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Strong Emission Enhancement in pH-Responsive 2:2 Cucurbit[8]uril Complexes

Stefan Schoder, Hendrik V. Schröder, Luca Cera, Rakesh Puttreddy, Arne Güttler, Ute Resch-Genger, Kari Rissanen and Christoph A. Schalley*

Abstract: Organic fluorophores, particularly stimuli-responsive molecules, are very interesting for biological and material sciences applications, but frequently limited by aggregation- and rotation-caused photoluminescence quenching. A series of easily accessible bipyridinium fluorophores is reported, whose emission is quenched by a twisted intramolecular charge transfer (TICT) mechanism. Encapsulation in a cucurbit[7]uril host yields a 1:1 complex exhibiting a moderate emission increase due to destabilization of the TICT state inside the apolar cucurbituril cavity. A much stronger is the fluorescence enhancement is observed in 2:2 complexes with the larger cucurbit[8]uril, which is caused by additional conformational restriction of rotations around the aryl-aryl bonds. As the cucurbituril complexes are pH switchable, this system represents an efficient supramolecular ON/OFF fluorescence switch.

Stimuli-responsive organic fluorophores have received great attention because of their potential as switchable biolabels,[1] sensors,[2] and components in organic light-emitting diodes.[3] Their design and synthesis[4] can be similarly challenging as the tuning and switching of their photophysical properties.[5] Particularly in water, organic chromophores with large hydrophobic π-systems often exhibit poor fluorescence due to aggregation-caused quenching (ACQ).[6] Conversely, solid-state fluorophores as potential alternatives often tend to emit only weakly in solution as long as they are in the monomeric state.[7]

To overcome these limitations and to introduce the possibility to tune the emission without the need of time-consuming synthetic modification, a supramolecular approach is promising. Because of their good solubility, low toxicity and strong host-guest interactions, host molecules such as calixarenes,[8] cyclodextrins,[9] and cucurbit[*n*]urils (CB[*n*])[10] have been used in aqueous media to investigate the complexation of a broad range of organic dyes.[11] Furthermore, a stimuli-responsive host-guest equilibrium can enable ON/OFF fluorescence switching as a result of complex formation and dissociation.[12]

Fluorescence enhancement by complexation with CB[*n*]s can be a result of prevented chromophore aggregation,[13] of restricted intramolecular rotation (RIR)[14] and of excimer formation.[15] Impressive examples of CB[8]-based tunable supramolecular polymers that form *J*-aggregates[16] and exhibit very high quantum yields[17] have been reported.

Herein, we present a series of structurally simple, yet versatile bipyridinium fluorophores **2**$^+$–**7**$^+$ (Figure 1) and their supramolecular complexation with CB[*n*]s (*n* = 7, 8) in water (Figure 1). This includes the study of three approaches of tuning the fluorescence properties of these fluorophores: (i) covalent modification of the guest, (ii) complexation with host molecules of varying size, i.e. CB[7] and CB[8], and (iii) (de)protonation of the fluorophores and their complexes.

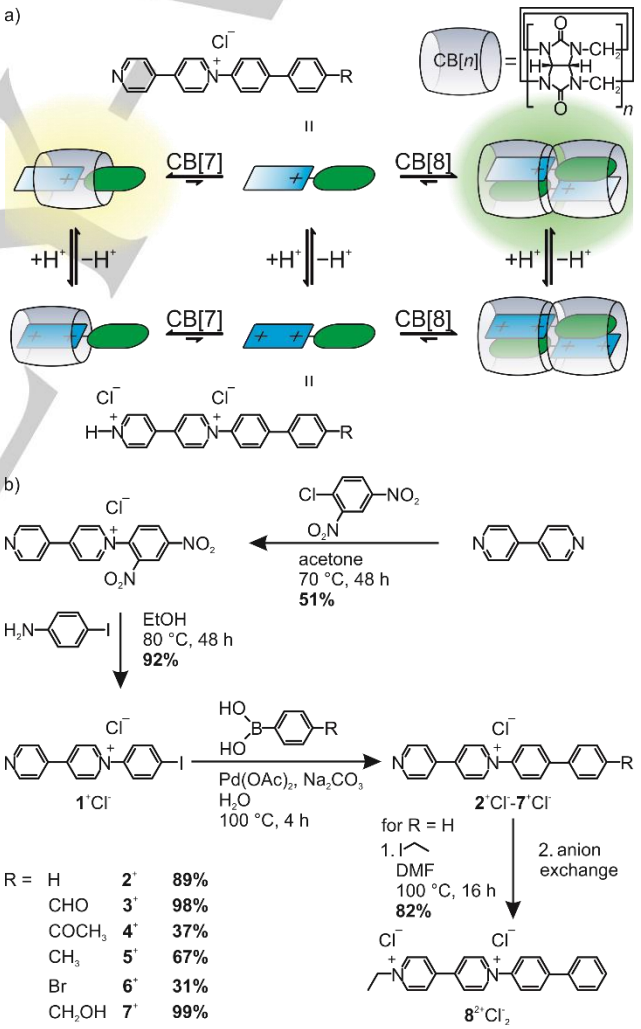

Figure 1. a) Complexation-induced emission enhancement and acid/base switching of a TICT fluorophore upon the addition of macrocyclic hosts CB[7] and CB[8] and b) synthesis of bipyridinium derivatives **2**$^+$Cl$^-$–**7**$^+$Cl$^-$ through Suzuki reaction in water and subsequent substitution of **2**$^+$Cl$^-$ to doubly charged **8**$^{2+}$Cl$^-_2$.

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The water-soluble bipyridinium compounds **2**$^+$–**7**$^+$ were synthesized in three steps from 4,4'-bipyridine (Figure 1, see Supporting Information for details). In the third step, different substituents were introduced by Suzuki reaction of **1**$^+$Cl$^-$ and the corresponding phenylboronic acids. The products were easily purified by a simple filtration. In addition, **2**$^+$Cl$^-$ was reacted to the corresponding permanently doubly charged *N*-ethyl viologen derivative **8**$^{2+}$Cl$^-_2$ by refluxing **2**$^+$Cl$^-$ with ethyl iodide in DMF. After an anion exchange to the chloride salt, 82% of **8**$^{2+}$Cl$^-_2$ were obtained. Compounds **2**$^+$Cl$^-$–**7**$^+$Cl$^-$ and **8**$^{2+}$Cl$^-_2$ are yellow, thermally stable (m.p. > 240°C) powders soluble in protic polar solvents including water. Simple anion exchange yields different salts of these cations, some of which like the PF_6^- salts are soluble in organic solvents. Several crystal structures of **2**$^+$ with different counterions as well as of **8**$^{2+}$Cl$_2$ confirm the identity of the products (Supporting Information).

The photophysical properties of **2**$^+$Cl$^-$–**7**$^+$Cl$^-$ in solution are summarized in Table 1 (for their electrochemical properties, see Table S1). All fluorophores show low-energy absorption bands at wavelengths between 310 and 321 nm. In agreement with time-dependent density functional theory (TD DFT) calculations (Supporting Information), we attribute these bands to HOMO-LUMO transitions, with the HOMO being centered on the biphenyl and the LUMO on the bipyridinium part (Figure S20). The substitution pattern has only a minor influence on the relative energies of the frontier orbitals and excitation energies (Table S1), but drastically affects the quantum yield (Figure 2a). This is in line with a twisted intramolecular charge transfer (TICT) mechanism in which the locally excited (LE) state relaxes to the twisted intramolecular charge transfer state (TICT state).[18] The barriers for rotation of the aromatic rings around their aryl-aryl C-C and C-N bonds were calculated to be smaller than 15 kJ mol^{-1} (Figure S21) which makes TICT formation possible. This affects the equilibrium between the LE and TICT state which hampers the radiative decay channel of the fluorophores and, thus, reduces the emission intensity. Different substituents are known to stabilize either the LE or the TICT state.[19] For example, considerably stronger fluorescence quenching in **2**$^+$Cl$^-$ compared to **3**$^+$Cl$^-$ demonstrates that the TICT mechanism is favoured for **2**$^+$Cl$^-$. The presence of a TICT state was further supported by TD DFT calculations (Figure 2c).

Table 1. Photophysical properties of **2**$^+$Cl$^-$–**7**$^+$Cl$^-$.

	R =	λ_{abs} [nm]	λ_{em} [nm][a]	φ [%][a]
2$^+$Cl$^-$	H	318	541	3
3$^+$Cl$^-$	CHO	310	499	26
4$^+$Cl$^-$	$COCH_3$	313	513	17
5$^+$Cl$^-$	CH_3	321	501	4
6$^+$Cl$^-$	Br	318	638	2
7$^+$Cl$^-$	CH_2OH	314	497	13

[a] $\lambda_{ex} = \lambda_{abs}$

In contrast, the protonated compounds **2**H^{2+}Cl$^-_2$–**7**H^{2+}Cl$^-_2$ and compound **8**$^{2+}$Cl$^-_2$ display virtually no emission in solution.

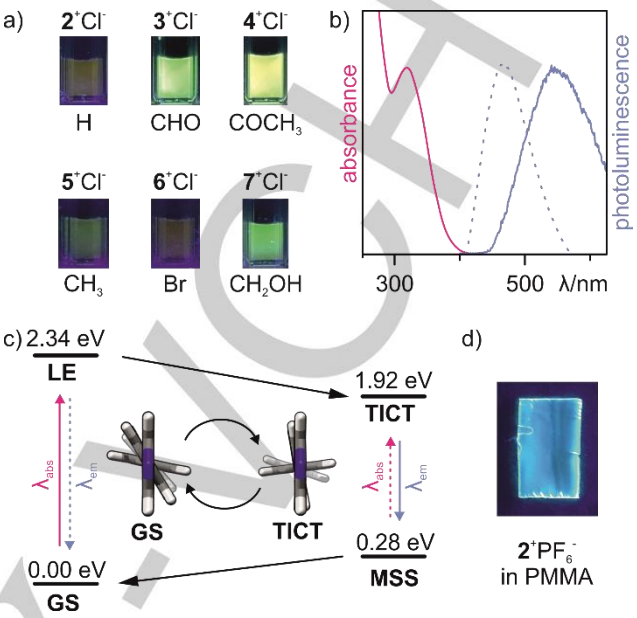

Figure 2. a) Photographs of aqueous solutions of **2**$^+$Cl$^-$–**7**$^+$Cl$^-$ (0.06 mM, 298 K, λ_{ex} = 366 nm). b) Absorption and photoluminescence spectra of **2**$^+$Cl$^-$ in H_2O and **2**$^+$$PF_6^-$ in a PMMA matrix (dashed line). c) TD DFT calculations of the ground and exited state structures with the corresponding singlet energy levels of **2**$^+$ (GS = ground state, LE = locally excited state, TICT = twisted intramolecular charge transfer state, MSS = meta-stable state). d) Photograph of **2**$^+$$PF_6^-$ embedded in a PMMA polymer matrix (0.02 wt. %, λ_{ex} = 366 nm).

Compounds **2**$^+$Cl$^-$–**7**$^+$Cl$^-$, as well as the PF_6^-, OTf^-, $Tosyl^-$, NO_3^-, ClO_4^-, NTf_2^-, and $BArF^-$ salts of **2**$^+$ exhibit solid state luminescence (Figure S2). Furthermore, compound **2**$^+$$PF_6^-$ and **2**$^+$$ClO_4^-$ show emission maxima at 470 nm when embedded with 0.02 wt.-% in a polymethylmethacrylate (PMMA) polymer matrix (Figures 2b,d, S3). In polymeric media like PMMA, the formation of the TICT state, involving molecular rotations in the exited state, is hindered and therefore radiative depopulation on the LE state (LE→GS transition) is favoured, yielding enhanced fluorescence.[20]

The structures of the host-guest complexes formed with equimolar amounts of CB[7] in solution can be derived from typical complexation-induced ^{1}H NMR shifts (Figures S8–S10). Irrespective of the protonation state, all guests **2**$^+$Cl$^-$–**7**$^+$Cl$^-$, **2**H^{2+}Cl$^-_2$–**7**H^{2+}Cl$^-_2$ and **8**$^{2+}$Cl$^-_2$ form 1:1 complexes, in which the (di)cationic half is located inside the host cavity. Encapsulation inside CB[7] induces a bathochromic shift of the π–π* absorption band and a blue shift in emission compared to the free guest (Figure S11). The quantum yields increase by factors of three and four for **2**H^{2+}Cl$^-_2$@CB[7] and **2**$^+$Cl$^-$@CB[7], respectively. This can be attributed to the highly unpolar chemical environment in the host.[11b] This change in polarity leads only to a minor shift of the equilibrium from the TICT state to the LE state.[21] Even though the excited fluorophore is well stabilized inside the cavity of CB[7], there is no significant restriction of intramolecular motion (RIM).[22] The aromatic rings of the guest can still rotate

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Table 2. Photophysical properties of **2**$^+$Cl$^-$@CB[7]–**7**$^+$Cl$^-$@CB[7]

	R =	λ_{abs} [nm]	λ_{em} [nm][a]	φ [%][a]
2$^+$Cl$^-$@CB[7]	H	328	528	10
3$^+$Cl$^-$@CB[7]	CHO	312	491	50
4$^+$Cl$^-$@CB[7]	$COCH_3$	315	499	36
5$^+$Cl$^-$@CB[7]	CH_3	330	499	8
6$^+$Cl$^-$@CB[7]	Br	327	549	4
7$^+$Cl$^-$@CB[7]	CH_2OH	320	496	30

[a] $\lambda_{ex} = \lambda_{abs}$

around the aryl-aryl bonds and thus the TICT mechanism of fluorescence quenching is not efficiently suppressed.[23]

The complexation of the fluorophores with CB[8] is described here exemplarily for **2**H^{2+}Cl$^-_2$ and **2**$^+$Cl$^-$ as a representative example. In a 1:1 mixture of **2**H^{2+}Cl$^-_2$ and CB[8], 2:2 complexes (**2**H^{2+}Cl$^-_2$)$_2$@CB[8]$_2$ form as confirmed by ^{1}H NMR experiments (Figure S13). Single crystals were obtained, in which two CB[8] hosts complex two protonated guests in a 2:2 complex (Figure 3a,b). Both CB[8] molecules are connected by (background) sodium ions, which also bind to a second 2:2 complex containing non-protonated guests (for details, see Supporting Information). The two protonated guests inside the CB[8] dimer adopt co-facial anti-parallel arrangement[24] with centroid-to-centroid contacts of 3.75 Å. Furthermore, the two guests manifest a nearly co-planar conformation with dihedral angles between the aryl rings of 17.6°, 22.7° and -19.0° due to the confinement in the CB[8] cavities. An excess of CB[8] does not change the complex stoichiometry, in case of an excess of the guest, however, a new set of signals appears for a 2:1 complex (Figure S14). Deprotonation of the guest molecules results in a set of signals shifted relative to the protonated complex indicating a 2:2 complex stoichiometry (**2**$^+$Cl$^-$)$_2$@CB[8]$_2$ also for the deprotonated guest (Figure 3d and S12).

The UV/Vis spectra of all CB[8] complexes show a bathochromic shift of the π-π* absorption band indicating dimer formation (Figure S16).[25] Compared to the corresponding CB[7] complexes, the CB[8] complexes of **2**H^{2+}Cl$^-_2$–**7**H^{2+}Cl$^-_2$ have significantly higher fluorescence quantum yields (φ), up to φ = 26% for the **3**H^{2+}Cl$^-_2$@CB[8] complex (Table 3). An amazingly strong emission enhancement is observed for all CB[8] complexes after guest deprotonation (Figure 3e). For example, (**2**$^+$Cl$^-$)$_2$@CB[8]$_2$ displays a φ of 82%. This corresponds to a 27-fold increase in comparison to the free fluorophore **2**$^+$Cl$^-$. Also, the fluorescence lifetime increases drastically by a factor of 100 (τ = 15.20 ns) (Figure S17). One (smaller) contribution to the fluorescence quantum yield increase is certainly again the unpolar CB[8] cavity as already observed for the CB[7] complexes that shifts the equilibrium from the TICT to the LE state. The major effect, however, is the restriction of intramolecular motion (RIM), i.e. hindered rotations around the aryl-aryl bonds caused by dimerization inside the cavity. Therefore, the strong fluorescence enhancement cannot be attributed solely to the prevention of TICT state formation, but is also caused by the combination of RIM and dimer formation inside the cucurbituril cavity. The relatively low φ value of complex (**6**$^+$Cl$^-$)$_2$@CB[8]$_2$ and especially the modest enhancement compared to the CB[7] complex (φ = 4% to 5%) are due to quenching by the heavy-atom effect of the bromo-substituent in the dimeric structure.[26]

The guest molecules can be further functionalized on the pyridine side by simple *N*-alkylation. As a result, the pH switch is eliminated. However, this easy-to-accomplish functionalization offers a point of attachment for other functional groups that may be useful for future applications, e.g. to attach the chromophores to biomolecules, sensors or surfaces. To investigate the effect of *N*-alkylation, the influence of complexation on the luminescence properties of **8**$^{2+}$Cl$^-_2$ were studied, revealing a strong luminescence enhancement after host addition e.g. from 0.2% to 7.8% for (**8**$^{2+}$Cl$^-_2$)$_2$@CB[8]$_2$ (Table S2, Figure S20, S21).

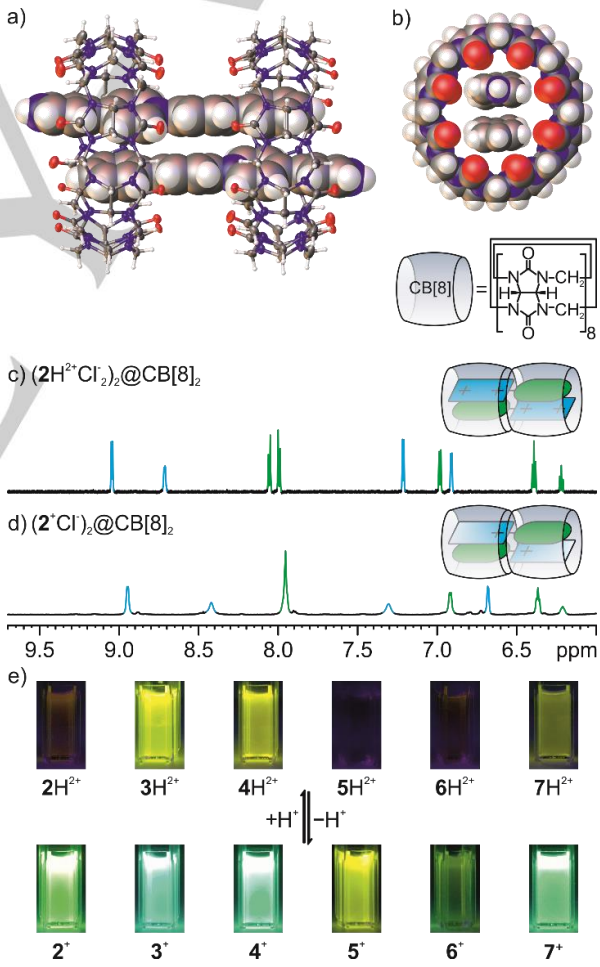

Figure 3. a) Side view and b) view along the cavity of the crystal structure of (**2**H^{2+}Cl$^-_2$)$_2$Na$_2$@CB[8]$_2$ (anions and bridging sodium ions omitted for clarity; for crystallographic details, see Supporting Information). Partial ^{1}H NMR spectra (700 MHz, 298 K, D_2O, 1.0 mM) of c) a 1:1 mixture of **2**H^{2+}Cl$^-_2$ and CB[8] and d) a 1:1 mixture of **2**$^+$Cl$^-$ and CB[8]; DCl (35% in D_2O) and K_2CO_3 were used to (de)protonate. e) Photographs of aqueous solutions of CB[8] complexes of **2**H^{2+}Cl$^-_2$–**7**H^{2+}Cl$^-_2$ and **2**$^+$Cl$^-$–**7**$^+$Cl$^-$ (0.06 mM, 298 K, λ_{ex} = 366 nm).

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Table 3. Photophysical properties of (**2**$^+$Cl$^-$)$_2$@CB[8]$_2$–(**7**$^+$Cl$^-$)$_2$@CB[8]$_2$ and (**2**H^{2+}Cl$^-_2$)$_2$@CB[8]$_2$–(**7**H^{2+}Cl$^-_2$)$_2$@CB[8]$_2$.

	R =	λ_{abs} [nm]	λ_{em} [nm][a]	φ [%][a]		R =	λ_{abs} [nm]	λ_{em} [nm][a]	φ [%][a]
(**2**H^{2+}Cl$^-_2$)$_2$@CB[8]$_2$	H	367	587	4	(**2**$^+$Cl$^-$)$_2$@CB[8]$_2$	H	328	498	82
(**3**H^{2+}Cl$^-_2$)$_2$@CB[8]$_2$	CHO	353	547	26	(**3**$^+$Cl$^-$)$_2$@CB[8]$_2$	CHO	336	478	80
(**4**H^{2+}Cl$^-_2$)$_2$@CB[8]$_2$	$COCH_3$	354	561	18	(**4**$^+$Cl$^-$)$_2$@CB[8]$_2$	$COCH_3$	336	482	78
(**5**H^{2+}Cl$^-_2$)$_2$@CB[8]$_2$	CH_3	391	560	10	(**5**$^+$Cl$^-$)$_2$@CB[8]$_2$	CH_3	360	536	42
(**6**H^{2+}Cl$^-_2$)$_2$@CB[8]$_2$	Br	380	601	2	(**6**$^+$Cl$^-$)$_2$@CB[8]$_2$	Br	353	521	5
(**7**H^{2+}Cl$^-_2$)$_2$@CB[8]$_2$	CH_2OH	366	551	12	(**7**$^+$Cl$^-$)$_2$@CB[8]$_2$	CH_2OH	341	489	43

[a] $\lambda_{ex} = \lambda_{abs}$

In conclusion, the effect of supramolecular complexation on the photophysical properties of simple charge-transfer dyes **2**$^+$–**7**$^+$ and their protonated forms in aqueous solution is reported. The free fluorophores are weakly emissive due to formation of a TICT state as indicated by experiment as well as theory. However, the compounds exhibit strong luminescence in the solid state and in viscous matrices like polymer blends, where molecular rotations are hindered. Complexation with CB[7] results in the formation of 1:1 complexes and the TICT state is destabilized in the unpolar environment inside the host cavity. In contrast, the fluorophores form 2:2 complexes with CB[8] with a cofacial antiparallel arrangement of the dyes as shown by ^{1}H NMR and a crystal structure. The 2:2 complexes exhibit a very strong emission increase due to RIM and dimer formation (27-fold increase for **2**$^+$ yielding φ = 82%). The two tuning parameters (change of pH and host–guest complexation) of the stimuli responsive system can be combined and are orthogonal to each other. This novel, yet simple strategy to implement a RIM-triggered luminescence enhancement in stimuli-responsive supramolecular CB[8] complexes is highly promising for the rational design of strongly emissive fluorophores for biological and material sciences applications.

Conflict of interests

The authors declare no conflict of interest.

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Keywords: Cucurbituril • fluorescence enhancement • host-guest complex • restriction of intramolecular motion • luminescence

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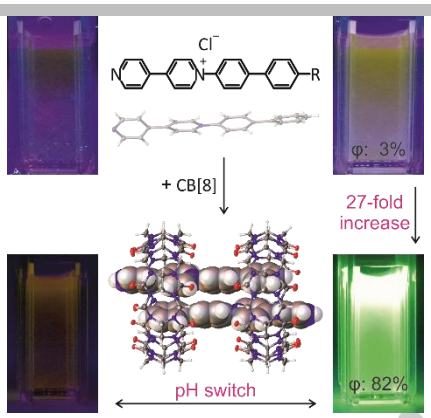
Confine to shine: A simple supramolecular approach to enhance and tune the luminescence properties of a set of pH-responsive TICT fluorophores in water is presented. Addition of CB[8] results in 2:2 complexes with up to a 27-fold increase in quantum yield. The complexation enforces restriction of intramolecular motions and an intermolecular charge transfer of a guest dimer in a confined space.



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Strong Emission Enhancement in pH-Responsive 2:2 Cucurbit[8]uril Complexes

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