Porphyrinoids

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Macrocyclic Transformations from Norrole to Isonorrole and an N-Confused Corrole with a Fused Hexacyclic Ring System Triggered by a Pyrrole Substituent

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Abstract: *Three kinds of fused porphyrinoids,* ***L2–L4****, possessing different types of corrole-based frameworks were synthesized from a pyrrole-substituted corrole isomer (norrole* ***L1****). Oxidation of* ***L1*** *afforded a unique N-C_{meso}-fused pyrrolyl isonorrole* ***L2****, involving the fusion of an auxiliary pyrrolic NH moiety with a meso-sp^3-hybridized carbon atom. Subsequently,* ***L2*** *underwent macrocycle transformations to give singly and doubly N-C_{Ar}-fused N-confused corroles,* ***L3*** *and* ***L4****, respectively.* ***L3*** *and* ***L4*** *contain fused [5.7.6.5]-tetra- and [5.6.7.7.6.5]-hexacyclic structures, respectively, prepared through lateral annulation. These skeletal transformation reactions from norrole to its isomer isonorrole and finally to N-confused corrole indicate that multiply fused porphyrinoids could be readily synthesized from pyrrole-appended confused porphyrinoids.*

Corrole is one of the most widely studied contracted tetrapyrrolic macrocycles containing four pyrrolic units interconnected at the α positions through three *meso*-carbon atoms in a (1.1.1.0) fashion (Figure 1).[1] Unlike the parent porphyrin skeleton, such a contracted core structure means that these compounds have potential as catalysts for oxidation because of the stabilization of high-valent metals through a markedly smaller and trianionic coordinating environment.[2] The compounds may also have potential as photosensitizers in the conversion of light to electrical energy.[2] Thus, it is of particular importance to develop a method for the functionalization of corroles for various applications.[3] However, a method for direct skeletal modification and further functionalization of a corrole core is still its infancy because such analogues are usually less stable compared to the parent corrole and often exhibit unexpected reactivity.[4]

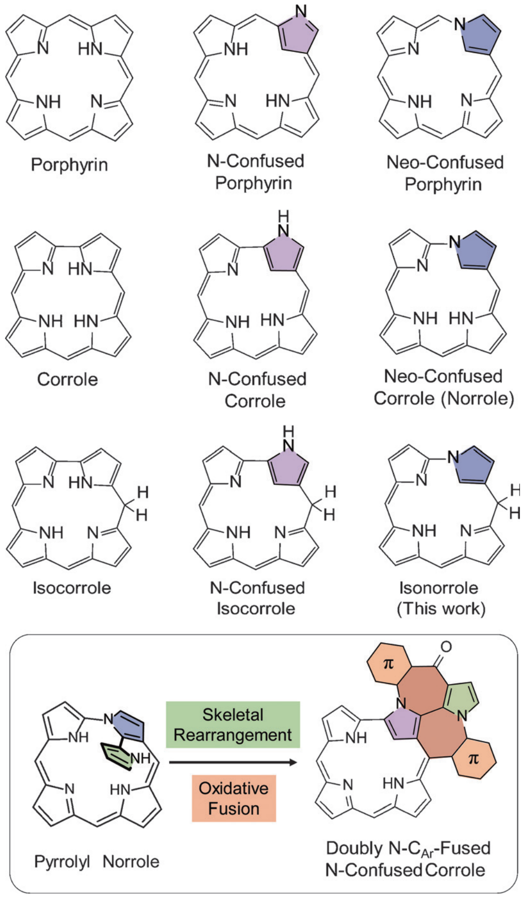

Figure 1. Chemical structures of porphyrin, corrole, and their analogues.

To address this issue, we envision that a "confusion approach"[5] can be systematically applied to obtain new electronic structures by varying the linking modes of pyrrolic subunits, for example C_α–C_β,[6] C_β–C_β,[7] or N–C_α[6c,8] (Figure 1). One of these derivatives, neo-confused porphyrinoids, have one pyrrolic unit linked through an N–C bond, affording electronically perturbed π-electron platforms with

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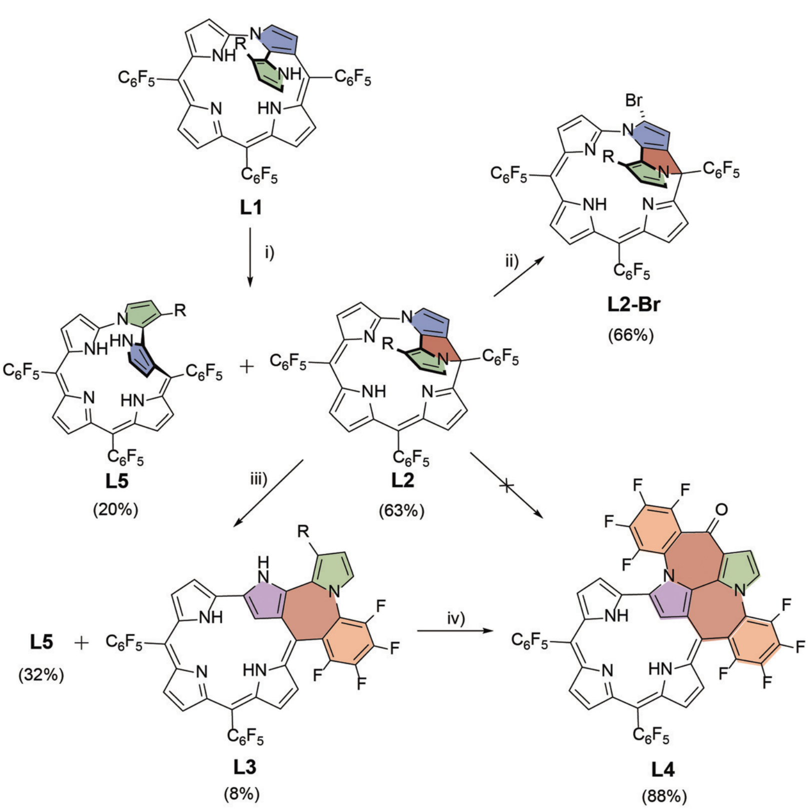
a polarized N−C covalent bond.[8] Notably, these compounds retain 18-π-electron conjugated circuits, and their resultant properties, such as extended UV/Vis absorption, tunable aromaticity, anion-binding ability, cation complexation, and oxidative coupling reactivity of the inner carbon atom, have been thus demonstrated.[9]

Oxidative fusion reactions have been found to be useful to create highly conjugated core skeletons such as electron-rich π-conjugated compounds.[4b,10] Herein, we focused on the pyrrolyl norrole (**L1**, Scheme 1), which has been reported to undergo an unusual ring expansion reaction to form pentaphyrin.[11] Taking advantage of the regioselective reactivity of the α-pyrrolic CH moieties as well as the structural flexibility originating from the interpyrrolic N−C linkage of neo-confused corrole, the auxiliary pyrrole appended at the adjacent α position of norrole is expected to trigger a fusion reaction through the weakly acidic pyrrole NH site.[12] Thus, in this study, analysis of the oxidative fusion of norrole **L1** led to the formation of N-C_{meso}-fused isocorrole isomer **L2** (Scheme 1, classified as an isonorrole). Different from the regular isocorroles,[13] isonorrole **L2** can be considered as a new class of tetrapyrrolic macrocycle, and it showed further reactivity for ring-fusion reactions.[14] The singly and doubly N-C_{Ar}-fused N-confused corroles (**L3** and **L4**) were subsequently generated by double skeletal rearrangement of N−C linkages (specifically the N−C_α and N−C_{meso} bonds). The core transformation from norrole to isonorrole and finally to N-confused corrole can alter the photophysical and electrochemical properties of the compounds as a result of the lateral annulation of the auxiliary pyrrole unit and the C_6F_5 moieties.



Scheme 1. Syntheses of **L2**–**L5**. Conditions: i) DDQ (1 equiv), CH_2Cl_2; ii) NBS, CH_2Cl_2; iii) toluene, reflux; iv) DMF, 30 °C. R = COC_6F_5.

Details of the syntheses are outlined in Scheme 1. Treatment of **L1**[11] with one equivalent of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CH_2Cl_2 yielded isonorrole **L2** in 63 % yield by N−C fusion of the appended pyrrolic NH moiety with the neighboring *meso*-carbon atom.[15] Under these conditions, the previously reported pentaphyrin **L5** was formed as the second major product.[11] Interestingly, **L2** undergoes a regioselective bromination reaction at one of the two free pyrrolic *α* positions to afford **L2-Br** in a yield of 66 % upon addition of *N*-bromosuccinimide (NBS, 0.9 equiv). Considering the presence of an sp^3-hybridized *meso*-carbon atom and a reactive interpyrrolic N−C linkage in the framework of **L2**, it is anticipated that **L2** may be susceptible to ring opening or skeletal transformation reactions if suitable conditions are applied. Consistent with this expectation, when a solution of **L2** in toluene was heated at reflux for 10 h, a skeletal rearrangement occurred with concurrent fusion of the appended pyrrolic nitrogen with the C_6F_5 moiety. The pyrrolyl-fused N-confused corrole **L3** was obtained in yield of 8 % accompanied by the formation of **L5** in 32 % yield. Since the N-confused corrole **L3** still contains a free pyrrolic NH site located close to the C_6F_5 moiety, one further fusion reaction could be expected.[16] With this in mind, **L3** was stirred in DMF for 4 h at 30 °C, leading to the formation of fused corrole **L4** which was obtained in 88 % yield. Interestingly, no reaction occurred when THF was used as the solvent instead of DMF, which implies that the basic solvent facilitates the reaction through deprotonation of the NH group of **L3** followed by its nucleophilic attack at the C_6F_5 moiety. In fact, **L4** was not formed upon heating the toluene solution of isonorrole **L2** at reflux, which may be ascribed to the nonbasic nature of the solvent. The structures of the products obtained in this study were characterized by various spectroscopic methods.

Combined with the structural analysis of **L2-Br** (see below), it should also be noted that **L2** was generated by oxidative dehydrogenation of **L1**. The ^{1}H NMR spectrum of **L2** in $CDCl_3$ shows only one resonance signal for an NH moiety ($\delta = 14.67$ ppm; see Figure S1 in the Supporting Information), whereas three signals for NH units are present in the spectrum of **L1**. The disappearance of signals for two NH protons is consistent with the oxidation-triggered ring-fusion reaction. The characteristic signal at $\delta = 68.3$ ppm in the ^{13}C NMR spectrum supports the proposed isonorrole structure with an sp^3-hybridized *meso*-carbon atom. As a result of the disruption of the conjugation in **L2**, the pyrrolic *β*−H signals lie in the range of $\delta = 5.8$–7.0 ppm, reflecting its nonaromatic character.

The X-ray crystal structure of brominated derivative **L2-Br** gave more solid evidence for the intrinsic structure of isonorrole (Figure 2a,c).[17] A [5.5.5]-tricyclic fused moiety formed by connection of the nitrogen atom of the appended pyrrole with the neighboring *meso*-carbon atom is evident in **L2-Br**. The *meso*-carbon atom is arranged as an sp^3-hybridized carbon with typical tetrahedral angles of approximately 109.5°. The tripyrrin unit (namely, pyrrole rings A–C) is nearly coplanar as a result of effective internal hydrogen-bond formation. The fused tricyclic unit (rings D–F) are lying approximately perpendicular to the tripyrrin with an interplanar angle of 72.1°, which is more severely distorted with respect to that of norrole (36.4°)[6c] because of the presence of the sp^3-hybridized *meso*-carbon atom. Based on the similarities between **L2-Br** and **L2** in the ^1H and ^{13}C NMR spectra (Figures S1–S6), a distorted isonorrole-like structure was proposed for compound **L2**.

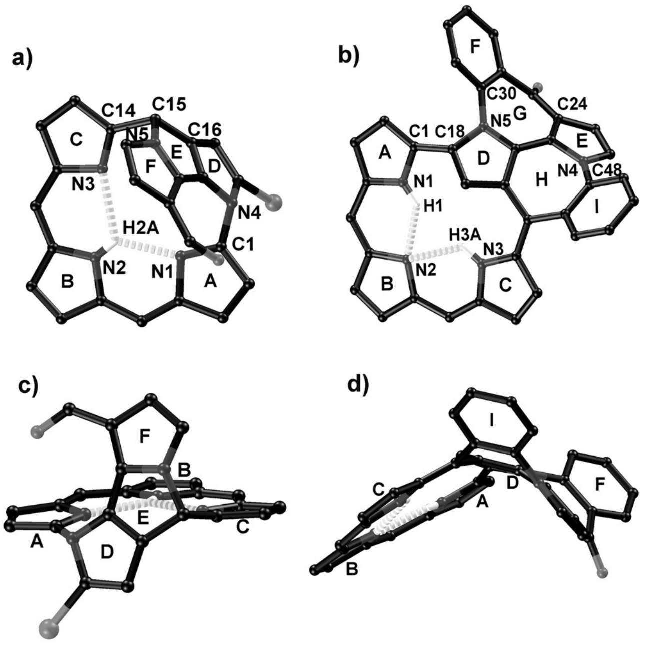


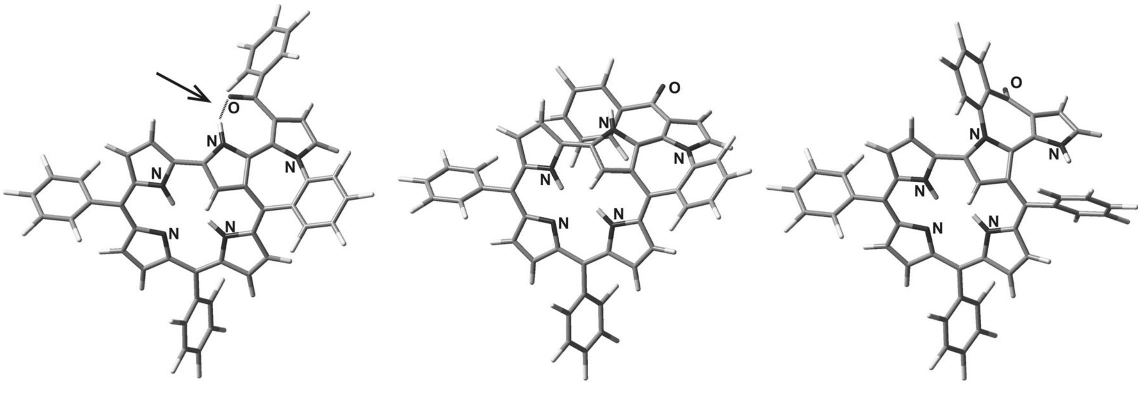
Figure 2. Complementary views of the molecular structures of a,c) **L2-Br** and b,d) **L4**.[17] C_6F_5 groups and hydrogen atoms attached to carbon atoms are omitted for clarity. The dotted lines represent hydrogen bonds.

Upon transformation of **L2** to **L3** and subsequently to **L4**, typical spectral features of an N-confused corrole[6c] were evident in the ^1H and ^{13}C NMR spectra (see the Supporting Information). In the ^1H NMR spectrum of **L3** (Figure S7), a resonance signal for an outer NH unit appears at lower field ($\delta = 13.20$ ppm) and two internal NH signals appear at relatively high field at $\delta = 8.52$ and 4.56 ppm. In addition, one resonance signal for an internal CH moiety appears upfield at $\delta = 2.12$ ppm. These features imply the recovery of aromaticity in the molecule, although the strength is likely weak judging from the maximum difference between the chemical shifts of peripheral CH moieties and those of interior CH or NH moieties ($\Delta\delta_{\text{CH-CH}} = 5.6$ ppm and $\Delta\delta_{\text{CH-NH}} = 3.2$ ppm; Figure S7).[6c,18] These results provide evidence for the skeletal rearrangement of isonorrole **L2** to the N-confused corrole derivatives **L3** and **L4**.

The ^1H NMR spectrum of **L4** was essentially the same as that of **L3** except for the loss of an outer NH signal (Figure S10). In the mass spectrum of **L4**, a mass loss of 20 units relative to **L3** suggests the further fusion of the outer NH unit with the neighboring C_6F_5 moiety. Further support for the formation of fused N-confused corrole skeletons in **L3** and **L4** was given by the unambiguous X-ray crystallographic analysis of **L4** (Figure 2b,d).[17] Structure determination revealed the presence of an N-confused corrole core skeleton in addition to two N-fused ring systems involving the linkage of the confused and the appended pyrrolic moieties with the neighboring C_6F_5 groups. The resulting [5.6.7.7.6.5]-hexacyclic ring unit (rings D–I) is highly distorted relative to the tripyrrin core unit (rings A–C). Specifically, pyrrole ring D is tilted from the tripyrrin mean plane by an angle of 44.1° and interplanar angles for rings D/E, D/F, and D/I are 36.3°, 43.4°, and 38.1°, respectively. The incorporated seven-membered rings in the peripheral ring system may introduce a strained curvature as previously found in warped nanographene.[19]

Considering the formation of doubly fused corrole analogue **L4**, from a mechanistic viewpoint the singly fused corrole **L3** can be regarded as an intermediate containing a fused [5.7.6.5]-tetracyclic ring with one of the pyrrolic NH moieties, specifically, either the N-confused or the appended one. To provide further details on the $N{-}C_{Ar}$ bond formation occurring in **L3**, the relative energies of the plausible isomers and conformers of **L3** were examined by DFT calculations (Figure 3). Owing to the proximity between the NH and the C_6F_5 moieties, model isomers **L3a′** and **L3b** are subject to severe intramolecular steric hindrance. It is found that the geometry of **L3a** is energetically more than 10 kcal mol^{-1} more stable than the other isomers as a result of effective hydrogen bonding between the outer NH moiety and the carbonyl O atom as well as the lack of intramolecular steric hindrance. This finding is in good agreement with the experimentally obtained results; an extraordinarily downfield shift of the signal for the outer NH moiety of **L3** was detected, in marked contrast to that obtained for the equivalent moiety on a reported N-confused corrole (for example, $\delta = 13.20$ ppm versus 9.24 ppm, respectively).[6c] Moreover, the chemical shift for the outer NH moiety in **L3** is insensitive to the solvent media (for example in $CDCl_3$ or $[D_6]$DMSO; Figure S13).[20] These observations may be rationalized by the presence of a strong intramolecular hydrogen bond between the outer NH and the carbonyl O atom. Thus, the structure of **L3a** can be described as the most probable conformer (Figure 3). Upon deprotonation of the pyrrolic NH moiety in **L3**, the rotation barrier for the C_6F_5 ring may decrease significantly to facilitate the formation of doubly fused product **L4**.

The UV/Vis absorption spectra of **L2**–**L4** exhibit two sets of broad bands with comparable intensities in the ranges of $\lambda = 340$–380 nm and 460–750 nm, respectively (Figure 4). The nonaromatic isonorrole **L2** has an almost featureless spectrum (that is, no vibronic fine structure), whereas the fused N-confused corroles **L3** and **L4** have spectra with vibronic fine



L3a
0.0 kcal mol^{-1}

L3a'
+10.54 kcal mol^{-1}

L3b
+11.81 kcal mol^{-1}

Figure 3. DFT-calculated relative energies for the possible isomers of **L3**. The arrow on **L3a** indicates the hydrogen bond.

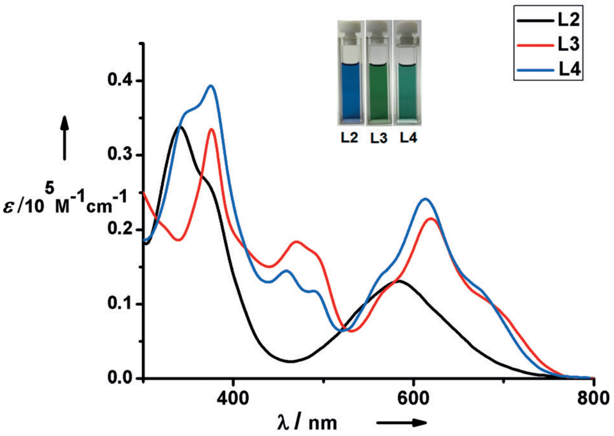


Figure 4. UV/Vis absorption spectra of **L2**–**L4** in CH_2Cl_2 and photographs showing the colors of the corresponding solutions in CH_2Cl_2.

structure in the Q-band region, similar to the spectrum for the reported N-confused corrole.[6c] The bathochromic shifts of the absorption bands for **L3** and **L4** relative to **L2** could be rationalized by the recovery of the conjugation framework in these two compounds. In addition, the peripheral fusion leads to an extension of absorption band edges by approximately 50 nm relative to that of N-confused corrole.[6c]

In an effort to calculate the HOMO–LUMO energy gaps for the corrole derivatives, the redox potentials of **L2-Br** and **L2**–**L4** (Figure S20 and Table S1) were determined by cyclic voltammetry in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. Isonorroles **L2** and **L2-Br** exhibit irreversible oxidation waves at 0.65 and 0.76 V (versus Fc/Fc$^+$). **L2** and **L2-Br** can be easily reduced, with reduction waves at −0.99 and −0.89 V, respectively. On the basis of these values, the HOMO–LUMO gaps for **L2** and **L2-Br** were calculated and were found to be almost identical with values of 1.64 and 1.65 V, respectively. Upon transformation to N-confused corroles **L3** and **L4**, the first oxidation potentials are determined at 0.49 and 0.55 V, and the first reduction potentials at −1.23 and −1.24 V, respectively. Using these values, electrochemical HOMO–LUMO gaps of 1.72 and 1.79 eV for **L3** and **L4**, respectively, could be calculated. The HOMO–LUMO gaps of **L2**–**L4** estimated from DFT calculations were 1.95, 2.12, and 2.18 eV, respectively, in reasonable agreement with those obtained from the electrochemical data (Figure S21).

Notably, **L2** had the smallest HOMO–LUMO gap among compounds **L2**–**L4**, which seems to be inconsistent with the fact that the lowest energy absorption band for **L2** appears at $\lambda = 581$ nm, a shorter wavelength relative to the equivalent bands at 620 and 612 nm for **L3** and **L4**, respectively. This inconsistency can be interpreted from further time-dependent DFT calculations, which indicates that the hypsochromic shift of **L2** arises from the noticeable admixture of the HOMO-1→LUMO into the HOMO→LUMO transition, thus enlarging the corresponding excitation energy (Table S2). In contrast, the corresponding absorption bands for **L3** and **L4** involve almost pure HOMO→LUMO transitions.

In summary, using the unique reactivity of the norrole-appended auxiliary pyrrole moiety in **L1**, we have synthesized three novel corrole isomers **L2**–**L4**. Notably, the oxidative fusion reaction of **L1** afforded N-C_{meso}-fused pyrrolyl isonorrole **L2** where one of the *meso*-carbon atoms is sp^3-hybridized. It was found that this species is highly reactive towards macrocycle transformation reactions. Isonorrole **L2** was successfully converted into singly and doubly N-C_{Ar}-fused N-confused corroles **L3** and **L4**. Unprecedented [5.7.6.5]-tetra- and [5.6.7.7.6.5]-hexacyclic fused ring structures involving lateral annulation were formed adjacent to the macrocyclic cores. The "confusion approach" products reported herein may be employed to develop further interesting heteroacene architectures whose properties can be easily modulated by metal coordination to the novel corrole-based macrocyclic units.

Acknowledgements

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[14] Isomerization from norrole to isonorrole seems infeasible judging by the fact that the calculated relative energy for isonorrole is $+7.34\ \text{kcal mol}^{-1}$ higher than that of norrole (Figure S28). However the oxidative fusion approaches should potentially work for producing the N-confused corrole species with the downhill driving force.

[15] Addition of triethylamine did not change the yield of **L2** noticeably, which indicates that intrinsic oxidative nucleophilic addition is predominant for this reaction.

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[17] CCDC 1434096 (**L2-Br**) and 1434097 (**L4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[18] The relatively weak aromatic character was also evaluated by the nucleus-independent chemical shift (NICS) values at the global centers of the macrocycles, **L3** and **L4**. The values of $\delta = -4.55$ and -5.18 ppm are similar to those of the corresponding N-confused corrole (i.e., -4.82 ppm).

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