TTF} \cdot \text{TCNQ}$,¹⁵ say, from 2229 to 2206 cm^{-1} . These red-shifts indicated that the negative charge density is largely localized on cyano-groups. Similar large blue- and red-shifts of $\text{C}_{60}(\text{CN})_2^-$ were absent or unclear in $(\text{NiCp}_2)_m \cdot \text{C}_{60}(\text{CN})_2 \cdot (\text{CS}_2)_x$ and $\text{FeCp}_2 \cdot \text{C}_{60}(\text{CN})_2$. For example, the 1430 cm^{-1} peak shifted just 3 cm^{-1} in $(\text{NiCp}_2)_m \cdot \text{C}_{60}(\text{CN})_2 \cdot (\text{CS}_2)_x$. Assuming 1430.4–1446.3 cm^{-1} as the diagnostic frequency couple and a linear correlation between the charge transfer amount and the peak shift as usual,¹⁶ we found that only *ca.* 0.18 unit charge was transferred from NiCp_2 to $\text{C}_{60}(\text{CN})_2$.

All these results could be understood by considering the redox potentials of the different metallocenes ($E^{\text{CoCp}_2/\text{CoCp}_2^+} = -0.9$, $E^{\text{NiCp}_2/\text{NiCp}_2^+} = -0.08$ and $E^{\text{FeCp}_2/\text{FeCp}_2^+} = 0.2$ V vs. SCE⁶) and $\text{C}_{60}(\text{CN})_2$.^{5b} Obviously CoCp_2 is the strongest electron donor among them and the only one with a redox potential

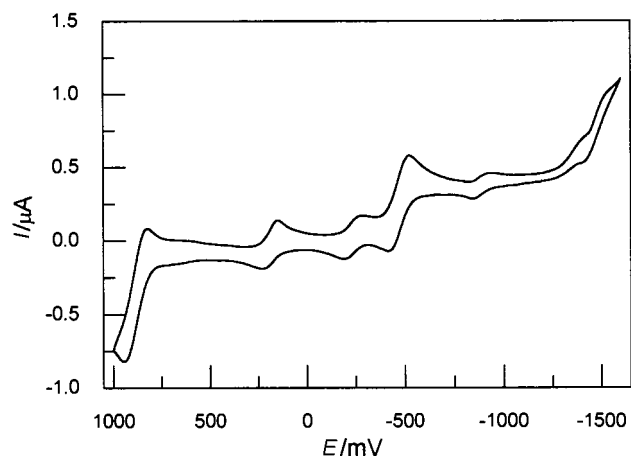


Fig. 3 Cyclic voltammety curve of $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$ at room temperature.

lower than the first redox potential of $\text{C}_{60}(\text{CN})_2$, so it can reduce $\text{C}_{60}(\text{CN})_2$ into $\text{C}_{60}(\text{CN})_2^-$ monoanion, but NiCp_2 is a relatively weak donor so there is only a minor charge transfer and no charge separated state $\text{NiCp}_2^+ \cdot \text{C}_{60}(\text{CN})_2^-$ for $(\text{NiCp}_2)_m \cdot \text{C}_{60}(\text{CN})_2 \cdot (\text{CS}_2)_x$, so it shows just relatively weak EPR peaks, which demonstrate it is not a mechanical mixture of NiCp_2 and $\text{C}_{60}(\text{CN})_2$. As to FeCp_2 , which is a poorer electron donor, there is essentially no intermolecular charge transfer from FeCp_2 to $\text{C}_{60}(\text{CN})_2$. These results are consistent with those of charge transfer complexes based on C_{60} and metallocenes.^{8,17} For example, C_{60} can cocrystallize with FeCp_2 to give $\text{C}_{60} \cdot 2\text{FeCp}_2$, in which ferrocene changes the packing manner of C_{60} , and almost no intermolecular charge transfer from FeCp_2 to C_{60} is observed.¹⁷

Cyclic voltammety

Cyclic voltammety † showed that $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$ underwent five quasireversible single electron processes at room temperature (Fig. 3), which suggest the electrochemical activities of both donor and acceptor. From left to right in Fig. 3, the first and the fourth waves were ascribed to Fc-Fc^+ and $\text{CoCp}_2-\text{CoCp}_2^+$, respectively. Compared with neutral $\text{C}_{60}(\text{CN})_2$ in pure ODCB,^{5b} the half-cell potentials [defined as $E_x = 0.5(E_{pc} - E_{pa})$] for the quasireversible waves of $\text{C}_{60}(\text{CN})_2^-$ in DMF showed large positive shifts, 242 and 223 mV for the first and second reduction waves, respectively (see Table 1). The different solvents used for cyclic voltammety are presumed to be the origin of the large shifts of reduction waves. This point was supported by the following observation: pure $\text{C}_{60}(\text{CN})_2$ showed 140 and 96 mV positive shifts for its first and second reduction waves in the mixed solvent ODCB-DMF (3:1, v/v), respectively. These results mean that the solvent polarity can change the electron accepting ability of $\text{C}_{60}(\text{CN})_2$, just like C_{60} .¹⁸

Mass spectroscopy

The complex $\text{C}_{60}(\text{CN})_2$ was undetectable in ESI-MS (electrospray ionization mass spectroscopy) with negative mode but showed just a single peak at $m/z = 772$ in APCI-MS (atmosphere pressure ionization mass spectroscopy). In contrast, $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$ showed two clear peaks corresponding to CoCp_2^+ cation ($m/z = 189.0$) and $\text{C}_{60}(\text{CN})_3^-$ anion ($m/z = 798.2$) in ESI-MS, respectively (Fig. 4). However, it is notable that $m/z = 798.2$ peak in negative mode exactly

† The room temperature cyclic voltammety experiments were performed at 2.5 mmol l^{-1} analyte concentration in dry DMF with Bu_4NBF_4 as supporting electrolyte, a silver-wire reference electrode, and a platinum disc working electrode. Ferrocene was used as an internal reference.

Table 1 Half-cell potentials for $\text{C}_{60}(\text{CN})_2$ and $\text{C}_{60}(\text{CN})_2^-$

Compound	Solvent	Half-cell potential/mV vs. Fc-Fc^+			
		E_1	E_2	E_3	E_4
$\text{C}_{60}(\text{CN})_2$	ODCB	-935	-1330	-1800	-2225
$\text{C}_{60}(\text{CN})_2$	ODCB-DMF (3:1 v/v)	-795	-1234	-1756	—
$\text{C}_{60}(\text{CN})_2^-$	DMF	-693	-1108	-1763	-2349

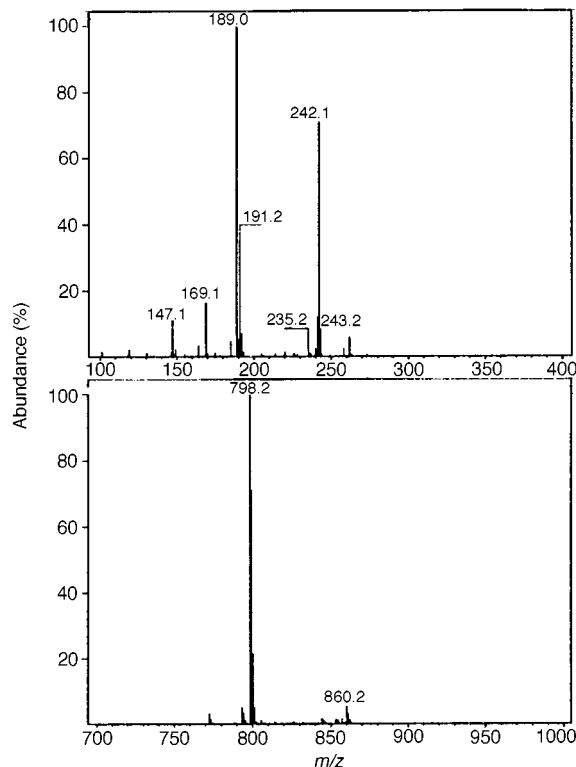


Fig. 4 The ESI-MS spectrum of $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$.

corresponds to a new species, $\text{C}_{60}(\text{CN})_3^-$, which may result from the following gas phase reaction in the MS process: $\text{C}_{60}(\text{CN})_2^- + \text{C}_{60}(\text{CN})_2 \longrightarrow \text{C}_{60}(\text{CN})_3^- + \text{C}_{60}(\text{CN})^{\cdot}$. Similar results were found during MS analysis of a CHCl_3 solution of $\text{C}_{60}(\text{CN})_2$, which showed a single peak at $m/z = 807.5$ corresponding to $\text{C}_{60}(\text{CN})_2\text{Cl}^-$, but this peak did not appear in those for C_{60} and C_{70} , undergoing chlorine addition to give C_{60}Cl^- and C_{70}Cl^- during MS analysis,¹⁹ so we consider that it is a common phenomenon for the anions of fullerenes and their derivatives to form adducts with a halogen atom or pseudo-halogen group in the MS process. In contrast with $\text{CoCp}_2 \cdot \text{C}_{60}(\text{CN})_2 \cdot \text{CS}_2$, there are no $\text{C}_{60}(\text{CN})_2$ peaks in the MS spectra of the $\text{FeCp}_2-\text{C}_{60}(\text{CN})_2$ system under the same conditions, which also suggests the absence of $\text{C}_{60}(\text{CN})_2^-$ anion. The $m/z = 772$ peak corresponding to $\text{C}_{60}(\text{CN})_2^-$ was observed with ESI-MS for $(\text{NiCp}_2)_m \cdot \text{C}_{60}(\text{CN})_2 \cdot (\text{CS}_2)_x$, which indicated that the presence of NiCp_2 was advantageous for the ionization of $\text{C}_{60}(\text{CN})_2$ due to the charge transfer, but no $m/z = 798$ peak was found because of the absence of $\text{C}_{60}(\text{CN})_2^-$ in the CT complex.

Theoretical calculations

AM1 Calculations show that the $\text{C}_{60}(\text{CN})_2$ molecule has non-degenerate HOMO-LUMO orbitals (B_2 and A_1 , respectively), and retains its symmetry (C_{2v}) and frontier orbitals upon addition of an electron. The charge density of $\text{C}_{60}(\text{CN})_2^-$ is mainly located on the two cyano-groups, in good agreement with the results from FTIR spectra and calculations of Khairallah and

Peel.²⁰ Neutral $C_{60}(CN)_2$ has a relatively large HOMO–LUMO energy gap, 6.5 eV, which is consistent with the absence of absorption in the NIR region for $C_{60}(CN)_2$. However, the HOMO–LUMO energy gap of $C_{60}(CN)_2^-$ monoanion is only 1.8 eV, slightly larger than the LUMO–LUMO+1 energy separation of neutral C_{60} (1.1 eV). Accordingly, the $C_{60}(CN)_2^-$ monoanion has a characteristic symmetry-allowed absorption band centered at 1226 nm and a symmetry-forbidden band at 906 nm, which are consistent with the observed spectra. In contrast to the C_{60}^- monoanion, which has a decreased symmetry compared with the I_h of neutral C_{60} , say D_{2h} , D_{3d} , or D_{5d} according to different calculations,²¹ the $C_{60}(CN)_2^-$ monoanion retains the C_{2v} symmetry and has non-degenerate HOMO–LUMO orbitals (A_1 and B_1 , respectively) so there is no Jahn–Teller effect for the $C_{60}(CN)_2^-$ monoanion and the shifts and splitting in FTIR spectra of $CoCp_2 \cdot C_{60}(CN)_2 \cdot CS_2$ might mainly result from the unbalanced charge density and the possible shape change along the C_{2v} axis.

Conclusion

We have synthesized novel charge transfer complexes based on dicyanodihydrofullerene and metallocenes, and found that there is complete charge transfer between $CoCp_2$ and $C_{60}(CN)_2$ to form $C_{60}(CN)_2^-$ monoanion and $CoCp_2^+$ cation. Only a minor charge transfer was found between $NiCp_2$ and $C_{60}(CN)_2$ whilst there is almost no intermolecular charge transfer from $FeCp_2$ to $C_{60}(CN)_2$. Also the characteristic absorption band of $C_{60}(CN)_2^-$ monoanion has been assigned by both experiments and theoretical calculations. All this behavior can be understood, based on the redox potentials.

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