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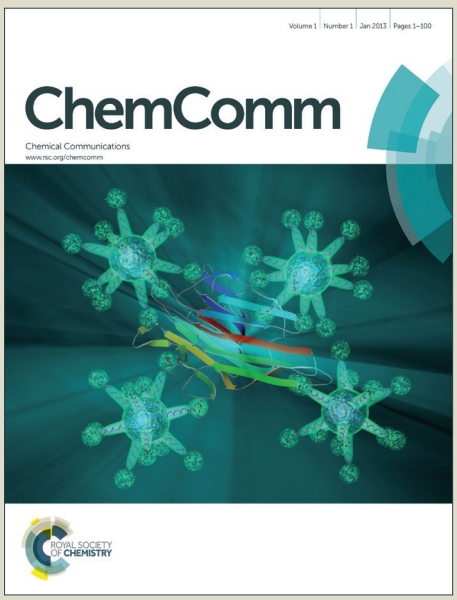

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Naohiro Kameta,* Mitsutoshi Masuda, and Toshimi Shimizu

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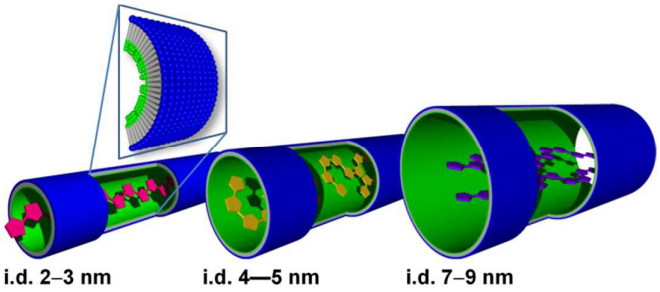

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Soft Nanotubes Acting as a Confinement Effecter and a Chirality Inducer for Achiral Polythiophenes

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Depending on their nanochannel sizes, soft nanotubes were able to not only control the conformation and aggregation state of encapsulated achiral polythiophene boronic acids but also induce chirality in the polythiophene chains that exhibit chiral recognition abilities for D, L-sugars.

Control of the conformation, aggregation and chirality of conjugated polymers presents a major challenge[1,2] to effectively maximize their chemical and physical potentials, which are applicable to optical/electrical materials, sensing devices, chiral catalysts and separations. Shinkai et al. have found that polysaccharides such as schizophyllan act as one-dimensional hosts to create chiral insulated polymer wires, in which the triple-stranded helical polysaccharides are wrapping single-chain achiral conjugate polymers through their self-assembly from the single-stranded polysaccharides in solvents.[3] This unique method can be widely available for various conjugated polymers, while other methods generally require precise designs and chemical modification for each conjugated polymer. The self-assembly of amphiphilic molecules into soft nanotubes[4] permits the encapsulation of conjugated polymers into their nanochannels with tunable sizes, surfaces and chiralities; notably, carbon, inorganic and metal nanotubes that do not self-assemble and that lack functionalized nanochannels are less useful for such encapsulation. The polysaccharides tune the cavity size according to guest sizes, while the soft nanotubes provide a relatively rigid cavity consisting of solid-state (i.e., crystalline) molecular membranes. Therefore, these soft nanotube systems enable us to clarify the effect of cavity size on the conformation of the encapsulated conjugated polymers. Herein we describe the confinement and chiral-induction effects, which are imparted by soft nanotubes having three different sized nanochannels self-assembled from wedge-shaped glycolipids (Tgly, Dgly and Mgly having a D-glucose unit, Fig. 1), on encapsulated achiral poly(thiopheneboronic acid) (PolyT-B(OH)$_2$, M_n = 24300, Fig. S1, ESI). We reveal that PolyT-B(OH)$_2$ encapsulated in the nanochannels is able to not only form complexes with sugars but also fluorescently recognize the chirality of the sugars.

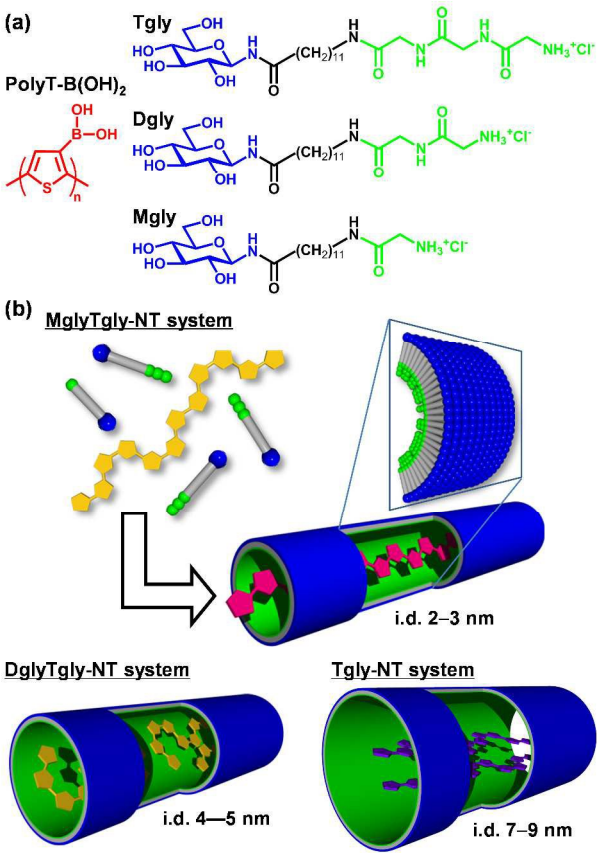


Fig. 1 (a) Chemical structures of polythiophene boronic acid (PolyT-B(OH)$_2$)) and wedge-shaped glycolipids (Tgly, Dgly and Mgly having a D-glucose unit) used to form soft nanotubes. (b) Schematic illustrations of one-dimensional extension, random-coil conformation and aggregation of PolyT-B(OH)$_2$ chain by encapsulation into the nanochannels of MglyTgly-NT, DglyTgly-NT and Tgly-NT, respectively.

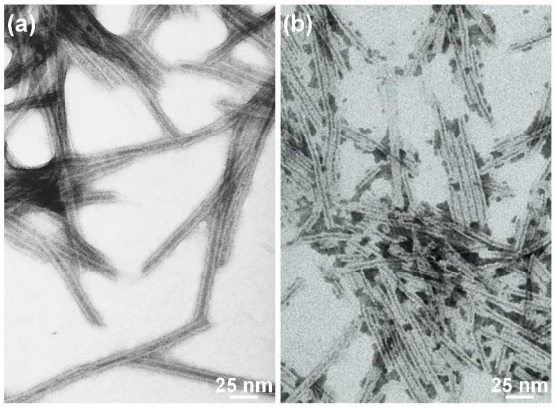


Fig. 2 Transmission electron microscopy images of (a) DglyTgly-NT and (b) MglyTgly-NT. The nanochannels of the nanotubes were visualized with 2 wt% phosphotungstate as a negative staining reagent.

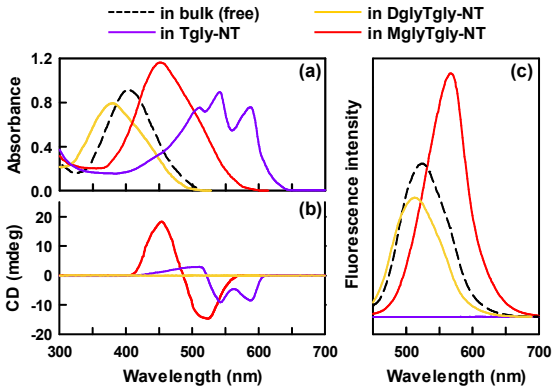


Fig. 3 (a) Absorption spectra, (b) circular dichroism (CD) spectra and (c) fluorescence spectra of free PolyT-B(OH)$_2$ in water/DMSO (v/v = 90/10) and of PolyT-B(OH)$_2$ encapsulated in nanotubes dispersed in water/DMSO (v/v = 90/10). [free PolyT-B(OH)$_2$] = [encapsulated PolyT-B(OH)$_2$] = 2.0 × 10^{-5} M.

As reported previously,[5] self-assembly based on the spray packing of Tgly produces nanotubes with nanochannels of 7–9 nm inner diameter and wall thickness of 3–4 nm, which is comparable to the molecular length of Tgly, 3.57 nm. The nanotubes (hereafter referred to as Tgly-NT) consist of a single-monolayer membrane, in which Tgly molecules pack in parallel fashion with the larger glucose headgroup and smaller amino headgroup located on the outer and inner surfaces of the tubular structure, respectively. In the present study, we constructed nanotubes with different inner diameters by co-assembling Tgly with Dgly or Mgly, although we have previously demonstrated that nanostructures composed solely of Dgly or Mgly are of nanofiber morphology, with widths of 10–25 nm (hereafter referred to as Dgly-nanofibers and Mgly-nanofibers, respectively).[5] Co-assembly experiments were performed as follows: Tgly (5.0 mg, 8.5 μmol) and either Dgly (4.5 mg, 8.5 μmol or 1.9 mg, 3.7 μmol) or Mgly (4.0 mg, 8.5 μmol or 1.5 mg, 3.7 μmol) were dispersed in 2 ml water/DMSO (v/v = 90/10) at room temperature. Then, 1 eq. NaOH was added to the resultant dispersions to weaken electrostatic repulsion among the glycolipids via neutralization of the ammonium groups. Co-assembly of Tgly with 50 mol% Dgly or 50 mol% Mgly yielded mixtures of nanotubes and nanofibers (Fig. S2, ESI), whereas that of Tgly with 30 mol% Dgly or 30 mol% Mgly selectively produced nanotubes, hereafter referred to as DglyTgly-NT or MglyTgly-NT, respectively. The DglyTgly-NT had inner diameters of 4–5 nm and the MglyTgly-NT had inner diameters of 2–3 nm (Fig. 2). The wall thickness of both types of nanotubes, 2–4 nm, was similar to that of the Tgly-NT, suggesting that both types of nanotubes also consisted of a single monolayer membrane of Tgly and Dgly or Mgly. Infrared spectroscopy showed that the lateral chain packing of the oligomethylene spacer in the DglyTgly-NT and MglyTgly-NT is assignable to a triclinic parallel type (Fig. S3, ESI), which is clearly distinguishable from the distorted hexagonal-type packing observed in the Dgly- and Mgly-nanofibers.[5] Therefore, the inner and outer surfaces of the DglyTgly-NT and MglyTgly-NT must have been occupied by the glucose headgroups and amino headgroups, respectively, as we observed previously for Tgly-NT. We have already reported that the inner diameters of nanotubes that consist of monolayer membranes of other wedge-shaped glycolipids as a single component decrease with decreasing length of the oligomethylene spacer.[6] It should be noted that in the present study we discovered the fine tuning of the inner diameter by co-assembly of two components with different numbers of glycine residues. Circular dichroism (CD) spectroscopy suggests that the contribution of twist packing (chiral packing),[5] rather than spray packing, to nanotube formation increased in the order of Tgly-NT < DglyTgly-NT < MglyTgly-NT (Fig. S4, ESI). These results indicate that the gap in the molecular packing created by the difference in the number of glycine residues between Tgly and Dgly or Mgly can promote membrane twisting and enhance the surface curvatures of membranes.

PolyT-B(OH)$_2$ was able to be encapsulated in the each nanotube channel with simultaneously formation of the nanotubes by above self-assembly in the presence of PolyT-B(OH)$_2$ (Fig. S5, ESI). In contrast, when PolyT-B(OH)$_2$ was added to a dispersion of the obtained, self-assembled nanotubes, it was not encapsulated. In aqueous solutions, the nanotube formation process was undisrupted in the presence of PolyT-B(OH)$_2$, owing to its poor complexation with glucose moieties without the 1-OH group in the glycolipids as described later. The encapsulated PolyT-B(OH)$_2$ was stored in the nanochannels at room temperature, and its release into bulk solution was negligible in all of the experiments described herein (Fig. S6, ESI). Figure 3a shows absorption spectra of free PolyT-B(OH)$_2$ in water/DMSO (v/v = 90/10) and of PolyT-B(OH)$_2$ encapsulated in the nanotube channels dispersed in the same aqueous solution. The ultraviolet/visible (UV/Vis) absorption maximum, 404 nm, of the free PolyT-B(OH)$_2$ is attributable to a random-coil conformation of polythiophene backbones.[7] The encapsulated PolyT-B(OH)$_2$ in the Tgly-NT had a larger red-shifted absorption band with three peaks, 511, 541 and 587 nm, which are assignable to vibronic absorptions in aggregated forms of polythiophene chains.[8] The absorption maximum of the encapsulated PolyT-B(OH)$_2$ in the MglyTgly-NT and DglyTgly-NT appeared at 452 nm and 380 nm, respectively. The red-shift observed in the MglyTgly-NT' spectrum, which is obviously different from that observed for the Tgly-NT, indicates an elongation of the effective conjugation length of the PolyT-B(OH)$_2$ backbone, with increased planar conformation. In contrast, the blue-shift observed in the DglyTgly-NT' spectrum suggests that the effective conjugation length shortened, possibly because of the further induction of the random-coil conformation in the nanochannel. Free PolyT-B(OH)$_2$ in the absence of the nanotubes formed non-specific aggregation in the solid state, which has a red-shifted absorption band at 542 nm and two shoulders (Fig. S7, ESI). In contrast, the encapsulated PolyT-B(OH)$_2$ in the nanotubes even in the solid state kept the above conformations observable in dispersions, since the absorption spectra of the solid-state samples were similar to those of the solution-dispersed samples. These results indicate that PolyT-B(OH)$_2$ is completely isolated in the nanotube channels and does not exist on the outer surface of the nanotubes. We also confirmed that nanotubes of appropriate inner diameters are

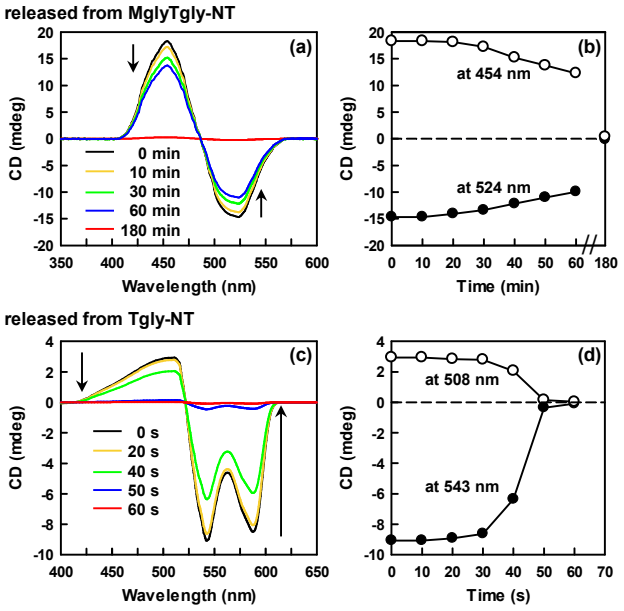
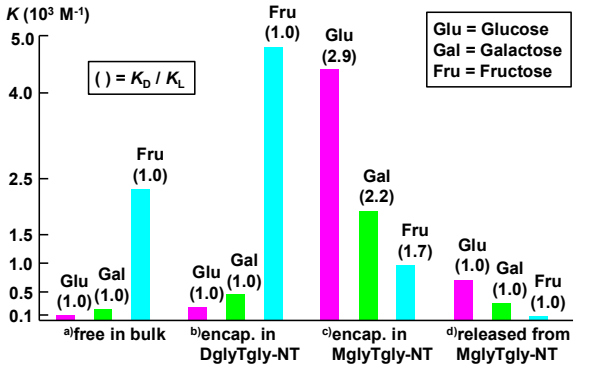


Fig. 4 Variation of (a, c) the CD spectra and (b, d) the CD intensities of the released PolyT-B(OH)$_2$ in water/DMSO/THF (v/v/v = 82/9/9) solution from the nanotubes. The samples were prepared as follows: The nanotubes encapsulating PolyT-B(OH)$_2$ were destructed by heating at 60 °C for 1 min in the presence of 1 eq. HCl. The disassembled components, Mgly and Tgly, were precipitated by addition of THF. The supernatant including the released PolyT-B(OH)$_2$ was subjected to CD spectroscopy. The time lapse (b, d) is counted just after the heating procedure.

able to control the folding and aggregation of PolyT-B(OH)$_2$ with a smaller molecular weight (M_n = 7680; Figs. S5 and S8, ESI). Considering the persistence length of polythiophenes, 2–3 nm,[9] we concluded that the MglyTgly-NT channels with diameters of 2–3 nm must have been suitable for the stretched conformation of PolyT-B(OH)$_2$ into a one-dimensional extension structure. In addition, the DglyTgly-NT channels, which had diameters of 4–5 nm, preserved the random-coil conformation of PolyT-B(OH)$_2$, thus preventing the aggregation that was observed in the 7–9-nm diameter nanochannels of Tgly-NT.

Figure 3b shows the CD spectra of the free PolyT-B(OH)$_2$ and the encapsulated PolyT-B(OH)$_2$ in the nanotubes. The free PolyT-B(OH)$_2$ was CD-inactive owing to its lack of chirality, so there was no Cotton effect. The encapsulated PolyT-B(OH)$_2$ in the MglyTgly-NT exhibits a split-type induced CD whose shape and negative/positive signs are characteristic of a left-handed helicity in the PolyT-B(OH)$_2$ backbone.[10] A similar induced CD has been observed for achiral polythiophenes encapsulated in schizophyllans.[11] Mimicking the right-handed helical structure of schizophyllans, the insulated polythiophene wire also had a right-handed helicity. This finding suggests that the MglyTgly-NT also have the ability to induce chirality in encapsulated molecules, although the helical direction of the MglyTgly-NT itself has not been prescribed. A nanotube (hereafter referred to as L-MglyTgly-NT), self-assembled from enantiomers (having a L-glucose unit) of Mgly and Tgly, gave a right-handed helicity to the encapsulated PolyT-B(OH)$_2$ (Fig. S9, ESI). The induced CD pattern of the encapsulated PolyT-B(OH)$_2$ in the Tgly-NT was consistent with that observed for aggregated polythiophenes covalently bonded with chiral substituents, supporting the mechanism of inducing chirality to the interchain π-π stacking among PolyT-B(OH)$_2$ molecules. In contrast, the PolyT-B(OH)$_2$ with a random-coil conformation encapsulated in the DglyTgly-NT was CD inactive, even though the DglyTgly-NT



Conformation of PolyT-B(OH)$_2$: a)b)random-coil; c)one-dimensional planer
Solutions: a)b)c)water/DMSO (v/v = 90/10); d)water/DMSO/THF (v/v/v = 82/9/9)

Fig. 5 Association constants of PolyT-B(OH)$_2$ with D-sugars (solid bars) or L-sugars (stripe bars).

possess chirality owing to the chiral packing of their glycolipids (Fig. S4, ESI). Upon heating at 60 °C for 1 min in the presence of 1 eq. HCl, PolyT-B(OH)$_2$ was compulsively released from the MglyTgly-NT to the bulk solution, and the MglyTgly-NT completely disassembled. The induced CD was retained for some time, disappearing completely only after 3 h (Fig. 4, upper), even though the disassembled components, MGly and Tgly, which exhibit no interaction with the released PolyT-B(OH)$_2$ (Fig. S10, ESI), were removed by precipitation using THF. This type of chiral memory phenomenon has been observed in other polymer and supramolecular systems.[1c,12] On the other hand, the induced CD of the PolyT-B(OH)$_2$ aggregation disappeared as soon as the disassembly of the Tgly-NT by the same heating process (Fig. 4, lower). Since single polythiophene chains hardly maintain the induced chiral conformation in the absence of chiral environments or without chiral interactions, the chiral memory observed in the MglyTgly-NT system will be attributable that the released PolyT-B(OH)$_2$ forms a self-association keeping partly the planer conformation (Fig. S11, ESI), which is distinguishable from the aggregation in the Tgly-NT system.

Fluorescence emission spectra of the encapsulated PolyT-B(OH)$_2$ strongly supported the conformations from the UV/Vis and CD spectroscopy measurements. The emission maximum of PolyT-B(OH)$_2$, 524 nm, shifted to a longer wavelength (566 nm) and was accompanied by an increase in fluorescence intensity upon encapsulation into the MglyTly-NT (Fig. 3c). We attribute these spectral changes to an extension of the effective conjugation length of the PolyT-B(OH)$_2$, which would have resulted from encapsulation into the MglyTgly-NT. In contrast, shortening of the effective conjugation length resulting from encapsulation into the DglyTgly-NT induced a shift in the emission maximum to a shorter wavelength, 513 nm, and was accompanied by a decrease in the fluorescence intensity. The degree of fluorescence quenching of PolyT-B(OH)$_2$, which had been aggregated by encapsulation into the Tgly-NT, was as expected in consideration of the strong interchain π-π stacking in the ground state, i.e., the quenching was similar to that observed in the solid-state PolyT-B(OH)$_2$.

The fluorescence intensities of free PolyT-B(OH)$_2$, encapsulated PolyT-B(OH)$_2$ in the DglyTgly-NT or MglyTgly-NT and compulsively released PolyT-B(OH)$_2$ from the MglyTgly-NT all sharply responded to complexation with D, L-sugars at pH 8.6–9.2 by means of boronate–ester formation[13] between the boronic acid moiety in PolyT-B(OH)$_2$ and the diol moiety in the sugars. The association constants (K) were determined by applying a nonlinear least-squares method based on the Benesi–Hildebrand equation to

the experimental plots (Fig. S12, ESI). The *K* values in the MglyTgly-NT system increased in the order of fructose < galactose < glucose (Fig. 5 and Table S1, ESI), whereas those in the free and the DglyTgly-NT systems exhibited the opposite trend, i.e., glucose < galactose < fructose. The former tendency can be seen in glucose sensors based on rationally designed diboronic-acid derivatives, whereas the latter one is generally observed in the complexation of phenylboronic acid with those sugars.[13] The differences in the conformations of PolyT-$B(OH)_2$, namely the one-dimensional planar conformation and random-coil conformation, strongly influenced its binding selectivity for sugars. Furthermore, in the MglyTgly-NT system, the *K* values for D-sugars were 1.7–2.9 times higher than those for L-sugars (parenthesis in Fig. 5 and Table S1, ESI), indicating that the encapsulated PolyT-$B(OH)_2$ with induced chirality exhibited a higher affinity for D-sugars. As expected, the encapsulated PolyT-$B(OH)_2$ in the L-MglyTgly-NT showed a higher affinity for L-sugars (Table S2, ESI). Although the PolyT-$B(OH)_2$ compulsively released from the MglyTgly-NT also had induced chirality due to the chiral memory effect, it failed to the chiral recognition. Therefore, the confined environment of the nanochannels must have cooperatively contributed to the chiral recognition of PolyT-$B(OH)_2$ in addition to enhancing its binding ability. In support of this conclusion, such chiral recognition was not observed in the DglyTgly-NT system, in which the encapsulated PolyT-$B(OH)_2$ had no induced chirality, nor was chiral recognition observed in the free PolyT-$B(OH)_2$ system (Fig. 5 and Table S1, ESI).

In conclusion, we were able to construct soft nanotubes with 2–3-, 4–5- or 7–9-nm inner diameters separately, which allowed encapsulated PolyT-$B(OH)_2$ to have the planar, one-dimensional conformation with an apparently longer conjugation length, the random-coil conformation and the aggregated conformation, respectively. Depending on the inner diameters of the nanotubes, we observed not only the induction of chirality to the achiral PolyT-$B(OH)_2$ upon encapsulation into the nanotubes, but also a chiral memory effect for PolyT-$B(OH)_2$ released upon destruction of the nanotubes. Furthermore, the chirality-induced PolyT-$B(OH)_2$ with the one-dimensional planar conformation was able to recognize the chirality of D, L-sugars in the nanochannels. Since soft nanotubes can provide suitable nanochannels with controllable sizes and functionalizable surfaces for various conjugated polymers, the system reported herein should enable application of conjugated polymers to optical/electrical materials, sensing devices, chiral catalysts and chiral separations.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis, TEM images, IR for the molecular packing analysis, encapsulation and release profiles, absorption and CD spectra for the conformational analysis, determination of *K* values. See DOI: 10.1039/c000000x/

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