Synthesis, Characterization, and Modification of Hyperbranched Poly(arylene oxindoles) with a Degree of Branching of 100 %**

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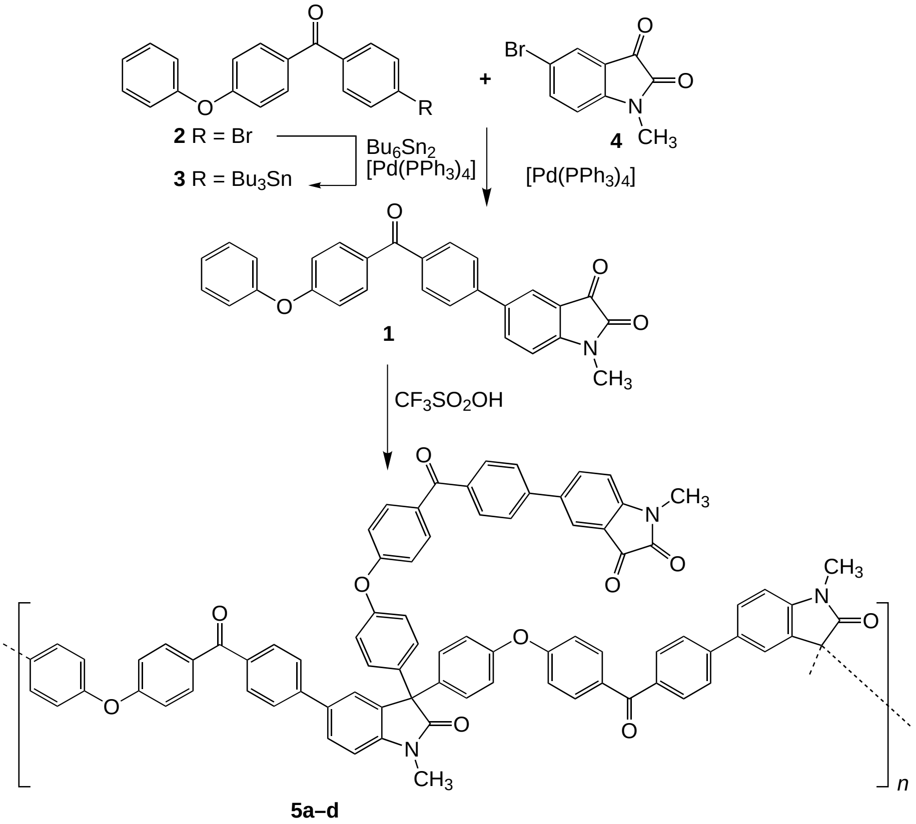

Scheme 1. Synthesis of the polymers **5a**–**d**.

Hyperbranched polymers are of high importance as readily available substitutes for dendrimers. Whereas the preparation of the latter requires a multistep synthesis, hyperbranched polymers can be obtained in a single step.[1] However, a degree of branching of 100%, which is a characteristic property of dendrimers, can be achieved only by postsynthetic modification[2] or when certain requirements for the monomer are met.[3] To date, the only example of a hyperbranched polymer (which necessarily consists exclusively of dendritic and terminal units) was based on an AB_2 monomer possessing an azine and a maleimide functional group, which react in a "criss-cross" cycloaddition.[4] However, to improve features such as accessibility, convenience of functionalization, and attractive physical properties, it is highly desirable to devise new strategies towards hyperbranched polymers with a degree of branching of 100%.

We applied the acid-catalyzed condensation of isatins[5] with aromatic compounds for the synthesis of hyperbranched poly(arylene oxindoles). The linear analogues have been shown to display a high glass-transition temperature (T_g) and excellent thermal stability.[6] The use of *para*-phenoxybenzophenones as the aromatic reaction partner results exclusively in *para*-substitution and hence in structural homogeneity of the polymer.[6] Therefore, the AB_2 monomer **1** was designed and synthesized by Stille coupling of the tin derivative **3** and 5-bromo-1-methylisatin (**4**)[7] (Scheme 1). The methyl group was introduced to enhance the solubility of both the monomer and the polymers and to facilitate the characterization of the latter by NMR spectroscopy. As it is known that this type of condensation of isatin and aromatic compounds exclusively yields 3,3-diaryl oxindoles,[5] we can exclude the possibility of the presence of linear units in the hyperbranched polymers obtained from **1**. The tin derivative **3** was obtained by palladium-catalyzed transmetalation of the bromide **2** and hexakis-*n*-butylditin. The bromide **2** was formed by Friedel–Crafts acylation of diphenyl ether (five-fold excess) with 4-bromobenzoyl chloride.

Monomer **1** was polymerized over 24 h using trifluoromethanesulfonic acid, to yield the polymers **5a**–**d**, which possess 3,3-diaryl oxindole groups as dendritic units and isatin residues at the periphery. These polymers were soluble in chloroform, dichloromethane, and toluene. They were poorly soluble in THF and insoluble in acetone. These solubility properties are in sharp contrast to the linear analogues which were only soluble in highly polar solvents such as *N*,*N*-dimethylacetamide and *N*-methylpyrrolidinone, or in the presence of strong acids.[6] As can be seen from Table 1, the obtained molecular weights are strongly dependent upon the reaction temperature and the concentration. At room temperature, only oligomers were obtained although, according to the literature,[6] the linear polymerization occurred readily at 25 °C. Higher temperatures and higher concentrations favor the formation of higher molecular-mass species. Higher molecular masses result in higher polydispersities. It should be emphasized that the molecular weights obtained by size-exclusion chromatography (SEC) are likely to be underestimated because of the compact structure of our macro-

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Table 1. Overview of the synthesized hyperbranched polymers.

Polymer	Temperature [°C]	Concentration [mg mL^{-1}]	Yield [%]	M_n[a] [g mol^{-1}]	M_w[a] [g mol^{-1}]	D[a]
5a	25	10	58	–[b]	–[b]	–[b]
5b	40	10	63	3900	4900	1.27
5c	60	10	68	4200	5700	1.37
5d	60	20	76	7100	20000	2.9

[a] GPC with chloroform as the eluent. [b] Only oligomers were obtained.

molecules. In the future, absolute molecular weights will be determined, to provide evidence for this assumption.

In the FTIR spectrum of the monomer, a strong absorption band at 1731 cm^{-1} is observed which can be attributed to both the carbonyl groups of the five-membered ring. Another absorption band of medium intensity at 1650 cm^{-1} is characteristic for the carbonyl group of the benzophenone unit. In the polymers, the latter absorption remains unaffected, yet two signals are observed for the carbonyl groups of the indole residues at 1742 and 1718 cm^{-1}, respectively. The first one can be assigned to both the carbonyl groups of the terminal isatin units, whereas the lactam carbonyl group of the dendritic diphenyloxindole residues gives rise to the latter. It is also possible to monitor the polymerization by UV spectroscopy. The monomer has an extinction coefficient of 789 $\text{L mol}^{-1}\,\text{cm}^{-1}$ at 437 nm. However, for the polymers, an apparent extinction coefficient of 427 $\text{L mol}^{-1}\,\text{cm}^{-1}$ was found at this wavelength. This is in agreement with the theoretical expectations that the ratio of terminal units (which can reasonably be expected to have an extinction coefficient close to that of the monomer) and the dendritic units (showing no absorbance in the visible region) should be close to (or over) 1,[8] which should give rise to an extinction coefficient of about half the value of the monomer.

In the ^{1}H NMR spectrum, extensive line broadening is observed (Figure 1). Two main clusters of signals for the CH_3 groups can be distinguished. The resonance signals at 3.37 ppm can be assigned to the internal (dendritic) groups, whereas the cluster at 3.31 ppm can be assigned to peripheral isatin residues. This assignment is supported by comparison of the chemical shifts of the latter peak and that arising from the methyl protons of the monomer. The observation that the ratio of the integral of the latter peak to the first is near 0.9 reflects again the expected ratio of terminal and dendritic units. The intensity of the peak at 7.80 ppm is lowered to the expected intensity for one proton with respect to the intensity of the signals of the monomer in this region. Indeed, the signals arising from the two protons which are *ortho* and *para* to the reactive isatin carbonyl group shift to ≈7.5 and ≈7.6 ppm, respectively, for the dendritic residues, but hardly move for the terminal units. Hence, the signal for the equivalent of only one proton per repeat unit will shift to the ensemble of signals between 7.49 and 7.6 ppm. Finally, it is clear that the protons which are *ortho* to the spiro center account for the resonance observed at 7.33 ppm.

In the ^{13}C NMR spectrum (see Supporting Information), analogous observations can be made. Multiple splitting is observed. Two clusters of almost equal intensity at 26.4 and 26.9 ppm account for the methyl groups. The signal at 61.6 ppm corresponds to the newly formed spiro carbon center. The cluster of signals at 177.3 ppm arises from the amide carbonyl group of the dendritic units. All NMR spectroscopic data are consistent with our assumption of a degree of branching of 100% as no traces of linear units could be observed.

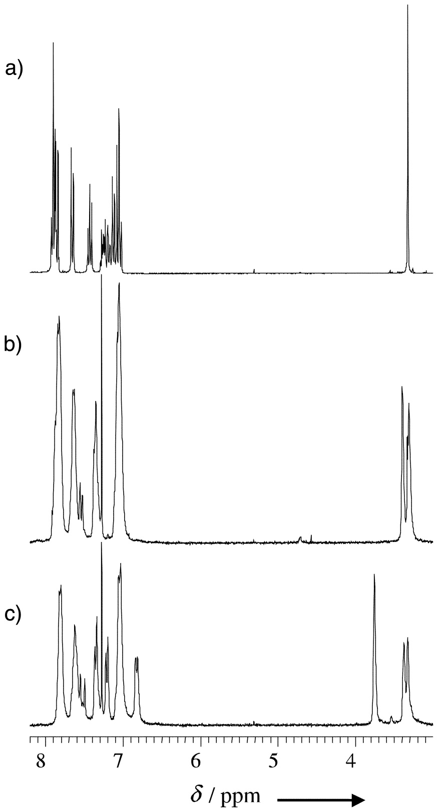
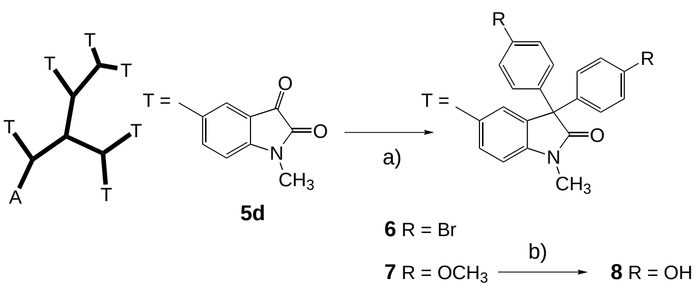


Figure 1. ^{1}H NMR spectrum in $CDCl_3$ of a) the monomer **1** and the hyperbranched polymers b) **5d** and c) **7** (see Scheme 2).

The glass-transition temperature of the polymer **5d** is 190 °C, which is significantly lower than that of the linear analogues in the literature.[6] The thermal stability was very good; no decomposition could be observed by heating at 420 °C under a nitrogen atmosphere (heating rate in both cases = 10 K min^{-1}).

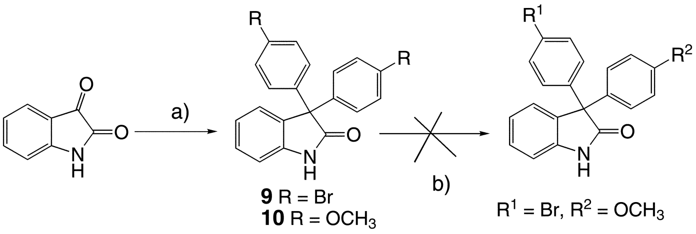
The isatin periphery of the hyperbranched polymers can easily be functionalized with differently substituted arenes in the presence of trifluoromethanesulfonic acid (Scheme 2). In this way, bromophenyl and methoxyphenyl substituents could readily be introduced, with complete conversion reached within 1 h, to yield the derivatives **6** and **7** (see Scheme 2). This conversion was confirmed by NMR spectroscopy. For instance, in the ^{1}H NMR spectrum of the methoxy derivative **7**, apart from the new signals from the methoxyphenyl



Scheme 2. a) Trifluoromethanesulfonic acid, bromobenzene (for the preparation of **6**) or anisole (for the preparation of **7**); b) BBr_3, $CHCl_3$. A = focal phenoxy residue.

substituents, another intensity shift of the equivalent of one proton in intensity from the signal at 7.80 ppm to the ensemble of signals between 7.50 and 7.65 ppm is observed, which indicates the disappearance of all the isatin residues. The functional groups introduced in this way allow further functionalization. As an example, the methoxyphenyl derivative was deprotected using BBr_3, which resulted in the polyhydroxy derivative **8**. These observations show that a large variety of functional groups can be introduced at the periphery of these hyperbranched macromolecules, which allows a convenient modification of their physical properties.

As exchange between the phenoxy residues of the incorporated monomers and the added aromatic compound, which is supposed only to react with the peripheral isatin moieties, could reduce the molecular weight of the hyperbranched poly(arylene oxindoles), we ran a control experiment to provide evidence for the absence of such an exchange. Therefore, compounds **9** and **10** were prepared by treatment of isatin and bromobenzene or anisole with trifluoromethanesulfonic acid (Scheme 3). These compounds were then left overnight in the presence of anisole (for **9**) or bromobenzene (for **10**), respectively, in the same acid. In neither case was evidence for exchange found. However, in the case of compound **10**, some decomposition occurred after long reaction times (> 24 h). As the hyperbranched polymers condensed within a short time (< 1 h) with the large excess of aromatic compound added, and as the electron-withdrawing benzophenone unit can be expected to stabilize the phenoxyphenyloxindole unit, we did not anticipate any problems arising from decomposition upon functionalization of the isatin periphery. By SEC, the molecular mass of the polymer **7** was found to be slightly higher (≈ 10 %) than that of the starting material **5d**. This clearly indicates that modification of the periphery of the polymers in the described way does not degrade the substrate.



Scheme 3. a) Trifluoromethanesulfonic acid and bromobenzene (for the preparation of **9**) or anisole (for the preparation of **10**); b) Trifluoromethanesulfonic acid, anisole (in combination with **9**) or bromobenzene (in combination with **10**).

In conclusion, we have shown that hyperbranched poly(arylene oxindoles) with a degree of branching of 100 % can be prepared in a convenient way. Moreover, these compounds show a high glass-transition temperature and excellent thermal stability. These polymers allow easy and extensive functionalization at the periphery which opens up a number of possibilities to modify their mechanical and physical properties. Further research towards the latter goal, as well as towards modification of the internal skeleton, is currently ongoing.

Experimental Section

Synthesis of 4-bromo-4′-phenoxybenzophenone (**2**): Thionyl chloride (20 mL) and one drop of DMF was added to 4-bromobenzoic acid (2 g, 10 mmol) and the mixture was heated under reflux for 2 h. The solvent was evaporated in vacuum, the residue dissolved in $(CH_2Cl)_2$ (10 mL) and added dropwise to a suspension of diphenyl ether (8.5 g, 50 mmol) and $AlCl_3$ (3.2 g, 24 mmol) in $(CH_2Cl)_2$ (150 mL) at room temperature. The mixture was heated under reflux for 10 min, cooled to room temperature, and poured onto crushed ice (ca. 200 g). The organic phase was separated and the solvent evaporated in vacuum. The bromide **2** was obtained as a white solid (3.2 g, 91 %) by crystallization from petroleum ether. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.03$ (d, ^3J (H-H) = 9 Hz, 2 H), 7.10 (d, ^3J(H-H) = 7 Hz, 2 H), 7.21 (t, ^3J(H-H) = 7 Hz, 1 H), 7.41 (d, ^3J(H-H) = 7 Hz, 2 H), 7.63 (AB system, 4 H), 7.79 ppm (d, ^3J (H-H) = 9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 117.2$, 120.2, 124.7, 127.1, 130.1, 131.3, 131.4, 131.5, 132.3, 136.7, 155.4, 161.9, 194.3 ppm; MS (EI, 70 eV): *m/z* 352 [M^+].

Synthesis of 4-(tris-*n*-butyltin)-4′-phenoxybenzophenone (**3**): $[Pd(PPh_3)_4]$ (3 mol %) was added to a solution of **2** (0.20 g, 0.57 mmol) and hexabutylditin (0.66 g, 1.14 mmol) in toluene under argon. The mixture was heated at 80 °C for 15 h, cooled to room temperature, and the solvent evaporated in vacuum. The tin derivative **3** was obtained as a clear oil (0.13 g, 40 %) after column chromatography (SiO_2, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.89$ (t, ^3J(H-H) = 8 Hz, 9 H), 1.10 (m, 6 H), 1.35 (m, 6 H), 1.56 (m, 6 H), 7.04 (d, ^3J(H-H) = 8 Hz, 2 H), 7.09 (d, ^3J(H-H) = 7 Hz, 2 H), 7.19 (t, ^3J(H-H) = 7 Hz, 1 H), 7.22 (t, ^3J(H-H) = 7 Hz, 2 H), 7.37 (d, ^3J(H-H) = 7 Hz, 2 H), 7.42 (d, ^3J(H-H) = 7 Hz, 2 H), 7.61 ppm (d, ^3J(H-H) = 8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.7$, 13.7, 27.3, 29.0, 117.1, 120.1, 124.5, 128.7, 130.0, 132.1, 132.5, 136.2, 137.3, 148.8, 155.6, 161.5, 195.8 ppm; MS (ES): *m/z* 564.3 [M^+].

Synthesis of the monomer **1**: 1-Methyl-5-bromoisatin (**4**; 97 mg, 0.40 mmol) and the tin derivative **3** (0.19 g, 0.34 mmol) were dissolved in toluene (4 mL). The solution was placed under argon and $[Pd(PPh_3)_4]$ (3 mol %) was added. The mixture was heated under reflux for 16 h. After cooling to room temperature, the solvent was evaporated in vacuum and **1** was obtained as an orange solid (106 mg, 72 %) after column chromatography (silica, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.31$ (s, 3 H; CH_3), 7.02 (d, ^3J(H-H) = 9 Hz, 1 H; 7-H isatin), 7.05 (d, ^3J(H-H) = 9 Hz, 2 H; *o*-H to OPh), 7.11 (d, ^3J(H-H) = 7 Hz, 2 H; *o*-H to COPhO), 7.18 (d, ^3J(H-H) = 7 Hz, 1 H; *p*-H to COPhO), 7.42 (t, ^3J(H-H) = 7 Hz, 2 H; *m*-H to COPhO), 7.64 (d, ^3J(H-H) = 8 Hz, 2 H; *o*-H to isatin), 7.84 (d, ^3J(H-H) = 9 Hz, 2 H; *m*-H to OPh), 7.87 (d, ^3J(H-H) = 8 Hz, 2 H; *m*-H to isatin), 7.89 (d, ^4J(H-H) = 2 Hz, 1 H; 4-H isatin), 7.90 ppm (dd, ^3J(H-H) = 9 Hz, ^4J(H-H) = 2 Hz, 1 H; 5-H isatin); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 26.4, 194.6, 183.1, 161.7, 158.2, 155.4, 151.0, 142.5, 137.1, 136.9, 136.0, 132.3, 131.7, 130.6, 130.0, 126.3, 124.6, 123.7, 120.1, 117.9, 117.1, 110.5 ppm; MS (EI, 70 eV): *m/z* 433 [M^+].

Preparation of polymer **5d**: The monomer (20 mg) was dissolved in trifluoromethanesulfonic acid (1 mL) and placed under argon. The mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the solution was added dropwise to vigorously stirred water (50 mL). After stirring for 30 min, the suspension was centrifuged (3600 r min^{-1}; 5 min) and the supernatant decanted. Water (10 mL) was added to resuspend the precipitate, which was shaken vigorously and again centrifuged. After decanting, acetone was added to the precipitate which was again shaken vigorously and centrifuged. This was repeated once more, after which the precipitate was dried in vacuum. The polymer was obtained as an orange-brown solid (15 mg, 76 %).

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[8] $\frac{T}{D}=\frac{n+1}{n-1}$ where T is the number of terminal units, D the number of dendritic units, and n the degree of polymerization. This equation is readily derived by observing the obvious facts that $T=D+1$ and $n=T+D$.

[(arene)Rh(cod)]$^+$ Complexes as Catalysts for [5+2] Cycloaddition Reactions[**]

Paul A. Wender* and Travis J. Williams

As part of our studies on the design and development of new metal-catalyzed [m+n] cycloaddition reactions, we previously reported the first examples of metal-catalyzed [5+2] cycloadditions of vinylcyclopropanes and tethered π systems.[1] In our initial and ongoing screening of catalysts for these reactions, rhodium(I) complexes have proven to be the most general. These complexes are active in both inter- and intramolecular cycloadditions. The latter reactions involve alkynes, alkenes, and allenes as the 2-π component and provide cycloadducts in high yields often at 25–40 °C.[2] This finding is consistent with earlier observations by our group[3] and others[4] on the utility of rhodium(I) in metal-catalyzed [4+2] cycloadditions of dienes and π systems. More recently, the groups of Gilbertson,[4e] Trost,[5] and Zhang[6] have reported other catalysts that are also effective in certain types of [5+2] cycloadditions.

Recently, Chung and co-workers have reported a readily prepared, air-stable naphthalene complex of rhodium ($[(C_{10}H_8)Rh(cod)]^+BF_4^-$) which is an efficient catalyst for [4+2] cycloaddition reactions of dienes and alkynes.[7] We have now examined the effectiveness of this and several related complexes in [5+2] cycloaddition reactions and have found them to be exceptionally effective in all cases studied, often providing cycloadducts in excellent yields in minutes at room temperature. The details of this study and X-ray crystallographic data on selected complexes are described herein.

Complex $[(C_{10}H_8)Rh(cod)]^+SbF_6^-$ (**1**) is prepared in a single step from commercially available $[\{RhCl(cod)\}_2]$[8] by treatment with $AgSbF_6$, followed by introduction of the naphthalene ligand.[9] The complex is air-stable at room temperature and retains its catalytic activity even after several months of storage.

Although complexes differing from **1** in only the counter ion have been reported,[7,9] characterization data available for these complexes do not directly establish the hapticity of the naphthalene ligand. Fortunately, with some effort, we were able to crystallize complex **1** from a concentrated dichloromethane solution under an anhydrous atmosphere. X-ray crystallographic analysis of these crystals led to the ORTEP representation of this complex given in Figure 1. This is apparently the first X-ray structure of a simple η^6 naphthalene–rhodium complex,[10] and is comparable to crystal structures that have been recorded for some similar ruthenium– and rhodium–naphthalene complexes.[11]

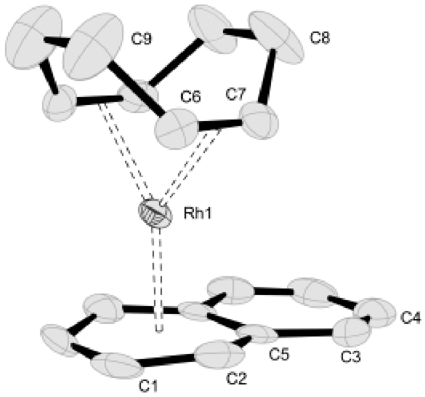

Figure 1. ORTEP diagram of $[(C_{10}H_8)Rh(cod)]^+SbF_6^-$ (**1**). Ellipsoids drawn at 50 % probability level.

Complex **1** was tested in a variety of [5+2] cycloaddition reactions and compared, where relevant, with some other effective catalysts (Table 1). The initial series was selected to explore the utility of the catalyst with a diverse variety of substitution patterns. Excellent results were obtained with vinylcyclopropanes tethered to terminal and internal alkynes, alkynoates, and alkenes. Substitution of the vinylcyclopropane is tolerated both on and adjacent to the cyclopropane

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