Synthesis and Photophysical Properties of C_{60}-carbazole Adducts

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Three C_{60}-carbazole adducts have been synthesized by 1,3-dipolar cycloaddition reaction. Intramolecular energy/electron transfer from carbazole to C_{60} was observed by steady-state absorption and fluorescence spectra. The fluorescence spectra of these adducts were similar to each other and dependent on the excitation wavelength and solvent.

Keywords   Fullerene, synthesis, intramolecular electron/energy transfer, cyclic voltammetry, fluorescence

Introduction

Fullerenes have fascinated many researchers during the last decade because of the large size and spherical shape of their delocalized π-electron system with high symmetry.[1] In particular, the unique three-dimensional structures of fullerenes make them a good candidate as an electron acceptor (A). The design of novel organofullerenes containing electron donor is a promising field due to the interesting optical and electronic properties they can display.[2] In addition, they have potential applications in photodynamic therapy because of the highly efficient photosensitization of singlet state molecular oxygen formation by C_{60} and C_{60} derivatives.[3] Because of their low reduction potentials,[4] one expects to find interesting charge-transfer chemistry between C_{60} and electron donor in both the ground state and the excited states. Due to that carbazole is a good electron donor, intermolecular photoinduced electron transfer (ET) between C_{60} and carbazole (hereafter abbreviated as Car) and poly(N-vinylcarbazole) has been thoroughly investigated.[5] In this paper, we report intramolecular photoinduced energy transfer (ENT) and electron transfer between N-alkylcarbazole and C_{60} moiety.

Results and discussion

Synthesis

In recent years, the 1,3-dipolar cycloaddition of azomethine ylide to C_{60} has been used extensively to prepare fullerene derivatives,[6] in which a pyrrolidine ring is fused with a 6,6-ring junction of C_{60}. Compounds **1a—c** were prepared as shown in Scheme 1.

Scheme 1

R=Me (**a**); Et (**b**); *n*-Bu (**c**)
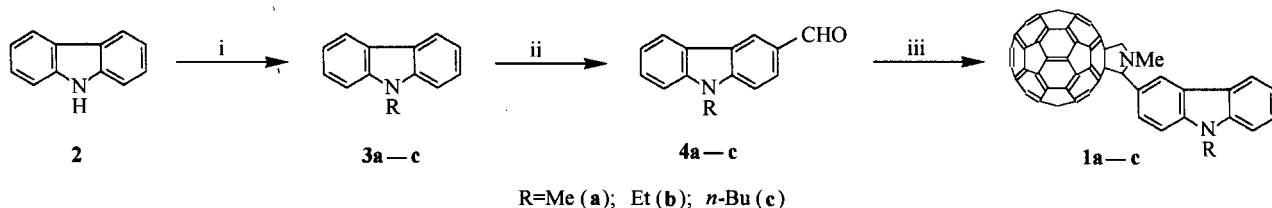
Reagents and conditions: i) NaH, RBr, tetrabutyl ammonium bromide (TBAB), toluene, reflux 3 h; ii) DMF, POCl₃, CHCl₃, reflux 2—3 h; iii) C_{60}, sarcosine, toluene, reflux 2—3 h.

Carbazole (2) was alkylated to give compounds 3a—c, which were converted into 4a—c by Vilsmeyer reaction using phosphoryl chloride and DMF in chloroform. The functionalization of C_{60} was based on the 1,3-dipolar cycloaddition of the azomethine ylide generated *in situ* from 4a—c. The reaction of C_{60} with 4a—c in the presence of an excess of N-methylglycine (sarcosine) in refluxing toluene afforded fulleropyrrolidine 1a—c in 42-46% yield. Compounds 1a—c were verified by ^{1}H NMR, ^{13}C NMR, FT-IR, ESI-MS, UV-VIS and FT-Raman spectra.

Electrochemical properties

Investigations about the redox behavior of the compounds 1a—c were carried out by cyclic voltammetry (CV). The redox potentials of 1a—c were measured in 1,2-dichlorobenzene (ODCB) at room temperature using Ferrocene/Ferricinium (Fc/Fc^{+}) couple as internal reference. Table 1 summarized the $E_{1/2}$ for 1a—c in ODCB with scan rate = 100 mV/s.

Table 1 $E_{1/2}$ (mV) for 1a—c in ODCB

	C_{60}	1a	1b	1c
$-E_{1/2}^{1}$	1123	1208	1164	1130
$-E_{1/2}^{2}$	1455	1613	1532	1501

$E_{1/2}$ values in mV (Fc/Fc^{+}, reference internal) of C_{60}[3] and compounds 1a—c ($C = 0.1$ mM) in o-dichlorobenzene (ODCB) solution (containing 0.1 M Bu$_4$NPF$_6$ as supporting electrolyte) at room temperature using Pt as working and counter electrodes.

Fig. 1 showed the cyclic voltammogram of compound 1a within the redox range of 1.0 to -2.0 V. Three one-electron reversible reduction processes were observed. The reduction potentials slightly shifted to more negative values with respect to C_{60}. It was interesting that the substitutent at nitrogen atom had some effects on the redox potentials. With the carbon chain prolonging, the reduction potentials slightly shifted toward positive region.

UV-Vis *absorption spectra*

The absorption spectra of 1a—c were measured in cyclohexane at room temperature. The spectra in the visible region had some common features, virtually independent of the attached carbazole derivatives. All the
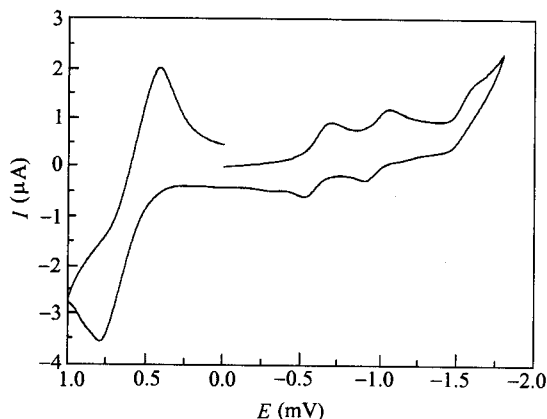

Fig. 1   Cyclic voltammogram of compound 1a ($SR = 100$ mV/s).

spectra exhibited a broad and weak absorption band around 702 nm with vibrational structures, which was the 0-0 transition and apparently shifted to the longer wavelength compared to that of C_{60} itself (ca. 620 nm). The sharp absorption at 432 nm, which was the characteristic band of the C_{60} monoadducts bonded at 6, 6-junction, was also observed in 1a—c. The absorption in the region shorter than 350 nm was an overlap of the absorption band of the attached carbazole and the C_{60} moiety. Thus, the whole spectra are simply interpreted as the sum of the absorption of the C_{60} and the attached carbazole. These results showed that there was lack of a strong through-bond electronic interaction between the C_{60} moiety and the attached carbazole derivatives, and also the lack of enough through-space interaction to modify the electronic state of C_{60} moiety. Solvents had some effects on the UV-Vis absorption spectra of the 1a—c. As an example, the absorption spectra of 1a in different solvents were shown in Fig. 2. In cyclohexane, the fine vibrational structures were relatively sharp, whereas in more polar solvents, the absorption bands in the range of 650—710 nm became broad and structureless, as in the case of other C_{60} cycloadducts.[7]

Fluorescence spectra

The fluorescence spectra of 1a—c were measured in cyclohexane, toluene, dichloromethane, and benzonitrile upon 432 nm excitation at room temperature. At this excitation wavelength, only the C_{60} moiety of 1a—c could be excited. The fluorescence behaviors of 1a—c

are almost the same. Fig. 3 showed fluorescence spectra of **1c** in various solvents excited at 432 nm. They afforded a relatively well-defined emission with maximum at 706, 710, 713, and 715 nm respectively, which could be reasonably assigned to the 0-0 component from C₆₀ moiety. The fluorescence spectra of **1c** showed that the emission peaks took a slight red-shift and the intensity decreased upon going to more polar solvents. The solvent dependence of the fluorescence of **1c** indicated that in polar solvents an extra deactivation path of the excited

state (S_1) of **1c** became available. As the population of a charge transfer state was energetically possible in polar solvents,[10(a)] this quenching path could be attributed to an intramolecular electron transfer that deactivates the excited state of C₆₀ moiety. It had been proved that the pyrrolidine "bridge" moiety was not involved in the quenching process in a bridged C₆₀-aniline system.[10(a)] Based on the previous report,[5(a)] the following processes might be responsible for the emission behavior of **1a—c** in polar solvents.

$$ C_{60} - Car \xrightarrow{h\nu \ (432 \ nm)} {}^1C_{60}^* - Car \xrightarrow{k_{et}^s} C_{60}^{-\bullet} - Car^{+\bullet} $$
$$ \downarrow isc $$
$$ {}^3C_{60}^* - Car \xrightarrow{k_{et}^T} C_{60}^{-\bullet} - Car^{+\bullet} $$

Fig. 2   UV-Vis spectra of **1c** in defferent solvents at room temperature ($C = 2 \times 10^{-5}$ M; paghlength, 1 cm. Insert from 600 to 750 nm).

Fig. 3   Fluorescence spectra of **1c** excited at 432 nm in different solvents at room temperature (Solid, in benzonitrile; Dot, in CHCl₃; Dash, in toluene; Dash-dot-dot, in cyclohexane).

Fig. 4 showed the fluorescence spectra of **1a** in cyclohexane upon excitation at 340 nm. Both carbazole and C₆₀ moiety can be excited under this excitation wavelength. The results show that the fluorescence intensity of C₆₀ moiety excited at 340 nm is higher than that at 432 nm and the carbazole emission in **1a** is almost quantitatively quenched (carbazole emission at 350—500 nm).[8] Since the energy level $S_{1(car)}$ was higher than $S_{1(C_{60})}$, the energy transfer from $S_{1(car)}$ to $S_{1(C_{60})}$ of **1a** obviously took place and sensitized the fluorescence emission of the C₆₀ moiety. In contrast to this, in polar solvents such as benzonitrile the emission behavior was quite different . The fluorescence intensity

Fig. 4   Fluorescence spectra of **1a** in cyclohexane ($C = 1 \times 10^{-5}$ M. Solid, Ex: 340 nm; Dot, Ex: 432 nm).

of C_{60} moiety excited at 340 nm and 432 nm was quite weaker in polar solvent than in nonpolar solvent, furthermore, the fluorescence intensity of C_{60} moiety excited at 340 nm was significantly lower than that at 432 nm in polar solvent (Fig. 5). This suggested that electron transfer dominated the behavior of **1a—c** to cause the fluorescence quenching. In addition, the results also suggested that carbazole absorbed 340 nm photons more efficiently than C_{60} moiety to form C_{60}-Car* which produces the charge separated state directly and made the fluorescence intensity very low. Because polar solvents could stabilize the radical pair, the energy of charge-separated radical was reduced and the efficiency of the electron transfer channel was enhanced. So energy transfer was a main process in nonpolar solvents, while electron transfer dominated the processes in polar solvents. Ito et al.[5(a)] reported that the direct excitation of C_{60} alone in benzonitrile at 355 nm did not generate $C_{60}^{\cdot-}$ radical anion, but could form PVCz radical cation by the direct excitation of PVCz in a polar solvent. They observed the $C_{60}^{\cdot-}$ and PVCz$^{+\cdot}$ when the benzonitrile solution of C_{60} and PVCz was excited at 355 and 532 nm respectively. Generally speaking, intramolecular electron transfer of **1a—c** is faster than intermolecular electron transfer between C_{60} and carbazole in polar solvent.
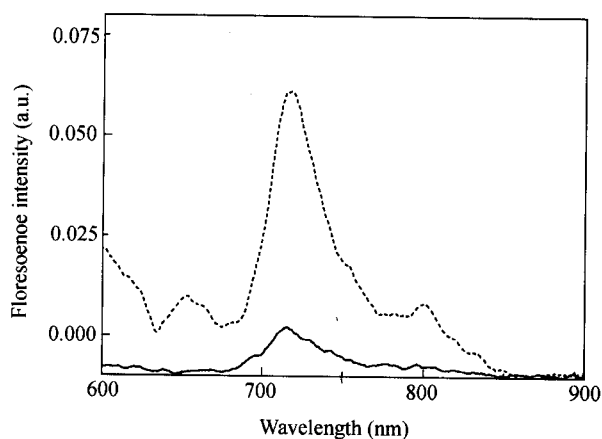

Fig. 5 Fluorescence spectra of **1c** in benzonitrile ($C = 1 \times 10^{-5}$ M. Solid, Ex: 340 nm; Dot, Ex: 432 nm).

In order to investigate the effect of $E^1_{1/2}$ of C_{60} moiety on ET, the fluorescence measurements for dyads **1a—c** were carried out in medium polar chloroform after considering very low emission in benzonitrile. Fig. 6 illustrated the fluorescence spectra for dyads **1a—c** excit-

ed at 432 nm in chloroform. The results showed that with the carbon chain prolonging, the fluorescence intensity decreased gradually. Considering the shift trend of the redox potential of **1a—c**, it can be deducd that the ability of accepting one electron was **1c > 1b > 1a**, and the ability of fluorescence quenching followed the same order.
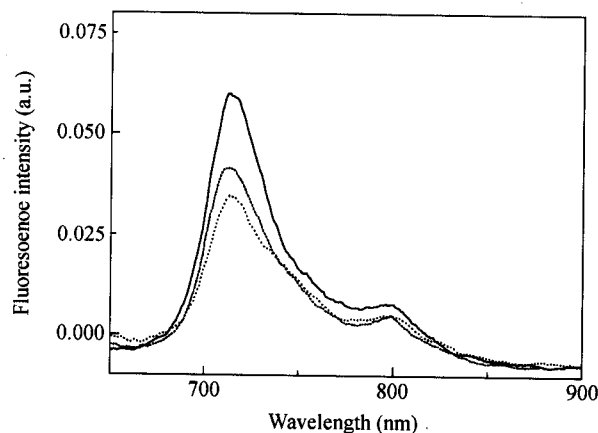

Fig. 6 Fluorescence spectra for **1a—c** excited at 432 nm in chloroform; pmt = 900 V. $C = 2 \times 10^{-5}$ M. Solid (**1a**), Short dash (**1b**), Dot (**1c**).

Fluorescence quantum yields and fluorescence lifetime

Table 2 summaried the fluorescence quantum yields (Φ_f) and fluorescence lifetime for **1a—c** at room temperature. Fluorescence quantum yields of the C_{60} derivatives **1a—c** in room temperature solutions (ca. 2×10^{-5} M) were determined quantitatively in reference to the yield of C_{60} ($\Phi_f = 3.2 \times 10^{-4}$).[9] Like other mono-functionalized fullerene derivatives reported in the literature,[7,10] compounds **1a—c** have fluorescence yields several times higher than the yield of pristine C_{60}, and Φ_f values decreased with the increasing of the polarity of the solvents. Fluorescence lifetime τ_T of **1a—c** was ca. 1.3 ns in toluene, which was very similar to that[11] of C_{60} (Due to the limitation of the instrument, the lifetime of **1a—c** could not be measured in benzonitrile).

Conclusion

In summary, this work synthesized and characterized three C_{60} derivatives of carbazole, and investigated their photophysical properties both in ground and in ex-

Table 2   Parameters of singlet states of C$_{60}$ and **1a—c** in toluene (Tol) and benzonitrile (BN)

	C$_{60}$	1a	1b	1c
$\Phi_f \times 10^4$ (in Tol)	3.2	14.1	13.8	13.2
τ_f (ns, in Tol)	1.245 ± 0.2	1.52 ± 0.15	1.324 ± 0.15	1.25 ± 0.17
$\Phi_f \times 10^4$ (in BN)	1.14	1.07	1.05	

cited states via absorption and fluorescence spectra. The results show that there is little electronic interaction between C$_{60}$ moiety and carbazole in the ground state. There has an enhanced fluorescence excited at 340 nm in nonpolar solvent and the intramolecular energy transfer between carbazole and C$_{60}$ is responsible for this. Also there has an intramolecular electron transfer from carbazole to C$_{60}$ in polar solvent, which quenchs the fluorescence. The contribution of these processes to the charge transfer remarkably depends on the experimental conditions such as medium and the excitation wavelength. In addition, the substituents at N-atom of carbazole have an effect on $E_{1/2}$ and fluorescence emission.

Experimental

Fullerene [60] was purchased from Tian-an Co. (> 99.9%), and the other reagents were purified before use. UV-NIR absorption spectra were recorded on a Shimadzu UV-3100PC spectrometer. Mass spectra were recorded on a Finnigan mat APISSQ-710 mass spectrometer. IR spectra were recorded on a Bruker IFS 66V FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 500 spectrometer. Chemical shifts (δ) are given in parts per million relative to TMS. Raman spectra were recorded on a Bruker RFS 100 Raman spectrometer. Electrochemical data were measured on an EG&G Potentiostat/Galvanostat Model 273 electrochemical analyzer. The one-compartment electrochemical cell was airtight with high-vacuum glass stopcocks connected to the Schlenk system. The working electrode consisted of a platinum microdisk, and the counter electrode consisted of a platinum wire. The quasi-reference electrode was a silver wire and ferrocene was used as an internal standard. All spectroscopic measurements were made at room temperature in non-degassed solvent which was purified before use, in standard quartz cells with a pathlength of 1 cm. Fluorescence emission and excitation spectra were recorded on an Aminco Bowman Series 2 spectrofluorimeter equipped with an R928 photomultipli-

er working at 850 V and pass width was 8 nm. The sample concentration was in the range of 10^{-5}—10^{-4} mol/L. C$_{60}$ in non-degassed toluene ($\Phi_f = 3.2 \times 10^{-4}$) was used as a standard[9] for the determination of the fluorescence quantum yields. The excitation wavelength was 520 nm, and the absorbances of the reference and the sample were adjusted to 0.14 at this wavelength. The fluorescence lifetime was determined on an SLM 48000 Multi-Frequency Phase Fluorometer,[12] using the frequency-domain method with glycogen as the reference. The averaged values were used to evaluate the fluorescence lifetime in order to minimize the experimental error.

Syntheses

A mixture of C$_{60}$ (90 mg, 0.12 mmol), the aldehyde **3a—c** (0.24 mmol), and N-methylglycine (55 mg, 0.60 mmol) in toluene (100 mL) was stirred under reflux for 2—3 h, then cooled down to room temperature, a solid residue was obtained after removing the solvent under reduced pressure, which was chromatographed on silica (GF$_{60}$) column. Elution with a mixture of CS$_2$ and toluene (6:1) gave the pure products **1a—c**.

1a ^{1}H NMR δ_H: 2.84(s, 3H, NCH$_3$), 3.85 (s, 3H, NCH$_3$(Ar)), 4.30(d, $J = 9.0$ Hz, 1H, CH$_2$-(*exo*), pyrrolidine), 5.01(d, $J = 9.0$ Hz, 1H, CH$_2$-(*endo*), pyrrolidine), 5.10(s, 1H, CH, pyrrolidine), 7.08(d, $J = 7.5$ Hz, 1H), 7.16(t, $J = 7.3$ Hz, 1H), 7.31(d, $J = 8.2$ Hz, 1H), 7.40(d, $J = 7.3$ Hz, 2H), 8.02(d, $J = 5.5$ Hz, 1H), 8.35(br. s, 1H); ^{13}C NMR δ_C: sample insufficiently soluble for satisfactory characterisation; IR (KBr) ν: 3416.5, 2921.2, 2776.7, 1602.2, 1492.1, 1462.0, 1426.9, 1332.6, 1248.8, 1183.2, 1122.2, 1047.2, 882.4, 768.9, 744.2, 598.3, 574.6, 526.5, 474.4 cm^{-1}. Raman ν: 217.2, 255.4, 274.0, 312.8, 337.8, 429.9, 453.7, 489.9, 511.9, 528.3, 553.9, 564.4, 726.6, 770.2, 995.9, 1091.3, 1231.1, 1460.7,

1570.4, 2946.0 cm^{-1}. UV-Vis (CH_2Cl_2) λ_{max}: 306, 432, 635, 701.5 nm; EIS-MS $m/z(\%)$: 957 (M + H$^+$, 100), 1913.7(2M + H$^+$, 36).

1b ^{1}H NMR δ_H: 1.45(t, J = 7.1 Hz, 3H, CH$_2$**CH$_3$**), 2.84(s, 3H, NCH$_3$), 4.30(d, J = 9.1 Hz, 1H, CH$_2$(exo), pyrrolidine), 4.32(q, J = 6.9 Hz, 1H, **CH$_2$**CH$_3$), 5.01(d, J = 9.1 Hz, 1H, CH$_2$(endo), pyrrolidine), 5.26(s, 1H, CH, pyrrolidine), 7.08(d, J = 7.5 Hz, 1H), 7.16(t, J = 7.3 Hz, 1H), 7.31(d, J = 8.2 Hz, 1H), 7.40(t, J = 7.3 Hz, 2H), 8.02(d, J = 5.5 Hz, 1H), 8.35(br.s, 1H); ^{13}C NMR (125 MHz, CS$_2$/CDCl$_3$ 2:1) δ_C: 13.94, 29.85, 37.56, 39.93, 68.69, 69.91, 83.99, 108.25, 119.1, 120.51, 125.15, 125.79, 126.96, 128.03, 128.77, 136.48, 139.71, 139.90, 141.43, 141.71, 141.90, 142.04, 142,29, 142.42, 142.75, 144.13, 144.43, 144.85, 144.94, 145.27, 145.63, 145.84, 146.05, 146.60, 153.59, 156.14; IR (KBr) ν: 3435.9, 2972.2, 2776.4, 1601.5, 1490.4, 1461.9, 1332.8, 1232.8, 1182.6, 1122.6, 1048.2, 768.2, 744.8, 725.7, 598.1, 553.2, 526.5 cm^{-1}; UV-Vis (CH_2Cl_2) λ_{max}: 298.5, 432, 702 nm. Raman ν: 256.2, 273.6, 311.6, 345.6, 429.9, 454.0, 490.0, 512.4, 553.0, 564.5, 718.0, 770.4, 1091.7, 1232.1, 1460.9, 1570.5, 1629.0, 2945.7 cm^{-1}; EIS-MS $m/z(\%)$: 971.0 (M + H$^+$, 100), 1941.5(2M + H$^+$, 50).

1c ^{1}H NMR (125 MHz, CS$_2$/CDCl$_3$ 2:1) δ_H: 0.97(t, J = 7.2 Hz, 3H, CH$_2$CH$_2$CH$_2$**CH$_3$**), 1.43(q, J = 7.6 Hz, 2H, CH$_2$CH$_2$**CH$_2$**CH$_3$), 1.85(br.s, 2H, CH$_2$**CH$_2$**CH$_2$CH$_3$), 2.84(s, 3H, NCH$_3$), 4.25(t, J = 7.0 Hz, 2H, **CH$_2$**CH$_2$CH$_2$CH$_3$), 4.30(d, J = 9.1 Hz, 1H, CH$_2$(exo), pyrrolidine), 5.01(d, J = 9.1 Hz, 1H, CH$_2$(endo), pyrrolidine), 5.09(s, 1H, CH, pyrrolidine), 7.15(t, J = 7.4 Hz, 1H), 7.31(d, J = 8 Hz, 1H), 7.37(t, J = 7.3 Hz, 1H), 7.87(br.s, 1H), 8.03(d, J = 6.7 Hz, 1H), 8.39(br.s, 1H); ^{13}C NMR δ_C: 13.11, 19.93, 28.96, 30.38, 39.19, 42.04, 68.82, 69.15, 83.25, 107.73, 118.15, 119.63, 121.79, 124.89, 126.14, 134.81, 135.72, 138.97, 139.19, 139.68, 140.67, 140.78, 140.95, 141.13, 141.29, 141.53, 141.65, 141.98, 142.11, 143.37, 143.60, 144.19, 144.50, 144.76, 144.89, 145.08, 145.18, 145.38, 145.53, 145.87, 146.23, 152.74, 152.85, 153.15, 155.41; IR (KBr) ν: 3433.6, 2955.6, 2777.7, 1600.7, 1490.0, 1463.1, 1332.3, 1245.1, 1212.6, 1182.2, 1038.5, 769.1,

744.8, 598.8, 553.5, 526.5, 477.7 cm^{-1}. Raman ν: 255.5, 273.2, 311.9, 430.1, 453.7, 489.4, 512.5, 553.8, 770.2, 1231.9, 1462.2, 1571.6, 2779.7 cm^{-1}; UV-Vis (CH_2Cl_2) λ_{max}: 301, 432, 702 nm; EIS-MS $m/z(\%)$: 999.2 (M + H$^+$, 100), 1997.9 (2M + H$^+$, 28).

Acknowledgement

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